Phenoxo-bridged Dinickel(II) Complexes of a Macrocyclic Ligand: Synthesis, Stereochemical Equilibria and Structure†

Kausik K. Nanda,[a] Ramprasad Das,[a] Michel J. Newlands,[b] R. Hynes,[c] Eric J. Gabe[c] and Kamalaksha Nag*,[a]

[a] *Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India*

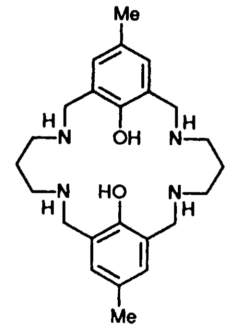
[b] *Department of Chemistry, Memorial University of Newfoundland, St. John's, Newfoundland, Canada A1B 3X7*

[c] *Division of Chemistry, National Research Council, Ottawa, Ontario, Canada K1A 0R6*

Dinuclear nickel(II) complexes of a tetraaminediphenol macrocyclic ligand (H_2L) of composition $[Ni_2L(B)_2][ClO_4]_2$ (B = NH_3, imidazole, pyridine, or pyrazine) have been synthesised and characterized. With pyrazole (Hpz) $[Ni_2L(pz)(H_2O)_2][ClO_4]$ and $[Ni_2L(pz)(Hpz)(H_2O)][ClO_4]$ complexes have been obtained in which pz^- appears to act as a bridging ligand. The equilibrium constants for the reaction $[Ni_2L(MeOH)_4]^{2+} + 2B \rightleftharpoons [Ni_2L(B)_2]^{2+} + 4MeOH$ [B = pyridine, 2-methylpyridine (2Me-py), 3Me-py, 4Me-py, imidazole, or pyrazine] in methanol solutions have been determined spectrophotometrically at room temperature. The X-ray structure of $[Ni_2L(py)_2][ClO_4]_2$ has been determined: monoclinic, space group $P2_1/n$, with $a = 9.251(1)$, $b = 11.457(2)$, $c = 18.555(2)$ Å, $\beta = 100.21(1)°$, and $Z = 2$. The structure was determined by direct methods and refined to $R = 0.053$ and $R' = 0.039$. In the complex cation the two nickel(II) centres are in square-pyramidal configuration with N_2O_2 in-plane donor sets, involving two phenoxide bridges and two *trans*-axially disposed pyridines. The distance between the two nickel centres is 3.206(5) Å.

Nickel(II) complexes of polyaza macrocyclic ligands, especially those of tetraaza macrocycles, probably have received more attention[1–4] than any other 3d metal ion complexes. In contrast, very few studies have been made of dinuclear nickel(II) complexes in which the two metal ions are placed in the same macrocyclic cavity. The known examples are limited to $[Ni_2L^1]Cl_2{\cdot}3H_2O$ **1**,[5] $[Ni_2L^2Cl_2]{\cdot}2H_2O$ **2**,[6] and the perchlorate or tetrafluoroborate salts of $[Ni_2L^2(py)_4]^{2+}$ **3**,[7] (py = pyridine), which were produced by template condensation of 2,6-diformyl-4-methylphenol with 1,2-diaminoethane (L^1) or 1,3-diaminopropane (L^2) in the presence of the metal salt. Complex **1** has been reported to be square planar, while **2** is square pyramidal, and **3** is tetragonally distorted octahedral. There is significant antiferromagnetic exchange interaction between the two metal centres in complexes **2**[8] and **3**.[7] None of these compounds, however, has been characterized by X-ray crystallography. In a recent communication we have reported[9] the synthesis, electrochemistry and structure of a novel dinickel(II) complex of the macrocyclic ligand H_2L with the composition $[Ni_2L(MeOH)_2(ClO_4)_2]{\cdot}2NHEt_3ClO_4$ **4**. This complex undergoes unprecedented stepwise two-electron oxidation producing $Ni^{II}Ni^{III}$ and $Ni^{III}Ni^{III}$ species and two-electron reduction producing $Ni^{II}Ni^{I}$ and $Ni^{I}Ni^{I}$ species.

One particular aspect of the chemistry of nickel(II) tetraaza macrocycles that has received considerable attention[10–18] is the thermodynamics of stereochemical equilibria involving low-spin four-co-ordinated species and high-spin five- or six-co-ordinated species. While a similar study is lacking with dinickel(II) complexes, it is worthy of note that although complex **1** does not interact with pyridine,[5] in complex **3** each of the metal centres has two pyridine donors.



H_2L

The present study is concerned with the interaction of several nitrogen-donor Lewis bases (B) with complex **4**. The resulting square-pyramidal $[Ni_2L(B)_2][ClO_4]_2$ complexes have been characterized and the crystal structure of $[Ni_2L(py)_2][ClO_4]_2$ has been determined. The equilibrium constants involving the formation of $[Ni_2L(B)_2]^{2+}$ species (B = pyridine, methylpyridines, pyrazine or imidazole) in methanol solutions are also reported.

