Kinetics and Mechanism of Formation of Nickel(II) Complexes of Nitrogen–Oxygen Donor Macrocyclic Ligands in Methanol, and the *X*-Ray Structure Determination of One of the Products, Dichloro(6,7,8,9,10,11,17,18-octahydro-5*H*-dibenzo[*e*,*n*][1,4]dioxa[8,12]diazacyclopentadecine)nickel(II)

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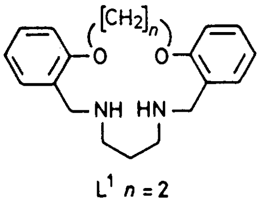
The kinetics of complexation of $NiCl_2$ in methanol with two O_2N_2-donor macrocyclic ligands have been studied by the stopped-flow technique. Complex formation involves a fast initial process controlled by the rate of methanol exchange for Ni^{II}, followed by a slower step which is postulated to involve a rearrangement of the ligand within the co-ordination sphere of the nickel(II) ion to form the final octahedral *trans*-dichloro-complex. An *X*-ray structure determination of the title complex [space group $P2_1/c$, $a = 14.442(4)$, $b = 10.867(3)$, $c = 18.617(5)$ Å, $\beta = 137.84(3)°$ (by heavy-atom method with 934 four-circle diffractometer data, R 0.063)] confirms a distorted *trans*-octahedral co-ordination geometry for the Ni^{II}.

THE kinetics of formation of metal complexes with macrocyclic ligands of both the polyether 'crown' type [1,2] and of those containing nitrogen [3-5] or sulphur [6] donors have recently been studied. Although most of these investigations have been carried out in aqueous media [3-5] several studies involving other solvents [2,6] have also been reported. The results from stopped-flow studies of the complexation of nickel(II) chloride in methanol with the O_2N_2-donor macrocycles L^1 and L^2 (ref. 7) are now reported, together with details of an *X*-ray structure determination of the complex of L^1. Previously [8] we described the isolation from methanol of a similar series of complexes of type $NiLX_2$ (X = Cl, Br, or NCS) which were assigned *trans*-octahedral geometries.



L^1 $n = 2$
L^2 $n = 3$

EXPERIMENTAL

Preparation of Reagents.—AnalaR grade nickel(II) chloride hexahydrate was dried by refluxing with thionyl chloride for 1 week as described previously.[9] The preparation and characterization of the macrocyclic ligands is given elsewhere.[7] AnalaR 'absolute' methanol was dried by distillation from magnesium turnings,[10] followed by storage over 3A molecular sieves. The water content was determined by Karl Fischer titration to be <0.01% (w/w). A nickel(II) chloride stock solution was prepared by dissolution of the anhydrous salt in dry methanol. Karl Fischer titration indicated a water content no higher than that of the dry solvent. Nickel analyses were performed using dimethylglyoxime. All the methanol solutions were prepared and handled under an atmosphere of dry nitrogen.

Kinetic Studies.—Spectrophotometric titrations were performed using a Beckman ACTA IV spectrophotometer. All the kinetic data were obtained using the stopped-flow system described elsewhere.[11] Since, as described below, the total reaction consisted of a fast initial step followed by a slower one, the data-acquisition system was modified to enable the operator to sample the photomultiplier output consecutively at two different time intervals. Typically, 50—60 samples were taken at 3 ms intervals, followed by another 50 samples at 50 ms intervals.

X-Ray Crystallography for $[NiL^1Cl_2]$.—*Crystal data.* $C_{19}H_{24}Cl_2N_2NiO_2$, $M = 442.0$; Monoclinic, $a = 14.442(4)$, $b = 10.867(3)$, $c = 18.617(5)$ Å, $\beta = 137.84(3)°$, $U = 1\,961$ Å^3, $D_m = 1.50$ g cm^{-3}, $Z = 4$, $D_c = 1.496$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.2 cm^{-1}, $F(000) = 920$. The space group $P2_1/c$ was deduced from systematic extinctions $0k0$ with $k = 2n + 1$ and $h0l$ with $l = 2n + 1$. For data collection and for refinement of the structure the space group $P2_1/n$ [$c = 12.513(3)$ Å, $\beta = 92.94(1)°$] was used.

