DALTON

Oxidative dehydrogenation of a saturated tetraaza macrocyclic nickel(II) complex: selective formation of nickel(II) complexes containing one or two imino groups†

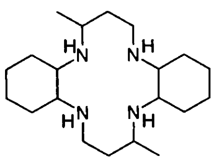
Shin-Geol Kang,*[a] Seong-Jin Kim,[a] Chee-Hun Kwak[b] and Jinkwon Kim*[c]

[a] *Department of Chemistry, Taegu University, Kyungsan 713–714, South Korea*
[b] *Department of Chemistry, Sunchon National University, Sunchon 540–742, South Korea*
[c] *Department of Chemistry, Kongju National University, Kongju 314–701, South Korea*

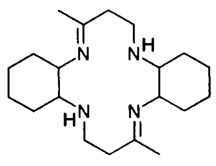
The reaction of the saturated polyaza macrocyclic nickel(II) complex $[NiL^1][ClO_4]_2$ (L^1 = *C-meso*-3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosane) with concentrated HNO_3 in water–methanol (1 : 1) solution yielded the low-spin nickel(III) complex $[NiL^1(NO_3)_2]ClO_4$. The latter is further oxidized in the presence of the acid to produce the diimine complex $[NiL^2]^{2+}$ (L^2 = 3,14-dimethyl-2,6,13,17-tetraazatricyclo-[16.4.0.$0^{7,12}$]docosa-2,13-diene). The monoimine complex $[NiL^3][ClO_4]_2$ (L^3 = *C-meso*-3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docos-5-ene) can also be prepared by the oxidative dehydrogenation reaction of $[NiL^1]^{2+}$ with HNO_3 in water–acetonitrile (1 : 1) solution. The square-planar nickel(II) complexes of L^2 and L^3 were characterized. The crystal structure of $[NiL^3][ClO_4]_2$ shows that the complex has a somewhat distorted square-planar geometry.

One of the most interesting aspects of polyaza macrocyclic complexes is that the ligand can be modified. Some transition-metal(II) complexes of polyaza macrocyclic ligands containing co-ordinated secondary amino groups are chemically oxidized to metal(II) complexes containing a higher degree of unsaturation in the ligand.[1-11] The reaction is largely affected by the nature of the central metal ion and the structure of the ligand. For example, iron(II) and ruthenium(II) complexes of L^4 react with mild oxidizing agents such as molecular oxygen to produce complexes of L^6.[1,2] On the other hand, oxidative dehydrogenation of the nickel(II) complex $[NiL^4]^{2+}$ requires much stronger oxidizing agents such as HNO_3 and produces $[NiL^7]^{2+}$.[2] Recently, the reactions of nickel(II) and iron(II) complexes of L^8 with H_2O_2 and O_2, respectively, were also reported to produce the corresponding complexes of the unsaturated bis(macrocyclic) ligand L^9.[3-6] It has been suggested that oxidative dehydrogenation of the metal(II) complexes is assisted by the central metal ion; the reaction begins with oxidation of the metal(II) to the metal(III) state, followed by oxidation of the ligand through disproportionation and/or intramolecular electron transfer from the ligand to the metal ion.[1-11]

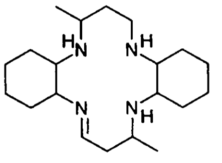
In this work the oxidative dehydrogenation of $[NiL^1][ClO_4]_2$ (L^1 = *C-meso*-3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosane), which contains both cyclohexane rings and C-methyl groups, was attempted in various solutions containing concentrated HNO_3 to investigate the effects of the substituents and solvents on the reaction. Interestingly, we obtained two types of unsaturated nickel(II) complexes $[NiL^2][ClO_4]_2$ (L^2 = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosa-2,13-diene) and $[NiL^3][ClO_4]_2$ (L^3 = *C-meso*-3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docos-5-ene) selectively from the reaction. This paper reports the selective preparation of the nickel(II) complexes of L^2 and L^3, along with the isolation of the nickel(III) complex $[NiL^1(NO_3)_2]ClO_4$ as an intermediate. The crystal structure of $[NiL^3][ClO_4]_2$ is also reported.



