Synthesis, Characterization and Structure of the Highly Sterically Congested Complex (3,14-Dimethyl-14-nitromethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docos-2-ene)nickel Diperchlorate and Structure of (3,14-Dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosa-2,13-diene)nickel Diperchlorate†

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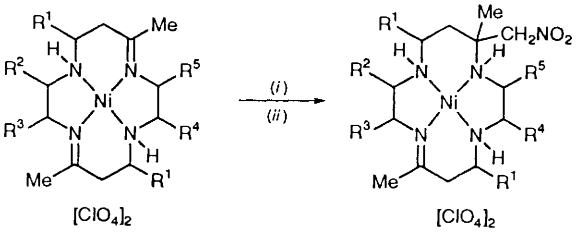
The reaction of the diimine complex $[NiL^1][ClO_4]_2$ (L^1 = 3,14-dimethyl-2,6,13,17-tetraazatricyclo[16.4.0.$0^{7,12}$]docosa-2,13-diene), containing cyclohexane subunits fused to the five-membered chelate rings, with nitromethane in the presence of triethylamine produced the highly sterically congested complex $[NiL^2][ClO_4]_2$ (L^2 = 3,14-dimethyl-14-nitromethyl-2,6,13,17-tetraazatricyclo-[16.4.0.$0^{7,12}$]docos-2-ene) containing one nitromethyl pendant arm. The electronic spectrum of $[NiL^2]^{2+}$ in nitromethane solution shows the d–d band at *ca.* 490 nm (ε = 170 $dm^3 mol^{-1} cm^{-1}$). The wavelength and the molar absorption coefficient are extraordinarily longer and larger, respectively, than those for square-planar nickel(II) complexes of L^1 and other related 14-membered polyaza macrocycles. The crystal structures of $[NiL^1][ClO_4]_2$ and $[NiL^2][ClO_4]_2$ revealed that the former has normal square-planar geometry with the nickel atom lying on the N_4 plane, whereas the latter has a severely distorted square-planar geometry with the metal atom 0.118 Å out of the mean plane of the donor nitrogen atoms. The steric effects of the substituents of the complexes on the geometry and the spectra are discussed. Crystal data: for $[NiL^1][ClO_4]_2$, monoclinic, space group $P2_1/n$, a = 10.423(3), b = 8.9375(6), c = 13.457(3) Å, β = 94.459(12)°, Z = 2, R = 0.056 and R' = 0.057 for 2349 independent reflections with $F_o^2 > 3\sigma(F_o^2)$; for $[NiL^2][ClO_4]_2$, monoclinic, space group $P2_1/n$, a = 11.968(3), b = 12.6208(14), c = 19.358(6) Å, β = 105.008(15)°, Z = 4, R = 0.046 and R' = 0.045 for 3382 independent reflections with $F_o^2 > 3\sigma(F_o^2)$.

A number of polyaza macrocyclic compounds with alkyl pendant arms have been prepared and investigated. Alkyl groups on the donor nitrogen atoms significantly affect the ligand-field strength, chemical properties, and structures of their nickel(II) complexes.[1–9] Although some chemical properties of macrocyclic complexes are also affected by alkyl groups attached to the carbon atoms, it has been generally observed that the effect is not as significant; in most cases, the ligand-field strength and the co-ordination geometry are rarely affected by the alkyl groups.[9–16] The effect of the *C*-alkyl groups has therefore received much less attention than that of the *N*-alkyl groups.

Recently, the nickel(II) complexes **2a**–**2d** containing one *C*-nitromethyl group were synthesised by the nucleophilic addition of nitromethanide to one of the imine bonds of **1a**–**1d** (Scheme 1).[16–18] However, in the case of **1e**, no such nucleophilic addition was observed, which was attributed to the steric hindrance of the methyl group(R^5) in the five-membered chelate ring.[16] In this work we have examined the reaction of the sterically congested complex $[NiL^1]^{2+}$, which contains cyclohexane rings fused to the five-membered chelate rings, with nitromethane anion to determine the effects of the cyclohexane rings. Somewhat surprisingly, it was found that the complex $[NiL^2]^{2+}$ is produced at low temperature, unlike **1e**. Moreover, the new complex exhibits quite interesting spectral properties; the wavelength and molar absorption coefficient of the d–d band are extraordinarily longer and larger, respectively, than those for $[NiL^1]^{2+}$ and other related nickel(II) complexes of 14-membered polyaza macrocycles. In order to understand the unusual spectral properties we determined the crystal structures of $[NiL^1][ClO_4]_2$ and $[NiL^2][ClO_4]_2$.



