Properties and Crystal Structure of a Four-co-ordinate Nickel(I) Complex with the Macrotricycle 1,3,6,8,12,15-Hexaazatricyclo[13.3.1.1^{8,12}]icosane†

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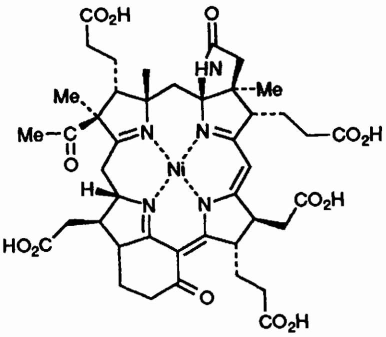
The four-co-ordinate nickel(I) macrocyclic complex *R,R,S,S*-[NiL]ClO$_4$ (L = 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]icosane) has been synthesized by the reduction of the corresponding nickel(II) complex *R,R,S,S*,-[NiL][ClO$_4$]$_2$·0.5H$_2$O with sodium amalgam in MeCN under nitrogen. It absorbs at 589 (ε = 620) and 355 nm (ε = 3020 dm^3 mol^{-1} cm^{-1}). The EPR powder spectrum shows the anisotropic axial *g* values of $g_{\parallel}$ = 2.272 and $g_{\perp}$ = 2.074. The complex crystallizes in the orthorhombic space group $P2_12_12_1$ with *a* = 8.681(2), *b* = 11.358(2), *c* = 19.146(4) Å and *Z* = 4. The structure was solved by the heavy-atom method and refined anisotropically to *R* = 0.0363 and *R'* = 0.0379 for 1551 observed reflections [$I > 3\sigma(I)$] measured with Mo-Kα radiation. It reveals a tetrahedrally distorted square-planar geometry having two sets of Ni–N bond distances, three at 1.978(3) (average) and one at 1.878(4) Å, without any noticeable expansion of the macrocyclic hole.

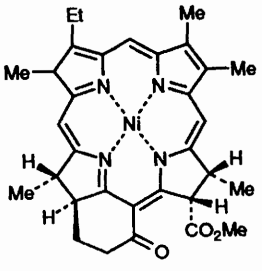
Recently, nickel(I) macrocyclic complexes have attracted considerable attention. This is because nickel(I) species were proposed to be involved in the electrocatalytic reduction of CO$_2$[1–3] and alkyl halides,[4–10] which was catalysed by nickel(II) tetraaza macrocyclic complexes. Furthermore, F$_{430}$, a nickel(II) hydrocorphinoid complex, is a prosthetic group of *S*-methyl coenzyme M reductase which catalyses the reductive cleavage of *S*-methyl coenzyme M to coenzyme M and methane in the final stage of carbon dioxide reduction in methanogenic bacteria.[11–14] An EPR signal detected with *Methanobacterium thermoautotrophicum* was attributed to a nickel(I) form of F$_{430}$ in the intact active enzyme.[15,16] However, few crystal structures of nickel(I) complexes with macrocyclic ligands[17,18] or porphyrin analogues[19] have been reported so far, and thus the structures of nickel(I) complexes have not been well documented.

It was generally assumed that the reduction of a nickel(II) macrocyclic complex to Ni^{I} would increase the Ni–N bond distances because of an additional electron in the $d_{x^2-y^2}$ orbital. However, extended X-ray absorption fine structure (EXAFS) data for nickel(I)–F$_{430}$ and –iBC indicated that the reduction of Ni^{II} resulted in two distinct sets of Ni^{I}–N bond distances with a slight expansion of the macrocycle core.[20–22] The structures of nickel(I) complexes with macrocycles L^1 and L^2 were reported by our laboratory[17] and that of L^3 by Fujita and co-workers.[18] They had square-planar geometry and showed two different sets of Ni–N bond distances; the differences between the two sets of distances were 0.04 for L^1, 0.12 for L^2 and 0.08 Å for L^3.[17,18] However, the complexes of the strained polycyclic systems L^1 and L^2 showed no expansion of the macrocyclic hole, whereas the monocyclic system L^3 showed an expansion of the Ni–N bond distances by *ca.* 0.10 Å, compared with the nickel(II) complexes. Furthermore, in the L^1 and L^2 systems there were two *cis* Ni–N bonds involving a six-membered chelate ring, while the complex of L^3 had two *trans* Ni–N bonds involving imine or amine nitrogens.