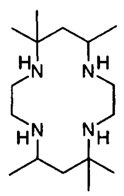
L^1



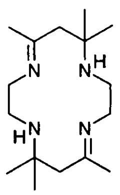
L^2



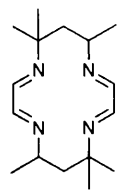
L^3



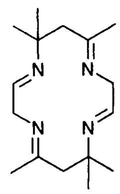
L^4



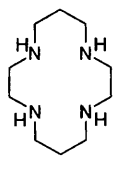
L^5



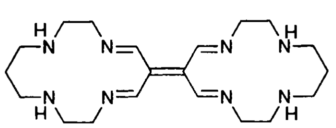
L^6



L^7



L^8



L^9

Experimental

Measurements

Infrared spectra were recorded as Nujol mulls on a Shimadzu IR-440 spectrophotometer, electronic spectra with a Shimadzu UV-160 spectrophotometer and NMR spectra with a Bruker WP 300 FT spectrometer. Conductance measurements were made with a Metrohm Herisau E518 Conductometer. Elemental

---

† *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}.

analyses were performed at the Korea Basic Science Institute, Seoul, Korea. Cyclic voltammograms were recorded using a Yanaco p-1000 Voltammetric Analyzer equipped with a FG-121B function generator and a Watanabe X-Y recorder. The electrochemical measurements were conducted in oxygen-free 0.1 mol dm^{-3} $NBu^n{}_4ClO_4$–acetonitrile solutions at 20 °C. Magnetic susceptibilities were measured with a Johnson Matthey MK-1 magnetic susceptibility balance. Molar susceptibilities were corrected for diamagnetism of the ligands and the anion by use of Pascal's constants.

Materials

All chemicals used in syntheses were of reagent grade. The complex $[NiL^1][ClO_4]_2$ was prepared as described previously.[12] **CAUTION**: perchlorate salts of complexes are potentially explosive materials and should be handled with care.

Syntheses

$[NiL^1(NO_3)_2]ClO_4$. An excess of concentrated HNO_3 (*ca.* 1.8 cm^3) was added to a hot (≈60 °C) water–methanol (1 : 1) suspension (*ca.* 10 cm^3) of the yellow nickel(II) complex $[NiL^1][ClO_4]_2$ (0.5 g). The mixture was stirred for *ca.* 5 min. During this period the yellow solid dissolved and then green crystals formed. These were filtered off at room temperature, washed with ethanol, and dried *in vacuo* (yield > 80%) (Found: C, 38.65; H, 6.55; N, 13.55. $C_{20}H_{40}ClN_6NiO_{10}$ requires C, 38.85; H, 6.50; N, 13.60%). Magnetic moment $\mu_{eff} = 1.85\ \mu_B$.

$[NiL^2][ClO_4]_2$. Addition of concentrated HNO_3 (*ca.* 1.8 cm^3) to a water–methanol (1 : 1) suspension of $[NiL^1][ClO_4]_2$ (0.5 g) yielded the green complex $[NiL^1(NO_3)_2]ClO_4$ as described above. The resulting suspension was further stirred on a hot water-bath (*ca.* 60 °C) for 1.5 h. During this period it became a homogeneous solution which turned yellow. The solution was filtered at room temperature to remove any insoluble material, and then an excess of $NaClO_4$ was added to the filtrate. The yellow crystals formed were filtered off, washed with ethanol, and recrystallized from hot water (yield ≈50%) (Found: C, 40.85; H, 6.10; N, 9.40. $C_{20}H_{36}Cl_2N_4NiO_8$ requires C, 40.70; H, 6.15; N, 9.50%). This complex was also prepared by stirring a hot (60 °C) methanol–water (1 : 1) suspension (10 cm^3) of $[NiL^1(NO_3)_2]ClO_4$ (*ca.* 0.5 g) and concentrated HNO_3 (*ca.* 1.5 cm^3).