1a $R^1 = R^2 = R^3 = R^4 = R^5 = H$ **2a**
1b $R^1 = R^2 = R^5 = H$; $R^3 = R^4 = Me$ **2b**
1c $R^1 = R^3 = R^5 = H$; $R^2 = R^4 = Me$ **2c**
1d $R^1 = Me$; $R^2 = R^3 = R^4 = R^5 = H$ **2d**
1e $R^1 = R^2 = R^4 = H$; $R^3 = R^5 = Me$

Scheme 1 (*i*) $MeNO_2$, NEt_3; (*ii*) $HClO_4$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Experimental

Measurements.—The IR spectra were obtained on a Shimadzu IR-440 spectrophotometer. Conductance measurements were made by using a Metrohm Herisau E518 conductometer. Visible spectra were obtained by using a Kontron Uvikon 860 UV/VIS spectrophotometer, NMR spectra with a Bruker WP 300 FT spectrometer. Elemental analyses were performed at the Kolon R & D Center, Kumi, Korea.

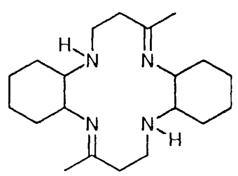
Materials.—All chemicals used in synthesis were of reagent grade and were used without further purification. The complex $[NiL^1][ClO_4]_2$ was prepared as described previously.[11]

Synthesis of $[NiL^2][ClO_4]_2$.—To a warm nitromethane (40 cm^3) suspension of $[NiL^1][ClO_4]_2$ (5.0 g, 9.0 mmol) was added triethylamine (6.0 cm^3). The mixture was stirred for 3–4 h at room temperature and stored in a refrigerator for several days. During this period it became a homogeneous solution which turned deep red-purple. The solution was acidified in an ice-bath with 60% perchloric acid and then filtered at room temperature. After more than half of the volume of the filtrate had been evaporated at room temperature, water–methanol (3 : 1, 50 cm^3) and 60% perchloric acid (5.0 cm^3) were added. The resulting solution was allowed to evaporate slowly at room temperature. The red crystals formed were filtered off, washed with water–methanol (1 : 1), and dried in air (yield ≈60%) (Found: C, 38.35; H, 6.00; N, 10.45. $C_{21}H_{39}Cl_2N_5NiO_{10}$ requires C, 38.70; H, 6.00; N, 10.75%. NMR: ^1H (CD_3NO_2), δ 1.42 (s, CMe), and 2.40 (s, N=CMe); ^{13}C (CD_3NO_2), δ 24.7, 25.2, 25.3, 25.4, 25.6, 26.2, 29.6, 29.8, 32.2, 33.9, 37.1, 37.7, 38.5, 43.5, 60.1, 60.9, 63.3, 69.2, 69.7, 80.7 ($-CH_2NO_2$) and 193.9 (C=N).

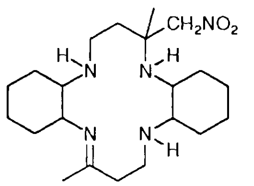
Crystal Structure Determination.—Crystals of $[NiL^2][ClO_4]_2$ suitable for the X-ray crystallographic work were obtained by dissolving the red solid in a 0.1 mol dm^{-3} $HClO_4$ acetonitrile solution, followed by the addition of a small amount of ethanol and water, and then allowing the solution to stand at room temperature. Single crystals of $[NiL^1][ClO_4]_2$ were obtained by recrystallization from acetonitrile–ethanol (5 : 1) solution.