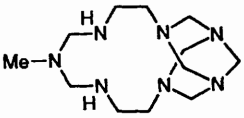
In order to establish the structural changes associated with the reduction of a nickel(II) complex, such as distortion of the co-ordination core and lengthening of Ni–N bond distances, we determined the crystal structure of the complex [NiL]ClO$_4$ (L = 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]icosane). It was shown previously that the core size of the square-planar nickel(II) complex of L is *ca.* 0.03 Å larger than that of L^2 and that ligand L is much more flexible than L^2 for accommodating the larger octahedral nickel(II) species in water.[23] Therefore, we anticipated that the structural behaviour of [NiL]ClO$_4$ might be different from those of nickel(I) complexes with L^1 and L^2. In this paper we describe the synthesis, properties and crystal structure of [NiL]ClO$_4$. Previously, we presented the spectra of the complex.[17] However, it was not possible to obtain satisfactory elemental analyses or determine the structure as we were not able to isolate the complex in crystalline form.



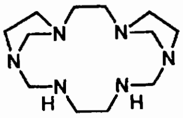
Ni–F$_{430}$



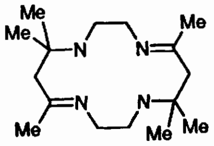
Ni–iBC



L^1



L^2



L^3

Experimental

All preparations, experiments and manipulations were conducted under nitrogen with strict exclusion of air by using

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Schlenk techniques. Nitrogen was purified by passing it through BASF and $CaCl_2$ columns. **CAUTION**: perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared, and be handled with great care.

Materials.—All solvents and reagents were purified according to the literature[24] and deaerated thoroughly prior to use. The complex $[Ni^{II}L][ClO_4]_2 \cdot 0.5H_2O$ was prepared as previously reported.[23]

Measurements.—Infrared spectra were recorded with a JASCO IR 810, electronic absorption spectra on a Shimadzu UV-260 and electron spin resonance spectra on a Bruker ER 200E-SRC spectrometer. Elemental analysis was performed by Galbraith Laboratories, TN, USA.

Synthesis of (R,R,S,S-1,3,6,8,12,15-*Hexaazatricyclo*[13.3.1.1^{8,12}]*icosane)nickel*(I) *Perchlorate*, *R,R,S,S*-[NiL]ClO_4.—The complex was prepared by a similar method to that previously reported for the synthesis of nickel(I) macrocyclic complexes.[17] The yellow complex *R,R,S,S*-$[NiL][ClO_4]_2 \cdot 0.5H_2O$ (2 g, 0.004 mol) and an excess of 5% Na-Hg (6 g, 0.01 mol) were suspended in MeCN (50 cm^3). The mixture was stirred at room temperature for 20 min. The resulting blue solution was filtered, concentrated to *ca.* 1/5th of the original volume, and then allowed to stand in a refrigerator for 2 d until deep blue crystals formed. These were filtered off, washed with MeCN, and dried *in vacuo*. Yield: 1.2 g, *ca.* 70% (Found: C, 37.70; H, 6.20; N, 18.85. Calc. for $C_{14}H_{30}ClN_6NiO_4$: C, 38.15; H, 6.85; N, 19.05%).

X-Ray Crystallography for R,R,S,S-[NiL]ClO_4.—A crystal was sealed in a thin-walled glass capillary under a nitrogen atmosphere.