$[NiL^3][ClO_4]_2$. To a hot (≈60 °C) water–acetonitrile (1 : 1) suspension (13 cm^3) of $[NiL^1][ClO_4]_2$ (*ca.* 1.0 g) was added dropwise concentrated HNO_3 (1.5 cm^3) with vigorous stirring until a homogeneous dark brown solution was produced. The solution was stirred for *ca.* 1 h, turning orange-red. Concentrated HNO_3 (*ca.* 0.5 cm^3) was added, and the mixture was further stirred for 1 h. During this period the homogeneous solution turned pale yellow. An excess of $NaClO_4$ was added at room temperature. The yellow crystals which formed were filtered off and washed with ethanol. The crude product often contains a small amount (< 5%) of $[NiL^2][ClO_4]_2$ as a by-product. The pure product was readily obtained by fractional recrystallizations of the crude product from hot water (yield ≈30%) (Found: C, 40.45; H, 6.55; N, 9.40. $C_{20}H_{38}Cl_2N_4NiO_8$ requires C, 40.60; H, 6.50; N, 9.45%). This complex was also prepared by stirring a hot (60 °C) homogeneous water–acetonitrile (1 : 1) solution (15 cm^3) of $[NiL^1(NO_3)_2]ClO_4$ (*ca.* 0.5 g) and concentrated HNO_3 (*ca.* 1.5 cm^3).

$[NiL][PF_6]_2$ ($L = L^2$ or L^3). To a warm acetonitrile suspension (*ca.* 5 cm^3) of $[NiL][ClO_4]_2$ (0.4 g) was added an excess of NH_4PF_6. The solid (NH_4ClO_4) formed was filtered off and water (10 cm^3) was added to the filtrate. A yellow solid was filtered off, washed with cold water, and dried in air.

$[NiL^2][PF_6]_2$ (Found: C, 35.25; H, 5.45; N, 8.30. $C_{20}H_{36}F_{12}N_4NiP_2$ requires C, 35.25; H, 5.35; N, 8.25%): NMR (CD_3NO_2) ^1H, δ 2.40 (s, Me); ^{13}C, δ 24.8, 25.3, 25.7, 29.1, 31.9, 37.2, 38.2, 62.9, 69.8 and 193 (C=N).

$[NiL^3][PF_6]_2$ (Found: C, 35.25; H, 5.70; N, 8.15. $C_{20}H_{38}F_{12}N_4NiP_2$ requires C, 35.15; H, 5.60; N, 8.20%): NMR (CD_3NO_2) ^1H, δ 1.21 (d, Me) and 1.92 (d, Me); ^{13}C, δ 12.4, 13.8, 22.6, 22.8, 23.1, 23.4, 27.4, 27.7, 28.1, 28.3, 31.4, 37.0, 40.1, 43.2, 45.6, 60.2, 60.9, 64.3, 69.9 and 170.0 (C=N).

Crystallography

Yellow crystals of $[NiL^3][ClO_4]_2$ were grown from water–acetonitrile. One (0.3 × 0.35 × 0.3 mm) was mounted on a thin glass fibre and intensity data were collected at 24 °C on an Enraf-Nonius CAD4 diffractometer equipped with monochromated Mo-Kα radiation (λ 0.710 73 Å). Unit-cell parameters were determined from a least-squares fit of 23 accurately centred reflections (19 < 2θ < 29°). Data were collected in the ω-scan mode. Three intense reflections (−5 −1 −4, −6 2 −4, −6 0 6) were monitored every 200 to check stability. Of the 3322 unique reflections measured, 2901 were considered observed $[F_o > 4\sigma(F_o)]$ and used in subsequent structure analysis. The intensity data were corrected for Lorentz-polarization effects. An empirical ψ-scan absorption correction was also applied. The SHELXS 86 program[13a] was utilized for the heavy-atom method. The structure refinements were performed with the SHELXL 93 program[13b] on F^2 data. Heavy atoms (Ni and Cl) were located by use of the heavy-atom method. Other non-hydrogen atoms were found from successive Fourier-difference syntheses. All oxygen atoms of disordered perchlorate anions were refined with a fixed site occupation factor of 0.5. Anisotropic thermal parameters for all non-hydrogen atoms were included in the refinements. All hydrogen atoms bonded to carbon atoms were included in calculated positions (C–H 1.00 Å) and U values assigned based approximately on that of the attached atom. The other hydrogens (NH) were included in located positions with U 0.08 Å^2. Anomalous dispersion terms were applied to the scattering of Ni. The final cycle of refinement led to the R indices listed in Table 2.