X-Ray data were collected on an Enraf-Nonius CAD4 diffractometer using Mo-Kα radiation at room temperature. Cell parameters and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. The intensities of three standard reflections, recorded every 3 h of X-ray exposure, showed no systematic changes. All the calculations were carried out with the Enraf-Nonius MOLEN package.[19] The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were also applied. The structures were solved by a combination of Patterson and Fourier difference methods and refined by full-matrix least squares. All the non-hydrogen atoms were refined anisotropically. For $[NiL^1][ClO_4]_2$ the hydrogen positions were found from the Fourier difference map and refined. The positions of hydrogen atoms in $[NiL^2][ClO_4]_2$ were idealized [d(C–H) = 0.95 Å] and included in the calculations of the structure factors as fixed contributions. In both cases each hydrogen atom was assigned an isotropic thermal parameter 1.2 times that of the attached atom. The final cycle of refinement led to the R indices listed in Table 1. The final positional parameters for $[NiL^1][ClO_4]_2$ and $[NiL^2][ClO_4]_2$ are listed in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.



L¹



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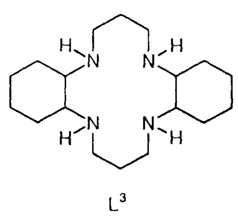

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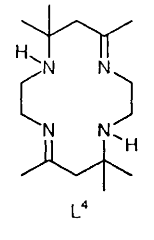

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Table 1 Crystal and refinement data for $[NiL^1][ClO_4]_2$ and $[NiL^2][ClO_4]_2$[a]

Complex	$[NiL^1][ClO_4]_2$	$[NiL^2][ClO_4]_2$
Formula	$C_{20}H_{36}N_4Cl_2NiO_8$	$C_{21}H_{39}Cl_2N_5NiO_{10}$
M	590.15	651.19
a/Å	10.423(3)	11.968(3)
b/Å	8.9375(6)	12.6208(14)
c/Å	13.457(3)	19.358(6)
β/°	94.459(12)	105.008(15)
U/Å³	1249.8(4)	2824.2(13)
Z	2	4
F(000)	620	1368
D_c/g cm⁻³	1.568	1.528
μ/cm⁻¹	10.4	9.35
Transmission coefficients	0.929–1.000	0.961–1.000
Crystal size/mm	0.3 × 0.4 × 0.4	0.3 × 0.4 × 0.4
Scan mode	ω/2θ	ω
2θ Limit/°	60	53
No. of data collected	4048	5508
No. of unique data	3858	5229
No. of unique data with $F_o^2 > 3\sigma(F_o^2)$	2349	3382
No. of variables	214	352
R[b]	0.056	0.046
R'[c]	0.057	0.045
Goodness of fit	0.65	0.48

[a] Details in common: monoclinic, space group $P2_1/n$ (no. 14); 23 °C; graphite monochromatic Mo-Kα radiation (λ = 0.709 26Å); take-off angle 2.0°; ω scan width = 0.8 + 0.35 tan θ; $w = 4(F_o)^2/[3\sigma(F_o)^2]^2$. [b] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [c] $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$; $w = 4F_o^2/\sigma^2(F_o^2)$; $\sigma(F_o^2) = [\sigma^2(I) + (pI)^2]^{\frac{1}{2}}$.

Table 2 Positional parameters for the non-hydrogen atoms of $[NiL^1][ClO_4]_2$ with estimated standard deviations (e.s.d.s) in parentheses

Atom	x	y	z
Ni	0	0	0.5
Cl	0.303 0(1)	0.126 3(1)	0.034 28(9)
O(1)	0.377 0(9)	0.153 8(9)	0.117 9(5)
O(2)	0.295 8(8)	−0.018 9(6)	0.008 3(6)
O(3)	0.183 5(7)	0.183(1)	0.044 4(8)
O(4)	0.340 5(8)	0.214 6(7)	−0.039 9(5)
N(1)	0.130 7(3)	0.147 0(4)	0.481 2(3)
N(2)	0.049 9(3)	0.028 2(4)	0.636 6(2)
C(1)	0.237 0(4)	0.092 4(5)	0.552 3(3)
C(2)	0.363 7(4)	0.178 5(6)	0.558 7(4)
C(3)	0.457 0(5)	0.097 2(7)	0.634 4(4)
C(4)	0.404 0(5)	0.076 7(7)	0.734 0(4)
C(5)	0.272 0(4)	−0.001 3(6)	0.725 4(3)
C(6)	0.182 0(4)	0.088 2(5)	0.652 8(3)
C(7)	−0.030 4(4)	0.036 3(5)	0.704 1(3)
C(8)	−0.162 6(4)	−0.027 9(7)	0.682 1(3)
C(9)	−0.162 9(5)	−0.170 7(6)	0.622 6(4)
C(10)	−0.002 2(5)	0.107 7(8)	0.803 5(4)