The fine green needle-shaped crystals obtained from methanol diffracted weakly. Data were collected on a crystal with dimensions *ca.* 0.15 × 0.04 × 0.03 mm, using a Philips PW1100 four-circle diffractometer and graphite monochromatized Mo-K_α radiation. A θ–2θ scan mode was used, and 3 252 reflections with $3.0 < \theta < 30°$ in one quadrant were measured. Reflections with a total intensity less than 500 counts were scanned twice to increase their accuracy. A scan speed of 0.05° s^{-1} and a scan width of 1.2° were used with the background measuring time equal to half the scan time. Three standard reflections were measured every 7 h during data collection and showed no significant variations in intensity.

The reflection intensities were calculated from the peak and background measurements using a program written for the PW1100 diffractometer.[12] The variance of the intensity, I, was calculated as the sum of the variance due to counting statistics and $(0.04I)^2$, where the term in I^2 was introduced to allow for other sources of error.[13] I and $\sigma(I)$

were corrected for Lorentz and polarization factors. No absorption corrections were applied. Equivalents were averaged and reflections for which $I \leqslant 3\sigma(I)$ were rejected to give 934 unique reflections.

Structure solution and refinement. The nickel atom and one chlorine atom were located from a Patterson map. A difference-Fourier synthesis revealed the position of all the remaining non-hydrogen atoms. Refinement with isotropic thermal parameters for all atoms converged at $R = 0.088$. In the final three cycles of refinement, anisotropic thermal parameters were assigned to the nickel, chlorine, and oxygen atoms. The two ortho-substituted benzene rings were refined as regular hexagons with a C–C distance of 1.395 Å. Hydrogen atoms were included in calculated positions, 'riding' at a fixed distance of 1.08 Å from the carbon atoms to which they are attached; the isotropic thermal parameters were fixed at 0.10 Å^2. This resulted in $R = 0.063$, $R' = 0.056$ $(= \Sigma||F_o| - |F_c||w^{\frac{1}{2}}/\Sigma|F_o|w^{\frac{1}{2}})$ where weights (w) were assigned to reflections as $w = 1/\sigma^2(F_o)$; the maximum- and average-shift-to-error ratios were 0.036 and 0.008 respectively. The final difference-Fourier map showed maxima and minima of electron density of 0.57 and −0.51 e Å^{-3} respectively. Atomic co-ordinates are given in Table 1. Thermal parameters, interatomic bond lengths and angles in the macrocyclic ligand, and final structure factors are given in Supplementary Publication No. SUP 22440 (10 pp.).*

TABLE 1

Refined atomic positional parameters [a] ($\times 10^4$)

Atom	X	Y	Z
Ni	926(2)	2 162(2)	3 637(2)
Cl(1)	576(3)	35(4)	3 327(4)
Cl(2)	1 403(3)	4 259(4)	3 871(4)
C(1a)	2 789(12)	1 242(16)	3 107(14)
O(1a)	2 351(7)	1 573(9)	4 097(8)
C(2a) [b]	2 498	803	4 958
C(3a) [b]	3 107	−192	4 944
C(4a) [b]	3 219	−958	5 836
C(5a) [b]	2 723	−728	6 742
C(6a) [b]	2 115	268	6 756
C(7a) [b]	2 002	1 034	5 864
C(8a)	1 367(11)	2 135(15)	5 918(12)
N(1a)	540(8)	2 025(11)	5 188(9)
C(9a)	−207(10)	2 899(16)	5 419(12)
C(1b)	2 552(12)	2 188(17)	2 316(14)
O(1b)	1 556(7)	2 269(11)	2 163(7)
C(2b) [b]	1 088	1 917	1 246
C(3b) [b]	1 471	1 136	502
C(4b) [b]	977	863	−455
C(5b) [b]	98	1 370	−669
C(6b) [b]	−284	2 151	75
C(7b) [b]	211	2 425	1 033
C(8b)	−219(12)	3 249	1 830
N(1b)	−314(8)	2 611(11)	2 890(9)
C(9b)	−948(12)	3 340(15)	3 586(13)
C(9c)	−1 029(10)	2 766(16)	4 684(12)

[a] Fractional co-ordinates are given for the $P2/_1n$ cell. The standard deviation of the least significant digit is included in parentheses in this and subsequent tables. [b] Refined as part of rigid groups.

All computations were performed using the SHELX programs (Dr. G. M. Sheldrick). Scattering factors and anomalous-dispersion corrections for nickel were taken from refs. 14 and 15.