Crystal data. $C_{14}H_{30}ClN_6NiO_4$, $M = 440.59$, orthorhombic, space group $P2_12_12_1$, $a = 8.681(2)$, $b = 11.358(2)$, $c = 19.146(4)$, $\beta = 90.0°$, $U = 1887.7(7)$ Å^3 (by least-squares refinement on diffractometer angles $2\theta = 16–24°$ for 25 reflections, $\lambda = 0.710\,73$ Å), $Z = 4$, $D_c = 1.543$ g cm^{-3}, $F(000) = 932$. Dark blue, air-sensitive crystals. Crystal dimensions *ca.* 0.30 × 0.33 × 0.39 mm, μ(Mo-Kα) = 11.33 cm^{-1}.

Data collection and processing. Enraf-Nonius CAD4 diffractometer, ω–2θ mode with ω-scan width = $1.0 + 0.35 \tan \theta$, ω-scan speed 2–7° min^{-1}, graphite-monochromated Mo-Kα radiation. 1938 Reflections observed ($3 < 2\theta < 50°$, $-h,k,l$) for $-10 \leqslant h \leqslant 0$, $0 \leqslant k \leqslant 13$, $0 \leqslant l \leqslant 22$ giving 1551 independent with $I > 3\sigma(I)$. No noticeable intensity change during the data collection at room temperature. The data were corrected for Lorentz-polarization, decay, and absorption with ψ-scan data.

Structure analysis and refinement. Conventional heavy-atom method followed by successive Fourier difference synthesis; refined by using SHELX 76.[25] Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and hydrogens in calculated positions with one, overall, refined U_{iso} (=0.08 Å^2). The weighting scheme $w = 1.5438/[\sigma^2(F_o) + 0.000\,337(F_o)^2]$. Final R and R' values were 0.0363 and 0.0379. The maximum shift-to-error ratio in the final least-squares cycle was less than 0.001 : 1. In the final Fourier difference function the ten largest peaks (0.36–0.23 e Å^{-3}) were all at chemically implausible positions.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and thermal parameters.

Results and Discussion

Synthesis and Properties.—The deep blue nickel(I) complex *R,R,S,S*-[NiL]ClO_4 was obtained by reduction of the nickel(II) complex *R,R,S,S*-$[NiL][ClO_4]_2 \cdot 0.5H_2O$[22] with sodium amalgam in MeCN under the strict exclusion of air. Its complex is oxygen and moisture sensitive. The EPR powder spectrum is presented in Fig. 1. It shows anisotropic axial g values ($g_{\parallel} = 2.272$ and $g_{\perp} = 2.074$) indicative of a square-planar d^9 electronic structure.[17,26–31] The UV/VIS spectrum of an acetonitrile solution of the complex shows a d–d transition at $\lambda = 589$ nm ($\varepsilon = 620$ dm^3 mol^{-1} cm^{-1}) which is *ca.* 140 nm to longer wavelength than that ($\lambda = 480$ nm, $\varepsilon = 28$ dm^3 mol^{-1} cm^{-1}) of the nickel(II) complex, with significantly increased absorption coefficient, in addition to a charge-transfer band at 355 nm ($\varepsilon = 3020$ dm^3 mol^{-1} cm^{-1}). Weaker ligand-field strength and increased absorption for Ni^I compared with Ni^{II} have been observed for other macropolycyclic systems.[17]

Crystal Structure of R,R,S,S-[NiL]ClO_4.—An ORTEP[32] view of the cation is presented in Fig. 2. Table 1 shows fractional coordinates and Table 2 shows the bond distances and angles. The overall structure is similar to that of the corresponding nickel(II) complex $[NiL][ClO_4]_2 \cdot 0.5H_2O$.[23] The Ni^I has a square-planar co-ordination by the two secondary amine nitrogens and two tertiary amine nitrogens of the fourteen-membered macrocyclic framework. The nickel atom is nominally in the co-ordination plane, displaced by 0.006 Å. The co-ordinated nitrogen atoms deviate tetrahedrally from the least-squares plane by 0.025–0.027 Å. The distortion of the