Table 3 Positional parameters for the non-hydrogen atoms of $[NiL^2][ClO_4]_2$ with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	0.021 96(5)	0.446 38(4)	0.782 57(3)	C(3)	0.010 2(4)	0.231 2(4)	0.828 0(3)
Cl(1)	0.220 5(1)	0.469 6(1)	0.659 05(6)	C(4)	0.195 9(4)	0.334 0(3)	0.865 5(2)
Cl(2)	0.264 6(1)	0.541 9(1)	1.136 82(8)	C(5)	0.260 9(4)	0.253 7(4)	0.919 3(2)
O(1)	−0.053 8(4)	0.652 7(4)	0.995 5(2)	C(6)	0.390 1(4)	0.264 7(4)	0.924 9(3)
O(2)	0.005 7(4)	0.771 0(3)	0.937 0(3)	C(7)	0.432 9(4)	0.376 4(5)	0.943 5(3)
O(3)	0.226 2(4)	0.560 1(3)	0.705 0(2)	C(8)	0.362 4(4)	0.457 6(4)	0.892 2(2)
O(4)	0.318 1(3)	0.465 4(4)	0.632 4(2)	C(9)	0.234 7(4)	0.445 8(4)	0.890 0(2)
O(5)	0.120 2(5)	0.483 7(5)	0.602 6(3)	C(10)	0.128 5(4)	0.625 8(4)	0.872 8(2)
O(6)	0.206 4(4)	0.376 7(3)	0.697 8(2)	C(11)	0.077 9(4)	0.699 4(4)	0.809 4(3)
O(7)	0.242 7(4)	0.447 8(5)	1.168 9(3)	C(12)	−0.034 8(4)	0.668 5(4)	0.759 3(3)
O(8)	0.288 2(6)	0.515 5(6)	1.072 4(3)	C(13)	−0.146 0(4)	0.537 9(4)	0.675 0(2)
O(9)	0.168 5(5)	0.604 2(5)	1.122 6(5)	C(14)	−0.196 6(5)	0.613 1(4)	0.613 1(3)
O(10)	0.360 6(6)	0.588 3(6)	1.176 4(5)	C(15)	−0.316 3(5)	0.574 3(5)	0.572 9(3)
N(1)	−0.072 0(3)	0.362 4(3)	0.707 2(2)	C(16)	−0.315 5(5)	0.460 6(5)	0.549 6(3)
N(2)	0.067 6(3)	0.334 3(3)	0.850 0(2)	C(17)	−0.260 9(4)	0.388 8(4)	0.612 4(3)
N(3)	0.155 6(3)	0.522 1(3)	0.840 6(2)	C(18)	−0.139 1(4)	0.427 7(4)	0.646 7(2)
N(4)	−0.031 1(3)	0.567 0(3)	0.721 3(2)	C(19)	−0.060 0(5)	0.220 3(4)	0.622 6(3)
N(5)	−0.002 9(4)	0.680 2(4)	0.952 8(2)	C(20)	0.043 8(4)	0.593 2(4)	0.916 5(3)
C(1)	−0.041 0(4)	0.267 8(4)	0.695 6(3)	C(21)	0.236 5(4)	0.677 5(4)	0.920 7(3)
C(2)	0.018 7(4)	0.197 2(4)	0.755 9(3)				

Table 4 Electronic spectral data

Complex	λ_{max}/nm(ε/$dm^3 mol^{-1} cm^{-1}$)[a]
$[NiL^1][ClO_4]_2$	439(77), 442(73),[b] 440(73)[c]
$[NiL^2][ClO_4]_2$	489(170), 488(171)[b]
$[NiL^3][ClO_4]_2$[d]	455(80)[c]
1a[e]	446(87), 448(82)[c]
1d[f]	442(80)[c]
2a[g]	445(82)[h]
2d[g]	452(53)[h]

[a] In nitromethane solution at 25 °C unless otherwise specified. [b] In acetonitrile solution. [c] In aqueous solution. [d] Ref. 20. [e] Ref. 12. [f] Ref. 13. [g] Ref. 16. [h] In 0.10 mol dm^{-3} $HClO_4$ solution.