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited of the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/65.

Results and Discussion

Nickel(III) complex of L^1

The nickel(II) complex $[NiL^1][ClO_4]_2$ is readily oxidized by concentrated HNO_3 in water, methanol, water–methanol or water–acetonitrile to the green nickel(III) complex $[NiL^1(NO_3)_2]ClO_4$. The latter is fairly stable in the solid state at room temperature. Its magnetic moment is 1.85 μ_B, which is consistent with a d^7 electronic configuration in octahedral geometry. In the infrared spectrum ν(N–H) of the secondary amino groups was observed at 3160 cm^{-1} and ν(ClO_4) at 1100 cm^{-1}. The spectrum shows a sharp peak at *ca.* 630 cm^{-1}, indicating non-co-ordination of the perchlorate anion. Peaks corresponding to the axially co-ordinated NO_3^- ions were also observed at 1480 and 1280 cm^{-1}, but no peak assignable to C=N bonds. The complex is moderately soluble in acetonitrile or water–acetonitrile (1 : 1), slightly soluble even in hot water or water–methanol (1 : 1). The electronic spectrum in acetonitrile shows maxima at 344 (ε ≈ 4.8 × 10^3) and 695 nm (ε ≈ 65 dm^3 mol^{-1} cm^{-1}). A similar spectrum was observed in nitromethane solution. The electronic spectra are comparable with those observed for related octahedral nickel(III) complexes of 14-membered tetraaza macrocycles.[14–17] The molar conductances measured in acetonitrile and nitromethane are 190 and 80 Ω^{-1}

cm^2 mol^{-1} at 20 °C, respectively, indicative of a 1 : 1 electrolyte. These data together with the elemental analysis are consistent with the formulation $[NiL^1(NO_3)_2]ClO_4$, in which two NO_3^- anions are co-ordinated to Ni^{III}. When the complex was dissolved in water–acetonitrile (1 : 1) the solution turned greenish brown and showed maxima at 390 and 555 nm. Furthermore, the molar conductance was 420 Ω^{-1} cm^2 mol^{-1}. These results strongly indicate that, in water–acetonitrile (1 : 1), the NO_3^- ions of $[NiL^1(NO_3)_2]^+$ are replaced by solvent molecules.[16]

Synthesis of unsaturated nickel(II) complexes

As described in the Experimental section, the reaction of $[NiL^1][ClO_4]_2$ with concentrated HNO_3 in a water–methanol (1 : 1) suspension precipitates the green solid $[NiL^1(NO_3)_2]ClO_4$. Further reaction of the resulting suspension with concentrated HNO_3 at *ca.* 60 °C, followed by addition of an excess of $NaClO_4$, produces the diimine complex $[NiL^2][ClO_4]_2$ as the main product. On the other hand, when a suspension of $[NiL^1][ClO_4]_2$ in water–acetonitrile (1 : 1) was treated with concentrated HNO_3 the crude product isolated contained the monoimine complex $[NiL^3][ClO_4]_2$ and a relatively small amount of $[NiL^2][ClO_4]_2$. Interestingly, the proportion of the two complexes in the crude product was strongly affected by the experimental conditions. It was found that the initial precipitation of the nickel(III) complex $[NiL^1(NO_3)_2]ClO_4$ in the course of the reaction decreases the relative amount of $[NiL^3][ClO_4]_2$ in the crude product; in the case of the reaction of concentrated HNO_3 with $[NiL^1][ClO_4]_2$ or $[NiL^1(NO_3)_2]ClO_4$ suspended in a small volume of water–acetonitrile (1 : 1), the relative amount of $[NiL^3][ClO_4]_2$ in the crude product was sometimes smaller than that of $[NiL^2][ClO_4]_2$. However, when concentrated HNO_3 was added to a hot (≈ 60 °C) water–acetonitrile (1 : 1) suspension of $[NiL^1][ClO_4]_2$ with vigorous stirring to prevent precipitation of the green solid $[NiL^1(NO_3)_2]ClO_4$ the main product was $[NiL^3][ClO_4]_2$ which can readily be isolated by fractional recrystallizations of the crude product from hot water (see Experimental section). The complex $[NiL^3][ClO_4]_2$ can be also prepared as a main product by the reaction of a hot homogeneous water–acetonitrile (1 : 1) solution of $[NiL^1(NO_3)_2]ClO_4$ with concentrated HNO_3. In all cases, an elevated temperature appears to be crucial for the oxidative dehydrogenation of $[NiL^1]^{2+}$ as we found that, even after prolonged stirring (> 1 d) of the reaction mixture at room temperature, the only complex isolated and characterized was $[NiL^1(NO_3)_2]ClO_4$.