RESULTS AND DISCUSSION

Equilibrium Studies.—For the concentration ranges used in the kinetic studies, spectroscopic titration of the nickel(II) solution with the respective macrocyclic ligands (methanol as solvent) gave no evidence for the formation of other than 1 : 1 complexes. Preliminary measurements indicate that the respective formation constants in methanol are greater than *ca.* 10^4 dm^3 mol^{-1} and hence any contribution from the reverse reaction can be ignored in the present system.

Kinetic Studies.—The rates of formation of metal complexes in aqueous solution are generally accepted to be controlled largely by the rate of exchange of water molecules between the co-ordination sphere of the metal ion and the bulk solvent (S).[16] For such systems, rapid

$$[\mathrm{MS_6}]^{n+} + \mathrm{L} \underset{}{\overset{K_0}{\rightleftharpoons}} [\mathrm{MS_6}]^{n+}\cdots\mathrm{L} \xrightarrow{k_1} [\mathrm{MS}_{6-x}\mathrm{L}]^{n+} + x\mathrm{S}$$

initial formation of an outer-sphere complex (of the ion–ion or ion–dipole type) is usually postulated which is characterized by the equilibrium constant K_0. This is then followed by a rate-determining step controlled by solvent exchange (first-order rate constant, k_1) to yield the product. The overall second-order formation rate constant (k_a) will be given by (1). Related complexation reactions in methanol have also been postulated [10,17,18] to occur by a similar dissociative ion-pair mechanism to the above.

$$k_a = k_1 K_0 \qquad (1)$$

In the present studies, preliminary experiments indicated that for each ligand system the reaction with $\mathrm{Ni^{2+}}$ in methanol consists of a fast initial step followed by a slower step. These experiments also showed that the rate of the initial reaction is dependent on both the initial nickel(II) and ligand concentrations, whereas the rate of the second reaction is independent of ligand concentration (in excess) at constant initial nickel(II) concentration. These observations suggest the reaction sequence (2). Accordingly, the experimental data (absorbance against time) were analysed in terms of equations (3) and (4) where a_0 and b_0 are the initial concentrations of $\mathrm{Ni^{2+}}$ and ligand and x and y are those of the intermediate and $[\mathrm{NiL}]^{2+}$ at any time (t). The absorbance (A) at time t is given by expression (5).

$$\mathrm{Ni^{2+}} + \mathrm{L} \xrightarrow{k_a} \text{Intermediate} \xrightarrow{k_b} [\mathrm{NiL}]^{2+} \qquad (2)$$

$$\mathrm{d}x/\mathrm{d}t = k_a(a_0 - x - y)(b_0 - x - y) - k_b x \qquad (3)$$

$$\mathrm{d}y/\mathrm{d}t = k_b x \qquad (4)$$

$$A = \varepsilon^{\mathrm{Ni}}(a_0 - x - y) + \varepsilon^{\mathrm{int}}x + \varepsilon^{\mathrm{c}}y \qquad (5)$$

For ligand $\mathrm{L^1}$ the reaction was followed at 635 nm and the data analysed using the Runge–Kutta numerical-integration method [19] for equations (3) and (4) in combination with (5) and the BMDX [20] non-linear least-squares program to determine the values of k_a and k_b which best reproduce the observed absorbance (A) of the reactant solution at any time. The values of $\varepsilon^{\mathrm{Ni}}$ and ε^{c} were measured independently, while the value of $\varepsilon^{\mathrm{int}}$ was

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

obtained as follows. When Ni^{2+} (1.30×10^{-2} mol dm^{-3}) was mixed with ligand L^1 (4.20×10^{-2} mol dm^{-3}) the formation of the intermediate was complete within *ca.* 30 ms, as indicated by the constancy of the observed absorbance after this time. The absorbance spectrum of the intermediate was recorded at 20 nm intervals over the range 500—700 nm. The position of the absorbance maximum (635 nm) was found to be the same as that for the complex, but the absorption coefficient for the intermediate (12.2 dm^3 mol^{-1} cm^{-1}) is significantly lower than that for the complex (16.6 dm^3 mol^{-1} cm^{-1}).