Results and Discussion

Synthesis and Properties.—The red complex $[NiL^2][ClO_4]_2$ containing one *C*-nitromethyl pendant arm is readily prepared by the reaction of $[NiL^1][ClO_4]_2$ with nitromethane in the presence of triethylamine at *ca.* 5 °C, followed by addition of an excess of perchloric acid. Keeping the reaction temperature below 15 °C appears to be crucial as we found that, at an elevated temperature (>30 °C), only the starting material $[NiL^1][ClO_4]_2$ was isolated even after prolonged stirring (>1 week) of the reaction mixture. It was expected that the complex of L^1 initially reacts with nitromethanide, formed by the reaction of nitromethane with the base, to produce the complex of a deprotonated form of L^2 as an intermediate.[16,17] However, all efforts to isolate the intermediate were unsuccessful.

The complex $[NiL^2][ClO_4]_2$ is soluble in nitromethane and acetonitrile but insoluble in water. It is extremely stable in the solid state and even in solutions containing a strong acid such as perchloric acid. The visible spectra of the complex in 1.0 mol dm^{-3} $HClO_4$, acetonitrile or nitromethane solution showed that less than 2% decomposition in 20 h at 25 °C. This result is quite similar to that observed for $[NiL^1]^{2+}$.[11] However, the complex of L^2 rapidly decomposes to yield $[NiL^1]^{2+}$ in acetonitrile solution containing triethylamine (0.1 mol dm^{-3}) even at room temperature. This behaviour is in contrast to the report that the addition of base to a solution of **2d** causes simple deprotonation of the pendant nitromethyl group.[17]

The IR spectrum of $[NiL^2][ClO_4]_2$ shows ν(N–H) of the co-ordinated secondary amino groups at 3165, 3200 and 3240 cm^{-1} and ν(ClO_4^-) at 1100 cm^{-1}. Single bands arising from the pendant nitro group and from the imine bond are observed at 1563 and 1635 cm^{-1}, respectively. The molar conductances measured in nitromethane and acetonitrile solutions of the complex are 148 and 261 Ω^{-1} cm^2 mol^{-1}, respectively, indicative of a 1 : 2 electrolyte. In the ^1H NMR spectrum two singlets for the methyl groups are observed at δ 1.4 and 2.4. The ^{13}C NMR spectrum showing 21 peaks (see Experimental section) is consistent with the structure of L^2 and indicates that only a single isomer of the complex was isolated.

The electronic spectra (Table 4) of $[NiL^2][ClO_4]_2$ in nitromethane and acetonitrile solutions show a d–d transition band at *ca.* 490 nm, indicating that the complex has a square-planar $Ni^{II}N_4$ chromophore. It is however quite interesting that the wavelength of the band is *ca.* 50 nm longer than that for the diimine complex $[NiL^1]^{2+}$,[11] and, moreover, *ca.* 40 nm longer than those for **2a**–**2d** containing one nitromethyl pendant arm.[16] Such a large red shift caused by the simple introduction of a *C*-nitromethyl group has not been observed in other systems. In the cases of **2a**–**2d**,[16] the bands appear at *ca.* 450 nm, which is similar to those for **1a**–**1d**.[12,13] Furthermore, the molar absorption coefficient (≈ 170 dm^3 mol^{-1} cm^{-1}) for $[NiL^2]^{2+}$ is more than twice those for **2a**–**2d** and the complexes of L^1 and L^3. These strongly indicate a more distorted structure of $[NiL^2]^{2+}$ due to the increased steric crowding caused by the presence of the cyclohexane subunit together with the methyl and nitromethyl pendant arms.