The reasons for the selective formation of the two unsaturated nickel(II) complexes from the reaction of $[NiL^1]^{2+}$ with HNO_3, depending on the reaction conditions, are not clearly understood at this time. However, it is clear that the nickel(III) species is an intermediate in each case; the reaction begins with the oxidation of the nickel(II) to nickel(III) species which undergoes metal-ion-assisted oxidative dehydrogenation of the ligand.[1–11] From the above results the following conclusions can be drawn. The major nickel(III) species formed in the heterogeneous water–methanol (1 : 1) suspension is the green solid $[NiL^1(NO_3)_2]ClO_4$ which is further oxidized to the nickel(II) complex of L^2. On the other hand, as expected from the electronic spectra and molar conductance of $[NiL^1(NO_3)_2]ClO_4$, the main nickel(III) species dissolved in the homogeneous water–acetonitrile (1 : 1) solution may be $[NiL^1(solv)_2]^{3+}$ (solv = MeCN or H_2O) which undergoes dehydrogenation to form the nickel(II) complex of L^3. To our knowledge, such a selective dehydrogenation of a polyaza macrocyclic nickel(II) complex depending on the solvent system has not been reported previously. We tentatively suggest that the oxidative dehydrogenation of $[NiL^1]^{2+}$ can be affected by the axial ligands of the nickel(III) species.

It has been reported that $[NiL^5]^{2+}$ is readily oxidized in a concentrated HNO_3 solution to produce $[NiL^7]^{2+}$.[7,10] However, all attempts at further oxidative dehydrogenation of $[NiL^2]^{2+}$ or $[NiL^3]^{2+}$ from the reaction of the complex with HNO_3 were unsuccessful. Under the present experimental conditions, the only complexes isolated were the starting materials; the addition of an excess of concentrated HNO_3 to the reaction mixture often results in decomposition of the complexes.

Properties of the unsaturated nickel(II) complexes

The infrared and electronic absorption spectra (Table 1) of $[NiL^2][ClO_4]_2$ prepared in the present work as well as ^{1}H and ^{13}C NMR spectra (see Experimental section) of its hexafluorophosphate salt are identical with those reported for N-*meso*-$[NiL^2]^{2+}$, which was synthesized from the reaction between nickel(II) ion and L^2·2HClO$_4$.[12] Other properties of the complex are also identical with those reported for N-*meso*-$[NiL^2]^{2+}$ previously.[12]

The monoimine complex $[NiL^3][ClO_4]_2$ is quite stable in the solid state and is soluble in polar solvents such as water, acetonitrile and nitromethane. The ^{1}H NMR spectrum of $[NiL^3][PF_6]_2$ shows two doublets at δ 1.21 and 1.92 for the two methyl groups and the ^{13}C NMR spectrum shows 20 peaks (see Experimental section). These data indicate that the complex contains only one imino group. The structure of $[NiL^3][ClO_4]_2$ was confirmed by X-ray crystallography (see below). The infrared spectrum shows ν(N–H) of the co-ordinated secondary amino groups at 3165 and 3190 cm^{-1}. A strong sharp band at *ca.* 630 cm^{-1} corresponding to the unco-ordinated perchlorate anions was observed. The most striking feature in the spectrum is that ν(C=N) of the imino group is observed at 1670 cm^{-1}, which is *ca.* 30 cm^{-1} higher than that observed for the complex of L^2. The molar conductance for $[NiL^3][ClO_4]_2$ measured in water is 205 Ω^{-1} cm^2 mol^{-1}, indicative of a 1 : 2 electrolyte. The electronic spectra (Table 1) measured in nitromethane, water and acetonitrile solutions show a d–d transition band at *ca.* 447 nm, indicating that the metal ion is in a square-planar Ni^{II}N$_4$ environment. In each solvent, the wavelength is intermediate between those of $[NiL^1]^{2+}$ and $[NiL^2]^{2+}$, supporting that the degree of unsaturation of a polyaza macrocyclic ligand strongly affects the ligand-field strength. The molar absorption coefficient for $[NiL^3]^{2+}$ is somewhat higher than those for the complexes of L^1 and L^2. This may be due to the more distorted structure caused by the asymmetric structure of the complex. The cyclic voltammograms of $[NiL^3][ClO_4]_2$ obtained in 0.1 mol dm^{-3} $NBu^n_4ClO_4$–acetonitrile solution showed one anodic and cathodic peak corresponding to a Ni^{II}–Ni^{III}, process. The oxidation potential [+1.13 V *vs.* saturated calomel electrode (SCE) at 20 °C] of the complex also falls between those for the nickel(II) complexes of L^1 (+1.08 V) and L^2 (+1.24 V). This result corresponds to the generally observed trend that stepwise increase in the unsaturation of a 14-membered tetraaza macrocyclic nickel(II) complex increases the degree of polarizability of the Ni–N bond and makes the oxidation of the complex a more unfavourable process.[12,18,19]