The preceding analyses reproduced the observed absorbances very well and gave values of k_a and k_b which were independent of initial reagent concentration; 52 experiments in which the concentration of $NiCl_2$ was varied over the range 0.652×10^{-2}—1.24×10^{-2} mol dm^{-3} and the ligand concentration over the range $1.01 \times 10^{-2} - 4.20 \times 10^{-2}$ mol dm^{-3} gave values of $k_a = (1.60 \pm 0.24) \times 10^3$ dm^3 mol^{-1} s^{-1} and $k_b = 0.72 \pm 0.34$ s^{-1} at 25 °C. Measurement of k_a and k_b at a number of temperatures between 10 and 30 °C (see Table 2) enabled activation parameters for each step to be calculated using the Eyring equation. Values of $\Delta H_a^\ddagger$ and $\Delta S_a^\ddagger$ of 59.8 ± 1.3 kJ mol^{-1} and 17.6 ± 3.8 J K^{-1} mol^{-1} were obtained, whereas the values for $\Delta H_b^\ddagger$ and $\Delta S_b^\ddagger$ were 56.9 ± 3.3 kJ mol^{-1} and -54.8 ± 11.7 J K^{-1} mol^{-1}, respectively.

TABLE 2

Effect of temperature [a] on k_a and k_b for ligands L^1 and L^2

		$10^{-3}k_a/dm^3\ mol^{-1}\ s^{-1}$		k_b/s^{-1}	
	$\theta_c/°C$	obs. [b]	calc. [c]	obs. [b]	calc. [c]
Ligand L^1					
	10.5	0.42 ± 0.03	0.44	0.27 ± 0.03	0.28
	14.0	0.61 ± 0.01	0.61	0.39 ± 0.06	0.38
	17.9	0.95 ± 0.08	0.87	0.65 ± 0.20	0.53
	22.4	1.31 ± 0.05	1.28	0.77 ± 0.15	0.76
	26.0	1.77 ± 0.06	1.74	1.07 ± 0.21	1.02
	30.0	2.36 ± 0.06	2.42	1.20 ± 0.38	1.40
$\Delta H^\ddagger/kJ\ mol^{-1}$		59.8 ± 1.3		56.9 ± 3.3	
$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$		17.6 ± 3.8		-54.8 ± 11.7	
% r.m.s. [d]		4.49		10.65	
Ligand L^2 [e]					
	14.3	0.46 ± 0.04	0.50		
	18.3	0.70 ± 0.03	0.67	$\Delta H^\ddagger/kJ\ mol^{-1}$	46.4 ± 4.6
	22.1	0.94 ± 0.11	0.86	$\Delta S^\ddagger/J\ K^{-1}\ mol^{-1}$	-31.4 ± 15.5
	26.0	1.02 ± 0.05	1.12	% r.m.s.	7.5
	29.4	1.51 ± 0.07	1.39		
	32.6	1.66 ± 0.11	1.71		

[a] $[Ni^{2+}]_0 = 1.06 \times 10^{-2}$ mol dm^{-3}, $[L^1]_0 = 0.021\,6$ mol dm^{-3}, and $[L^2]_0 = 0.019$ mol dm^{-3}. [b] Average and standard deviation from at least six individual determinations. [c] Calculated using the activation parameters summarized above. [d] % r.m.s. defined as $100[(1/n)\Sigma(k_{obs.} - k_{calc.})^2/k^2]^{\frac{1}{2}}$. [e] Very small absorbance change for second step caused large errors in the determination of k_b. Hence, the activation parameters were not determined.

An estimate of K_0 may be made using the Fuoss equation,[21] $K_0 = \frac{4}{3}\pi N_A a^3$, where a is the centre-to-centre distance of closest approach of the solvated metal ion and the reacting site of the ligand. If a is taken as 6 Å for the present system,[18] a value of 0.55 dm^3 mol^{-1} is obtained for K_0 and k_1 is found from equation (1) to be 2.9×10^3 s^{-1}. However, in view of the considerable uncertainties [18,22] surrounding the estimation of K_0, the above value of k_1 is unlikely to be of high accuracy. Nevertheless, from a comparison of this value * with the reported [23] value for methanol exchange for Ni^{2+} (k_{ex} 1.0×10^3 s^{-1}), as well as from a comparison of the value found for $\Delta H_a^\ddagger$ (59.8 ± 1.3 kJ mol^{-1}) with that reported for $\Delta H_{ex}^\ddagger$ (66.1 kJ mol^{-1}),[23] it seems that the intermediate complex formation for this system follows the dissociative ion-pair mechanism [16-18] established for other nickel complexation reactions.