Structure Analyses.—The ORTEP[21] drawings of the complexes $[NiL^1][ClO_4]_2$ and $[NiL^2][ClO_4]_2$ are shown in Figs 1 and 2, respectively, with the atomic labelling for the non-hydrogen atoms.

The diimine complex $[NiL^1][ClO_4]_2$ has a square-planar geometry around the metal centre and has N-*meso* conformation with an inversion symmetry. The N_4 plane [N(1), N(2), N(3), N(4)] is planar and the Ni atom is situated at the inversion centre of the plane. The shortest Ni···O(ClO_4) distance is 3.069 Å, showing that the anion is not co-ordinated. Selected bond distances and angles of the complex are summarized in Table 5. The Ni–N(1) and Ni–N(2) bond distances are 1.924(3) and 1.888(3) Å, respectively, indicating a low-spin nickel(II) complex.[8,20,22-24] The Ni–N_{amine} [Ni–N(1)] distance is somewhat longer than the Ni–N_{imine} [Ni–N(2)] distance as is usual. Each Ni–N distance of the complex falls between those for N-*racemic*-$[NiL^4][ClO_4]_2$ [Ni–N_{amine} 1.915(4), Ni–N_{imine} 1.884(5) Å] and N-*meso*-$[NiL^4][ClO_4]_2$ [Ni–N_{amine} 1.938(2), Ni–N_{imine} 1.907(2) Å].[23] The N(1)–C(9) and N(2)–C(10) bond distances correspond to the single and double bonds, respectively. The N–Ni–N bond angles somewhat deviate from

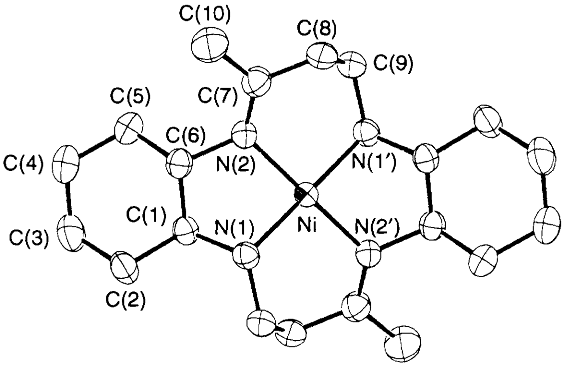

Fig. 1 An ORTEP drawing of [NiL^1]$^{2+}$ in [NiL^1][ClO$_4$]$_2$ with the atomic labelling scheme

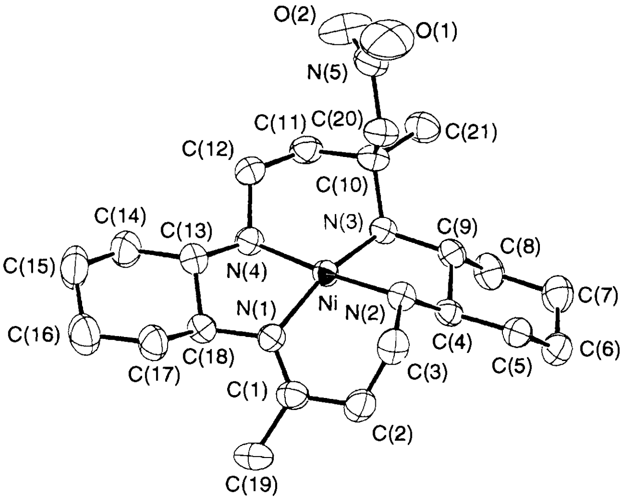

Fig. 2 An ORTEP drawing of [NiL^2]$^{2+}$ in [NiL^2][ClO$_4$]$_2$ with the atomic labelling scheme

Table 5 Selected bond distances (Å) and angles (°) for [NiL^1][ClO$_4$]$_2$*

Ni–N(1)	1.924(3)	Ni–N(2)	1.888(3)
N(1)–C(1)	1.489(5)	N(1)–C(9′)	1.477(6)
N(2)–C(6)	1.479(5)	N(2)–C(7)	1.284(6)
C(1)–C(2)	1.526(6)	C(1)–C(6)	1.509(6)
C(2)–C(3)	1.535(7)	C(3)–C(4)	1.499(8)
C(7)–C(8)	1.500(6)	C(7)–C(10)	1.491(7)
C(8)–C(9)	1.506(8)		