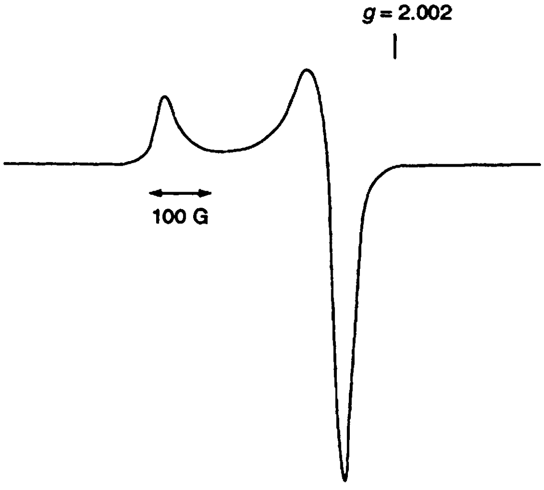


Fig. 1 The EPR powder spectrum of [NiL]ClO_4 measured at room temperature

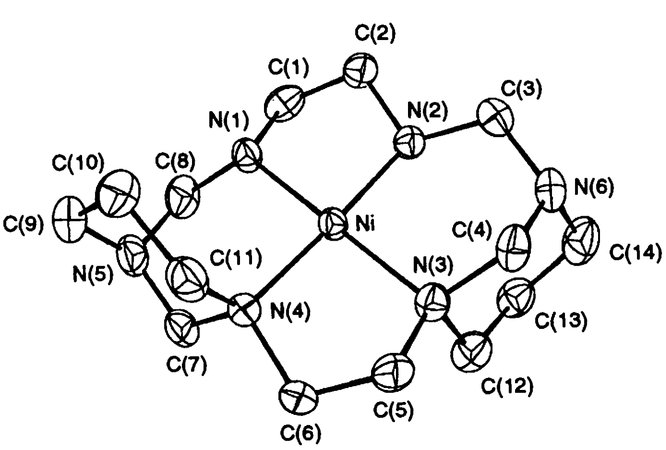


Fig. 2 An ORTEP drawing of the cation in [NiL]ClO_4. The atoms are represented by 50% probability thermal ellipsoids

Table 1 Positional parameters for $[NiL]ClO_4$

Atom	*x*	*y*	*z*
Ni	0.2906(1)	0.4712(1)	0.1305(0)
N(1)	0.4532(5)	0.5801(4)	0.1341(3)
N(2)	0.4315(6)	0.3604(4)	0.1752(3)
N(3)	0.1197(5)	0.3549(4)	0.1247(3)
N(4)	0.1475(6)	0.5874(4)	0.0881(2)
N(5)	0.3473(7)	0.7263(5)	0.0540(3)
N(6)	0.2312(7)	0.2158(4)	0.2071(3)
C(1)	0.5966(7)	0.5211(6)	0.1515(3)
C(2)	0.5596(7)	0.4307(5)	0.2053(3)
C(3)	0.3629(8)	0.2786(6)	0.2296(3)
C(4)	0.1020(7)	0.2895(6)	0.1923(3)
C(5)	−0.0221(7)	0.4239(6)	0.1117(4)
C(6)	0.0163(7)	0.5174(6)	0.0598(3)
C(7)	0.2208(8)	0.6528(5)	0.0302(3)
C(8)	0.4781(8)	0.6583(6)	0.0757(3)
C(9)	0.2940(10)	0.8152(5)	0.1042(3)
C(10)	0.2077(9)	0.7627(6)	0.1641(3)
C(11)	0.0853(7)	0.6760(5)	0.1395(4)
C(12)	0.1364(9)	0.2644(6)	0.0673(4)
C(13)	0.2638(8)	0.1772(5)	0.0802(3)
C(14)	0.2535(9)	0.1264(5)	0.1540(4)
Cl	0.2528(2)	0.5696(2)	0.3653(1)
O(1)	0.3072(9)	0.6854(6)	0.3636(6)
O(2)	0.3764(6)	0.4904(5)	0.3761(3)
O(3)	0.1485(8)	0.5601(8)	0.4209(4)
O(4)	0.1777(9)	0.5469(7)	0.3020(3)