Crystal structure of $[NiL^3][ClO_4]_2$

The crystal structure of the diimine complex $[NiL^2][ClO_4]_2$ prepared from the reaction of the metal ion with L^3·2HClO$_4$ has been reported.[20] The structure shows that the complex has a square-planar geometry around the metal centre and has N-*meso* conformation with an inversion symmetry. The Ni–N (imine) and Ni–N (amine) distances of $[NiL^2]^{2+}$ were reported to be 1.888(3) and 1.924(3) Å, respectively.

The ORTEP[21] drawing of the complex cation $[NiL^3]^{2+}$ is shown in Fig. 1 with the atomic labelling for the non-hydrogen atoms. The complex has a somewhat distorted square-planar co-ordination geometry with a *trans*-(III) type conformation.

Table 1 Infrared and electronic spectral data

Complex	IR (cm^{-1}) ν(C=N)	IR (cm^{-1}) ν(N–H)	Electronic,[a] λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})
$[NiL^1][ClO_4]_2$[b]		3185	463 (73), 459 (70),[c] 465 (66)[d]
$[NiL^2][ClO_4]_2$	1640	3200	439 (77), 440 (73),[c] 441 (73)[d]
$[NiL^3][ClO_4]_2$	1670	3165 3190	446 (87), 445 (90),[c] 447 (90)[d]

[a] In nitromethane solution at 25 °C unless otherwise specified. [b] Ref. 12. [c] In acetonitrile solution. [d] In aqueous solution.

Table 2 Crystal and refinement data for $[NiL^3][ClO_4]_2$

Formula	$C_{20}H_{38}Cl_2N_4NiO_8$
M	592.15
Crystal symmetry	Monoclinic
Space group	$P2_1/a$ (no. 14)
a/Å	13.922(2)
b/Å	12.754(2)
c/Å	15.301(4)
β/°	98.543(9)
U/Å^3	2686.6(9)
Z	4
D_c/g cm^{-3}	1.464
μ/cm^{-1}	9.7
Transmission coefficients	0.948–1.000
2θ Limit/°	46
No. unique data	3322
No. observed data [$F_o > 4\sigma(F_o)$]	2901
No. variables	394
$R1$[a]	0.0647
$wR2$[b]	0.1782
Goodness of fit	1.115

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_c|$. [b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$; $w = 1/[\sigma^2(F_o^2) + (0.1171P)^2 + 4.242P]$; $P = [\max(F_c^2, 0) + 2F_o^2]/3$.