N(1)–Ni–N(2)	83.9(1)	N(1)–Ni–N(2′)	96.1(1)
Ni–N(1)–C(1)	101.0(2)	Ni–N(1)–C(9′)	116.0(3)
Ni–N(2)–C(6)	112.0(3)	Ni–N(2)–C(7)	123.4(3)
C(1)–N(1)–C(9′)	116.3(3)	C(6)–N(2)–C(7)	121.8(3)
N(1)–C(1)–C(2)	117.9(4)	N(1)–C(1)–C(6)	105.6(3)
C(2)–C(1)–C(6)	110.4(4)	C(1)–C(6)–C(5)	109.2(3)
N(2)–C(6)–C(1)	106.9(3)	N(2)–C(6)–C(5)	115.0(4)
N(2)–C(7)–C(8)	118.5(4)	N(2)–C(7)–C(10)	124.4(4)
C(7)–C(8)–C(9)	113.2(4)	C(8)–C(9)–N(1′)	112.9(4)

* Numbers in parentheses are e.s.d.s in the least significant digits.

Table 6 Selected bond distances (Å) and angles (°) for [NiL^2][ClO$_4$]$_2$*

Ni–N(1)	1.916(3)	Ni–N(2)	1.907(3)
Ni–N(3)	1.952(3)	Ni–N(4)	1.934(3)
O(1)–N(5)	1.199(7)	O(2)–N(5)	1.198(6)
N(1)–C(1)	1.289(6)	N(1)–C(18)	1.488(5)
N(2)–C(3)	1.483(6)	N(2)–C(4)	1.487(5)
N(3)–C(9)	1.507(5)	N(3)–C(10)	1.522(6)
N(4)–C(12)	1.485(6)	N(4)–C(13)	1.482(5)
N(5)–C(20)	1.489(7)	C(1)–C(2)	1.497(6)
C(4)–C(5)	1.518(6)	C(10)–C(20)	1.537(7)

N(1)–Ni–N(2)	96.8(1)	N(1)–Ni–N(3)	160.4(2)
N(1)–Ni–N(4)	86.2(1)	N(2)–Ni–N(3)	85.5(1)
N(2)–Ni–N(4)	174.1(2)	N(3)–Ni–N(4)	93.3(1)
C(1)–N(1)–C(18)	119.8(4)	C(3)–N(2)–C(4)	115.7(3)
C(9)–N(3)–C(10)	117.1(3)	C(12)–N(4)–C(13)	111.8(3)
Ni–N(1)–C(1)	120.5(3)	Ni–N(1)–C(18)	112.6(3)
Ni–N(2)–C(3)	115.2(3)	Ni–N(2)–C(4)	103.8(3)
Ni–N(3)–C(9)	109.9(2)	Ni–N(3)–C(10)	115.3(2)
Ni–N(4)–C(12)	115.0(3)	Ni–N(4)–C(13)	106.4(3)
N(1)–C(1)–C(2)	121.1(4)	N(1)–C(1)–C(19)	123.8(4)
N(3)–C(10)–C(20)	103.7(3)	N(3)–C(10)–C(21)	112.3(4)
N(5)–C(20)–C(10)	116.4(4)	N(3)–C(9)–C(8)	114.7(4)
O(1)–N(5)–O(2)	123.1(5)	O(1)–N(5)–C(20)	115.5(5)

* Numbers in parentheses are e.s.d.s in the least significant digits.

those of the ideal square-planar geometry, as is often observed for complexes of 14-membered tetraaza macrocycles; the bond angles involved in the five-membered chelate rings are reduced to 83.9(1)°, but those in the six-membered rings are expanded to 96.1(1)°. The five-membered chelate rings have a *gauche* conformation. The cyclohexane subunits adopt a chair conformation with the diamino groups in a *trans* geometry.