Table 2 Bond distances (Å) and angles (°) for $[NiL]ClO_4$

Ni–N(1)	1.878(4)	N(4)–C(11)	1.507(8)
Ni–N(2)	1.952(5)	N(5)–C(7)	1.453(8)
Ni–N(3)	1.990(4)	N(5)–C(8)	1.434(8)
Ni–N(4)	1.986(5)	N(5)–C(9)	1.469(8)
N(1)–C(1)	1.453(7)	N(6)–C(3)	1.415(8)
N(1)–C(8)	1.443(7)	N(6)–C(4)	1.428(8)
N(2)–C(2)	1.484(7)	N(6)–C(14)	1.451(8)
N(2)–C(3)	1.518(8)	C(1)–C(2)	1.489(8)
N(3)–C(4)	1.500(8)	C(5)–C(6)	1.493(8)
N(3)–C(5)	1.481(7)	C(9)–C(10)	1.494(10)
N(3)–C(12)	1.512(8)	C(10)–C(11)	1.523(9)
N(4)–C(6)	1.491(7)	C(12)–C(13)	1.505(9)
N(4)–C(7)	1.479(7)	C(13)–C(14)	1.528(10)
N(2)–Ni–N(1)	86.4(2)	C(11)–N(4)–C(7)	107.9(4)
N(3)–Ni–N(1)	178.9(2)	C(8)–N(5)–C(7)	112.3(5)
N(3)–Ni–N(2)	93.7(2)	C(9)–N(5)–C(7)	111.2(5)
N(4)–Ni–N(1)	92.7(2)	C(9)–N(5)–C(8)	115.4(5)
N(4)–Ni–N(2)	177.9(2)	C(4)–N(6)–C(3)	113.5(5)
N(4)–Ni–N(3)	87.2(2)	C(14)–N(6)–C(3)	117.3(6)
C(1)–N(1)–Ni	110.3(3)	C(14)–N(6)–C(4)	112.1(6)
C(8)–N(1)–Ni	119.3(4)	C(2)–C(1)–N(1)	107.0(5)
C(8)–N(1)–C(1)	109.5(5)	C(1)–C(2)–N(2)	105.3(5)
C(2)–N(2)–Ni	107.0(3)	N(6)–C(3)–N(2)	114.7(5)
C(3)–N(2)–Ni	116.7(4)	N(6)–C(4)–N(3)	112.4(5)
C(3)–N(2)–C(2)	110.9(5)	C(6)–C(5)–N(3)	107.6(5)
C(5)–N(3)–Ni	106.2(3)	C(5)–C(6)–N(4)	108.0(5)
C(5)–N(3)–C(4)	108.8(5)	N(5)–C(7)–N(4)	112.2(5)
C(12)–N(3)–Ni	114.8(4)	N(5)–C(8)–N(1)	115.9(5)
C(12)–N(3)–C(4)	107.5(4)	C(10)–C(9)–N(5)	112.7(5)
C(12)–N(3)–C(5)	108.5(5)	C(11)–C(10)–C(9)	111.8(6)
C(6)–N(4)–Ni	105.8(3)	C(10)–C(11)–N(4)	112.6(5)
C(7)–N(4)–Ni	111.8(4)	C(13)–C(12)–N(3)	113.5(5)
C(7)–N(4)–C(6)	108.9(5)	C(14)–C(13)–C(12)	111.0(6)
C(11)–N(4)–Ni	113.6(4)	C(13)–C(14)–N(6)	113.1(5)
C(11)–N(4)–C(6)	108.6(5)		

nitrogen donors is slightly increased compared with those in the nickel(II) analogue in which the nitrogens deviate by 0.019–0.020 Å and the Ni^{II} is 0.02 Å out of the plane.