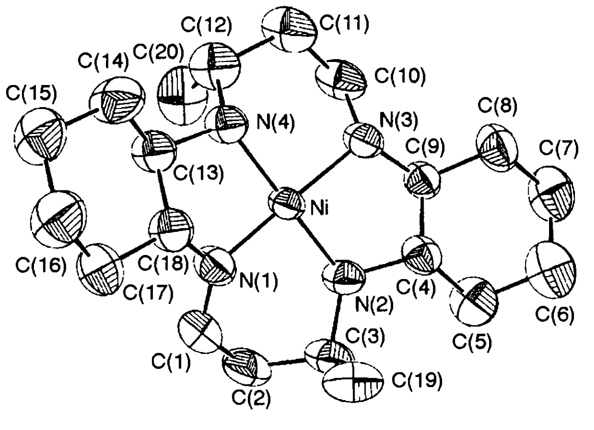


Fig. 1 An ORTEP drawing of $[NiL^3]^{2+}$ in $[NiL^3][ClO_4]_2$ with the atomic labelling scheme

The saturated six-membered chelate ring and the cyclohexane rings adopt a chair conformation. Selected bond distances and angles are listed in Table 3. The N(1)–C(1) bond distance [1.291(9) Å] is much shorter than other N–C bond distances and corresponds to the C=N double bond. The four Ni–N distances range from 1.862(5) to 1.930(5) Å; the Ni–N(1) (imine) distance is shorter than Ni–N (amine) distances as usual. Despite a substantial variation, the average Ni–N distance (1.906 Å) of the complex is comparable with that of the diimine complex $[NiL^2]^{2+}$ (1.907 Å)[20] or those of the reported low-spin square-planar nickel(II) complexes of 14-membered tetraaza macrocycles,[22–24] indicative of a low-spin nickel(II) complex. One of the most remarkable structural features of the complex is that the bond angles about the metal ion somewhat deviate from ideal square-planar angles; the N(1)–Ni–N(3) and N(2)–Ni–N(4) angles are 173.5(2) and 175.9(2)°, respectively, and the metal ion is displaced *ca.* 0.0215 Å out of the mean NiN_4 plane. Furthermore, the N(1)–Ni–N(2) angle is apparently larger than N(3)–Ni–N(4). The N(1)–C(1)–C(2) and C(1)–N(1)–C(18) bond angles are close to 120°, in agreement with in-plane sp^2 hybridization at the C(1) and N(1) centres, and are much larger than the remaining N–C–C or C–N–C angles. The C(1)–N(1)–Ni bond angle is much larger than C(10)–N(3)–Ni. The introduction of the C(1)–N(1) double bond also increases the C(3)–N(2)–Ni angle; the C(3)–N(2)–Ni angle [119.8(4)°] is distinctly larger than C(12)–N(4)–Ni angle [115.4(4)°] in the saturated chelate ring.

Table 3 Selected bond distances (Å) and angles (°) for $[NiL^3][ClO_4]_2$

Ni–N(1)	1.862(5)	Ni–N(2)	1.910(5)
Ni–N(3)	1.930(5)	Ni–N(4)	1.925(5)
N(1)–C(1)	1.291(9)	N(1)–C(18)	1.466(8)
N(2)–C(3)	1.509(8)	N(2)–C(4)	1.504(8)
N(3)–C(9)	1.480(8)	N(3)–C(10)	1.503(9)
N(4)–C(12)	1.506(9)	N(4)–C(13)	1.493(8)
N(1)–Ni–N(3)	173.5(2)	N(2)–Ni–N(4)	175.9(2)
N(1)–Ni–N(2)	95.7(2)	N(3)–Ni–N(4)	92.6(2)
N(1)–Ni–N(4)	86.2(2)	N(2)–Ni–N(3)	86.0(2)
C(1)–N(1)–C(18)	121.7(6)	C(3)–N(2)–C(4)	114.8(5)
C(9)–N(3)–C(10)	111.5(5)	C(12)–N(4)–C(13)	113.5(5)
N(1)–C(1)–C(2)	121.1(6)	N(1)–C(18)–C(13)	105.4(5)
N(2)–C(3)–C(2)	106.1(6)	N(2)–C(4)–C(9)	104.4(5)
N(3)–C(10)–C(11)	109.8(6)	N(3)–C(10)–C(11)	109.8(6)
N(4)–C(12)–C(11)	107.7(6)	N(4)–C(13)–C(18)	106.3(5)
C(1)–N(1)–Ni	127.7(5)	C(10)–N(3)–Ni	116.8(4)
C(3)–N(2)–Ni	119.8(4)	C(12)–N(4)–Ni	115.4(4)

As described above, the wavelengths of the d–d band of $[NiL^3]^{2+}$ are somewhat longer than that of $[NiL^2]^{2+}$ in spite of the similar average Ni–N bond distance. It can be suggested that the weaker ligand field and the larger molar absorption coefficient in the visible spectrum of $[NiL^3]^{2+}$, compared to those of $[NiL^2]^{2+}$, is strongly related to the distorted structure.