As expected from the solution data, [NiL^2][ClO$_4$]$_2$ has a distorted square-planar geometry with a *trans*-(III) type conformation. The cyclohexane rings also have a chair conformation. The saturated six-membered chelate ring adopts a chair conformation and the nitromethyl group on C(10) is axial. The nitromethyl group and the cyclohexane ring containing C(8) are *anti* with respect to the macrocyclic plane. The intramolecular Ni ··· O(1) and Ni ··· O(2) distances are 5.113 and 5.109 Å, respectively, and the shortest intermolecular Ni ··· O(NO$_2$ group) distance is 4.398 Å. This indicates that the nitro group of the complex is not involved in co-ordination. The shortest Ni ··· O(ClO$_4$) distance is 3.197 Å, which is somewhat longer than that of [NiL^1][ClO$_4$]$_2$. Selected bond distances and angles for the complex L^2 are listed in Table 6. The Ni–N bond distances range from 1.907(3) to 1.952(3) Å. Despite a substantial variation, the average value (1.927 Å) is comparable with that of [NiL^1][ClO$_4$]$_2$ or those of the reported low-spin square-planar nickel(II) complexes of L^3,[20] L^4(*meso*),[23] and other 14-membered polyaza macrocycles,[8,20,22–26] which are in accord with the low-spin nickel(II). It should be pointed out that the d–d band of [NiL^2]$^{2+}$ is observed at much longer wavelength than those for the complexes of L^1, L^3,[20] L^4,[23] and other macrocycles[8,20,22–26] in spite of the similar average Ni–N bond distance. This strongly indicates that the unusually weak ligand field of [NiL^2]$^{2+}$ is not directly related to the Ni–N distances. One of the most remarkable structural features of the complex is that the angles about the nickel ion significantly deviate from the ideal square-planar angles with N(1)–Ni–N(3) 160.4(2)°. Furthermore, each of the four co-ordinated nitrogen atoms [N(1)–N(4)] is displaced by *ca.* 0.21 Å from their mean plane. The metal ion is also displaced in the same direction as the nitromethyl pendant arm, 0.118 Å out of the mean N$_4$ plane, whereas that in the complex of L^1 or L^3 (ref. 20) is not displaced or is displaced less than 0.018 Å out of the plane. Unfortunately, direct comparison of the crystal structure of [NiL^2][ClO$_4$]$_2$ with those of **2a**–**2d** cannot be made at this time, because the structures of the latter complexes are not available. The severe distortion of [NiL^2][ClO$_4$]$_2$ may be attributed to the non-bonded repulsions between the substituents on C(9) and C(10). The distances N(3)–C(9) and N(3)–C(10) are longer than those of other N–C bonds. Furthermore, the C(9)–N(3)–C(10) bond angle [117.1(3)°] deviates considerably from the ideal tetrahedral angle. These can be also attributed to the severe repulsions between the substituents on C(9) and C(10).

The crystallographic study thus suggests that the unusually weak ligand field of the complex and the large molar absorption coefficient in the visible spectrum may be due to the severe angle distortion and the displacement of the nickel out of the mean plane of the nitrogen donors. This result differs from those observed for various *N*-alkylated macrocyclic nickel(II) complexes. Alkylation on the donor nitrogens of a tetraaza macrocyclic nickel(II) complex lengthens the Ni–N bond distances, and the weakening of the ligand field caused by the *N*-alkylation has generally been attributed to the increased Ni–N bond distances due to the steric repulsions between the *N*-alkyl groups and proximate hydrogens.[1-9]

Conclusion

Although the cyclohexane subunits in $[NiL^1][ClO_4]_2$ or the nitromethyl pendant arm in complex **2a** rarely affect the ligand-field strength and/or the geometry, the introduction of the nitromethyl group into the complex of L^1 to give $[NiL^2][ClO_4]_2$ results in severe steric crowding leading to severe distortion of the structure and significant weakening of the ligand field. This work clearly shows that the ligand-field strength and geometry of a macrocyclic nickel(II) complex can be strongly affected by steric hindrances of the substituents at the carbon atoms next to the donor nitrogens. To our knowledge, $[NiL^2][ClO_4]_2$ is a rare 14-membered polyaza macrocyclic complex which has strongly distorted square-planar geometry and an extraordinarily weak ligand field caused by the simple steric crowding of the substituents at carbon.

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