The complex contains two 1,3-diazacyclohexane ring moieties which are fused to amino functions at the bridgehead position of the six-membered chelate rings. The macrocyclic ligand adopts thermodynamically the most stable *R*,*R*,*S*,*S* (*trans*-III[33]) configuration, in which hydrogen atoms on the secondary nitrogens are on the same side of the 1,3-diazacyclohexane sub-ring moieties in a six-membered chelate ring. The 1,3-diazacyclohexane rings are located opposite and nearly perpendicular (95.3 and 86.6°) to the co-ordination plane. The corresponding nickel(II) complex also adopts the *R*,*R*,*S*,*S* conformation.[23] This means that no conformational change of the macrocycle occurs during the reduction of the latter. The six- and five-membered chelate rings assume a chair and a *gauche* conformation, respectively. The two 1,3-diazacyclohexane rings have chair conformations.

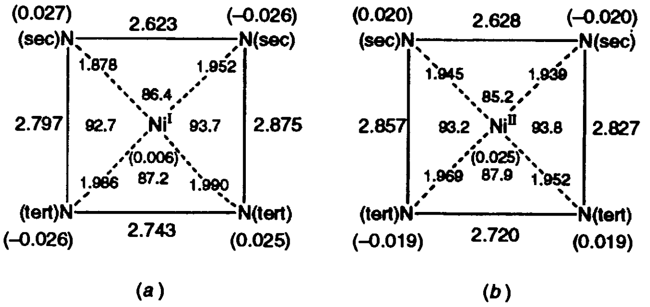
The C–N bond distances involving unco-ordinated bridgehead tertiary amines N(5) and N(6), ranging from 1.415(8) to 1.469(8) Å [average 1.442(3) Å], are shorter than normal aliphatic C–N bond distances (1.52 Å). The bond angles involving these nitrogens are 111–117°. This indicates a significant contribution of sp^2 hybridization in the unco-ordinated tertiary nitrogens. Similar shortening of C–N bond distances involving unco-ordinated tertiary nitrogens was observed for other complexes including $[NiL][ClO_4]_2{\cdot}0.5H_2O$[23] and the nickel(I) complexes of L^1 and L^2.[17]

The Ni–N bond distances of the present nickel(I) complex are 1.990(4), 1.986(5), 1.952(5) and 1.878(4) Å. The two Ni–N (tertiary) bonds are identical [average 1.988(2) Å], but there is a big difference in the Ni–N (secondary) bond distances, 1.952 and 1.878 Å. The nickel(I) complex of L^2 also showed different Ni–N (secondary) (1.972 and 1.850 Å) and different Ni–N (tertiary) bonds (1.897 and 1.975 Å).[17] Presumably, the nickel(I) complexes have a strong tendency for distortion of the core without making differentiation between the tertiary and the secondary nitrogen donors. The Ni–N bonds in the present complex, therefore, are considered as three long bonds consisting of two Ni–N (tertiary) and one Ni–N (secondary) bonds and one short Ni–N (secondary) bond. The average Ni–N bond distance of the three long bonds is 1.978(3) Å, and the short Ni–N (secondary) bond distance is 1.878(4) Å. That is, this complex has two different sets of Ni–N bond distances in analogy with other nickel(I) complexes.[17,18] Although only a few crystal structures of nickel(I) macrocyclic complexes have been reported so far,[17,18] the occurrence of the two different sets of long and short Ni^{I}–N bonds is common to all. In Table 3 Ni–N bond distances of various nickel(I) complexes are summarized and compared with those of the nickel(II) analogues. For the nickel(I) complexes of L^1 and L^2 two *cis* bonds involving a six-membered chelating ring form a set. In $[NiL^1]ClO_4{\cdot}MeCN$ the secondary and the tertiary nitrogen donors form different sets of Ni–N bonds. However, in $[NiL^2]ClO_4$, differentiation of Ni–N bonds was not related to tertiary and secondary nitrogens. The major difference between the present and the other nickel(I) complexes is that three Ni–N bonds form a set in the former whilst two form a set in the latter. In the nickel(II) complex of L a slight difference exists between Ni–N bond distances corresponding to secondary and tertiary nitrogens: average 1.942(1) and 1.961(1) respectively.[23] Compared with this nickel(II) complex, the difference between the Ni–N bonds in the nickel(I) complex is significantly greater. The overall average Ni–N bond distance [1.948(2) Å] is, however, rather similar to that [1.951(2) Å] of the nickel(II) complex, indicating no noticeable expansion of the macrocyclic hole in the nickel(I) complex. A structural comparison between the nickel-(I) and -(II) complexes of L is shown in Scheme 1. In $[NiL]ClO_4$ the N–Ni–N bite angles of five-membered chelate rings are 86.4(2) and 87.2(2)° and those of the six-membered chelate rings are 92.7(2) and 93.7(2)°. The N••• N bite distances of the five-membered chelate rings are 2.623(6) and 2.743(6) Å and of the six-membered chelate rings are 2.797(6) and 2.875(6) Å. As seen in Scheme 1, the N••• N bite distances