A series of 46 similar experiments with ligand L^2 (λ 655 nm) gave $k_a = (1.37 \pm 0.21) \times 10^3$ dm^3 mol^{-1} s^{-1}, $\Delta H_a^\ddagger = 46.4 \pm 4.6$ kJ mol^{-1}, and $\Delta S_a^\ddagger = -31.4 \pm 15.5$ J K^{-1} mol^{-1}. Limitations imposed by a very small absorbance change during the reaction as well as the low solubility of the product prevented a reliable determination of k_b for this ligand. However, it seems clear that in general terms the mechanism parallels that discussed above for the formation of $[NiL^1Cl_2]$ in methanol.

It is evident that complex formation in both cases involves the usual initial outer-sphere contact of the ligand and solvated Ni^{2+}. The formation of the intermediate complex is then controlled by the rate of methanol exchange for Ni^{2+} (or possibly $NiCl_2$), while the first-order conversion of the intermediate complex into the final *trans*-dichloro-complex (see below) may be attributed to a rearrangement of the ligand within the co-ordination sphere of the Ni^{2+}. For other macrocyclic ligand systems it has been demonstrated [5,6,24] that the rate-determining step in the formation kinetics is not

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* Both $NiCl_2$ and $NiLCl_2$ ($L = L^1$ or L^2) give conductance values in methanol which indicate that these compounds are not appreciably dissociated (values less than expected for a 1 : 1 electrolyte) in methanol. It has been shown (see ref. 18) that the presence of a chloride substituent in the inner sphere of Ni^{II} in methanol has an accelerating effect on the rates of reaction with various ligands. Rate enhancements of between 2 and 60 were observed for the reactions with a number of aromatic heterocyclic amines.

controlled by the dissociation of the first co-ordinated solvent molecule. For two such systems involving Cu^{2+} it has been reported[6,24] that the observed formation rate constants reflect the fact that the rate-determining step in these systems is shifted from the usual (with simple polydentate ligands) first metal–ligand bond formation to the point of second-bond formation. Essentially, such an effect has been ascribed to the added steric constraints associated with macrocyclic ligands. Our results also indicate that additional processes apart from the initial metal–ligand contact may be important in the formation kinetics of such systems.

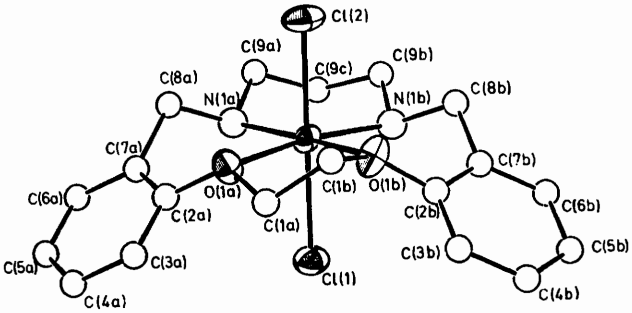


FIGURE 1 The complex $[NiL^1Cl_2]$, showing the atom-labelling scheme used in Table 1

For the complex $[NiL^1Cl_2]$ isolated from methanol an *X*-ray structure determination has confirmed a *trans* co-ordination geometry for the nickel(II) ion (Figure 1). The neutral complexes are well separated in the solid state (Figure 2), with the closest intermolecular contact (Table 3) involving a relatively weak[25] hydrogen bond between the amine hydrogen of N(1b) and a neighbouring Cl(1). The most marked deviations from a regular octahedral arrangement of donors about the nickel(II) ion are the different co-ordinate bond lengths to the three types of donor atoms N, O, and Cl and the deviations of the angles O(1a)–Ni–O(1b) and N(1a)–Ni–N(1b) from 90° (Table 4). The small angle defined by the O(1a) and O(1b) donors is a necessary consequence of these being present in the smaller (five-membered) chelate ring and of them being more distant from the nickel ion than the *N*-donors of the macrocycle.