Conclusion

The diimine complex $[NiL^2]^{2+}$ and the monoimine complex $[NiL^3]^{2+}$ can be prepared selectively by reactions of the saturated complex $[NiL^1]^{2+}$ with HNO_3. This work clearly shows that the oxidative dehydrogenation reaction is strongly affected by the transient nickel(III) species.

Acknowledgements

S.-G. Kang acknowledges the Ministry of Education, Republic of Korea for financial support through the Basic Science Research Program (BSRI-95-3403). J. Kim and C.-H. Kwak are grateful to the Ministry of Education for financial support (BSRI-95-3429) and to the Center of Molecular Science, Korea Advanced Institute of Science and Technology for the X-ray data collection.

References

1 C. K. Poon and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1981, 1019 and refs. therein.
2 C. J. Hipp, L. F. Lindoy and D. H. Busch, *Inorg. Chem.*, 1972, **11**, 1988.
3 A. McAuley and C. Xu, *Inorg. Chem.*, 1992, **31**, 5549.
4 H. S. Mountford, L. O. Spreer, J. W. Otvos, M. Calvin, K. J. Brewer, M. Richter and B. Scott, *Inorg. Chem.*, 1992, **31**, 718.
5 H. S. Mountford, D. B. MacQueen, A. Li, J. W. Otvas, M. Calvin, R. B. Frenkel and L. O. Spreer, *Inorg. Chem.*, 1994, **33**, 1748.
6 M. P. Suh, G.-Y. Kong and I.-S. Kim, *Bull. Korean Chem. Soc.*, 1993, **14**, 439.
7 S. C. Tang and R. H. Holm, *J. Am. Chem. Soc.*, 1975, **97**, 3359.

8 G. C. Gordon, S.-M. Peng and V. L. Goedken, *Inorg. Chem.*, 1978, **17**, 3578.
9 V. L. Goedken and D. H. Busch, *J. Am. Chem. Soc.*, 1972, **94**, 7355.
10 E. K. Barefield and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 108.
11 R. A. Kolinski, B. Korybut-Daszkiewicz and Z. Kubaj, *Inorg. Chim. Acta*, 1982, **57**, 269.
12 S.-G. Kang, J. K. Kweon and S.-K. Jung, *Bull. Korean Chem. Soc.*, 1991, **12**, 483.
13 G. M. Sheldrick, (*a*) SHELXS 86 User Guides, Crystallographic Department, University of Göttingen, 1985, (*b*) SHELXL 93 User Guides, Crystallographic Department, University of Göttingen, 1993.
14 K. D. Whitburn and G. S. Laurance, *J. Chem. Soc., Dalton Trans.*, 1979, 139.
15 E. S. Gore and D. H. Busch, *Inorg. Chem.*, 1973, **12**, 1.
16 R. I. Haines and A. McAuley, *Inorg. Chem.*, 1980, **19**, 719.
17 A. McAuley and S. Subramanian, *Inorg. Chem.*, 1991, **30**, 371.
18 F. V. Lovecchio, E. G. Gore and D. H. Busch, *J. Am. Chem. Soc.*, 1974, **96**, 3109.
19 S.-G. Kang and J. K. Kweon, *Bull. Korean Chem. Soc.*, 1992, **13**, 256.
20 S.-G. Kang, M.-S. Kim, D. Whang and K. Kim, *J. Chem. Soc., Dalton Trans.*, 1994, 853.
21 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
22 M. P. Suh, S.-G. Kang, V. L. Goedken and S.-H. Park, *Inorg. Chem.*, 1991, **30**, 365.
23 K. Kobiro, A. Nakayama, T. Hiro, M. Suwa and T. Tobe, *Inorg. Chem.*, 1992, **31**, 676.
24 N. F. Curtis, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979.

Received 29th December 1995; *Paper* 5/08434B