Table 3 The Ni–N bond distances (Å) in nickel-(I) and -(II) complexes of various macrocycles[a]

	Nickel(I) complex				
Macrocycle	short	long	δd[b]	Nickel(II) complex	Ref.
L	1.878(4)	1.978(3)	0.100	1.951(2)	This work
L^1	1.893(2)	1.936(2)	0.043	1.918(3)	17
L^2	1.859(7)	1.974(7)	0.115	1.923(4)	17
L^3	1.988(7)	2.063(6)	0.075	1.907(2), 1.938(2)	18
	1.979(7)	2.068(6)	0.089		
F_{430}[c]	1.88(3)	2.03(3)	0.15	1.90(2)	20
iBC[c]	1.85(5)	2.00(3)	0.15	1.93(2)	21

[a] Crystal structure data unless otherwise specified. [b] Difference between long and short Ni–N bonds. [c] EXAFS data.



Scheme 1 Structural comparison between $[Ni^IL]ClO_4$ (*a*) and $[Ni^{II}L][ClO_4]_2$ (*b*), showing Ni–N bond lengths, bite distances (Å) and bite angles (°). The numbers in parentheses are the deviations of the atoms from the least-squares plane comprising the four nitrogen donors. sec = Secondary, tert = tertiary

of the nickel(I) complex, which may be a measure of the hole size, are not always longer than those of the nickel(II) complex.

Although the crystal structures of nickel(I)–F_{430} and –iBC have not been reported, analyses of EXAFS data for their derivatives suggested the existence of two sets of long and short Ni–N bonds.[20,21] However, it is not clear whether the number of bonds in each set is one, two, or three. Considering the present results, the possibility of the formation of a set by the three Ni–N bonds in nickel(I)–F_{430} and –iBC cannot be excluded.

It is evident that the reduction of Ni^{II} to Ni^I induces increased distortion of the co-ordination geometry without expansion of the macrocyclic hole. The relatively large absorption coefficient of the d–d transitions of the nickel(I) complex may be attributed to distortion of the co-ordination sphere. In contrast to our results, the nickel(I) complex of the tetraaza monocyclic ligand L^3 showed Ni–N bonds which were significantly longer than those of the corresponding nickel(II) complex.[18] It seems that the holes of polycyclic macrocycles L^1, L^2 and L are too rigid to be enlarged, but monocycle L^3 may be flexible enough to expand its hole size upon reduction of Ni^{II} to Ni^I. It is presumed that distortion of the co-ordination core involving Ni–N bonds is common in square-planar nickel(I) complexes, but that expansion of the macrocyclic hole is very much dependent on the ligand flexibility. However, X-ray crystallographic studies on nickel(I) complexes with various types of macrocycles, especially with more symmetric ligands, are necessary.

Acknowledgements

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