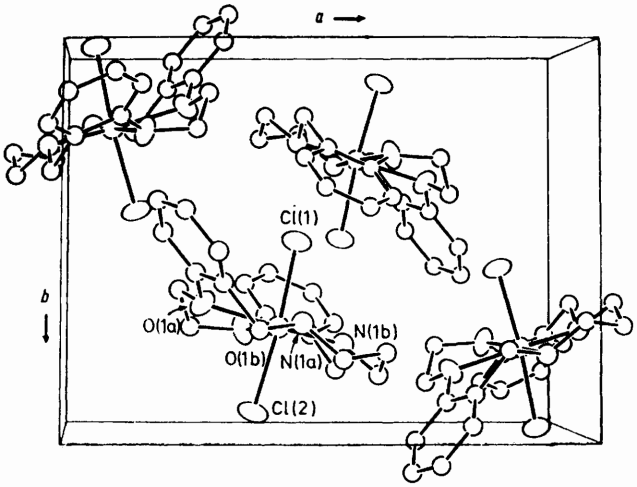


FIGURE 2 The contents of the unit cell viewed along *c*

TABLE 3

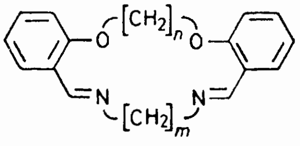
Intermolecular contacts <2.8 Å, excluding H–H contacts

Atoms	Distance/Å	Atoms	Distance/Å
$H(N1a) \cdots Cl(1^{I})$	2.47	$H(4a) \cdots C(5b^{II})$	2.72
$H(3b) \cdots Cl(2^{II})$	2.68	$H(5b) \cdots Cl(1^{III})$	2.74
$H(4a) \cdots C(4b^{III})$	2.71	$H(6b) \ldots O(1a^{IV})$	2.76

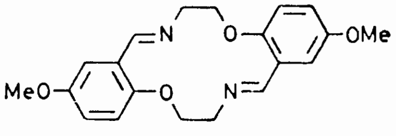
* Hydrogen atoms are given the number of the carbon atom to which they are attached, and the second atom is related to the positions given in Table 1 by the operations:

I $-x, -y, 1 + z$; III $-x, -y, -z$;
II $\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$; IV $-\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$

The lengths of the two Ni–O bonds vary significantly, and both exceed the sum of the covalent radii[26] of octahedral Ni^{II} (1.39 Å) and O (0.66 Å). In *cis* complexes of the related di-imine ligands L^3 and L^5 even greater variations of metal–oxygen bond lengths have been observed.[27,28] For such relatively weak metal–donor interactions the bond lengths are probably influenced significantly by geometric requirements which minimize strain in the macrocyclic ligands. Conformational effects in the free ligands L^1—L^4, $[NiL^1Cl_2]$, and related metal complexes are the subject of current investigations.[29]



L^3 $m = 3, n = 2$
L^4 $m = 3, n = 3$



L^5

The Ni–N(1a) and Ni–N(1b) distances fall within a range (2.03—2.16 Å) observed for the co-ordinate bonds from neutral sp^3-hybridized nitrogen atoms in

TABLE 4

Interatomic bond lengths (Å) and angles (°) in the co-ordination sphere of the complex

Lengths	
Ni–Cl(1)	2.393(5)
Ni–Cl(2)	2.395(6)
Ni–O(1a)	2.204(10)
Ni–O(1b)	2.102(9)
Ni–N(1a)	2.052(11)
Ni–N(1b)	2.036(11)
Angles	
Cl(1)–Ni–Cl(2)	174.9(2)
Cl(1)–Ni–O(1a)	87.0(3)
Cl(1)–Ni–O(1b)	90.5(3)
Cl(1)–Ni–N(1a)	91.0(4)
Cl(1)–Ni–N(1b)	89.1(4)
Cl(2)–Ni–O(1a)	89.2(3)
Cl(2)–Ni–O(1b)	85.4(3)
Cl(2)–Ni–N(1a)	92.5(4)
Cl(2)–Ni–N(1b)	93.9(4)
O(1a)–Ni–O(1b)	78.7(4)
O(1a)–Ni-N(1a)	91.6(4)
O(1a)–Ni–N(1b)	167.7(4)
O(1b)–Ni–N(1a)	170.1(4)
O(1b)–Ni–N(1b)	89.7(4)
N(1a)–Ni–N(1b)	100.1(5)

macrocyclic high-spin nickel(II) complexes,[30] and exceed the range of values (1.80—1.94 Å) found [31] in comparable low-spin complexes.

The configuration adopted by the macrocycle contrasts markedly with that found [27] for the precursor di-imine ligand L^3 in a *cis*-cobalt(II) complex in which the macrocycle is folded, giving a β-*cis* configuration.

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