Results and Discussion

The bluish green crystals of complex **4** become wine red in methanol. The electronic spectrum of this solution (Table 1) is typical of a six-co-ordinate nickel(II) complex indicating that the species existing in solution is $[Ni_2L(MeOH)_4]^{2+}$. The wine-red solution gradually becomes bright green on treatment with increasing amounts of nitrogen-donating ligands (B) such as ammonia, imidazole (Him), pyridine (py), or pyrazine (pyz), and complexes of composition $[Ni_2L(B)_2][ClO_4]_2$ **5**–**8** can be isolated. Preliminary studies showed that reaction (1) takes

---

† *Supplementary data available:* see Instructions for Authors. *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Electronic spectral data and magnetic moments of the complexes

	Complex	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})	μ_{eff} per Ni$^{II\,a}$
4	$[Ni_2L(MeOH)_2(ClO_4)_2]\cdot2NHEt_3ClO_4$^{b}	1160(7), 810(8), 750(9), 500(100), 375(400)	3.07
5	$[Ni_2L(NH_3)_2][ClO_4]_2$^{c}	1475(17), 850(10), 780(12), 620(32), 365(500)	3.01
6	$[Ni_2L(Him)_2][ClO_4]_2$^{d}	1550(24), 850(18), 785(17), 630(50), 370(780)	2.75
7	$[Ni_2L(py)_2][ClO_4]_2$^{e}	1525(22), 840(13), 790(14), 625(45), 380(890)	2.68
8	$[Ni_2L(pyz)_2][ClO_4]_2$^{f}	860, 750, 620, 370	2.84
9	$[Ni_2L(\mu\text{-}pz)(H_2O)_2][ClO_4]$^{c}	960(28), 595(16), 365(150)	2.98
10	$[Ni_2L(\mu\text{-}pz)(Hpz)(H_2O)][ClO_4]\cdot H_2O$^{g}	940(27), 590(22), 360(130)	3.02

[a] At 298 K. [b] In MeOH. [c] In dimethylformamide. [d] In MeCN. [e] In MeOH–py(1:1). [f] In Nujol. [g] In Me_2CO.

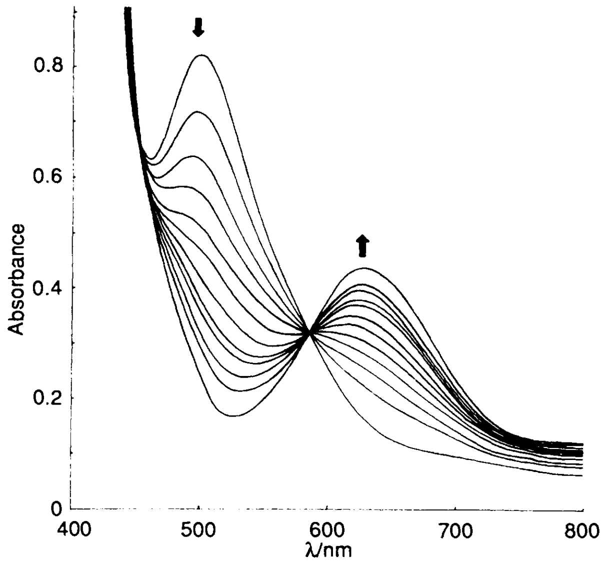


Fig. 1 Visible spectral changes of complex **4** (1.007 × 10^{-2} mol dm^{-3}) in MeOH upon addition of varying amounts of 4-methylpyridine: 0, 1.004 × 10^{-2}, 2.01 × 10^{-2}, 3.01 × 10^{-2}, 4.02 × 10^{-2}, 6.02 × 10^{-2}, 8.03 × 10^{-2}, 10.04 × 10^{-2}, 12.05 × 10^{-2}, 16.06 × 10^{-2}, 20.08 × 10^{-2} and 40.16 × 10^{-2} mol dm^{-3}. The arrow ↑ indicates the increase in concentration of $[Ni_2L(4Me\text{-}py)_2]^{2+}$

$$[Ni_2L(MeOH)_4]^{2+} + 2B \rightleftharpoons [Ni_2L(B)_2]^{2+} + 4MeOH \quad (1)$$

place reversibly. When 1 equivalent each of complex **4**, pyrazole (Hpz) and triethylamine are mixed in methanol a blue complex of composition $[Ni_2L(\mu\text{-}pz)(H_2O)_2][ClO_4]$ **9** is obtained. However, the same reaction with excess of pyrazole affords $[Ni_2L(\mu\text{-}pz)(Hpz)(H_2O)][ClO_4]\cdot H_2O$ **10**. Both complexes **9** and **10** behave as 1:1 electrolytes (Λ_M *ca.* 125 S cm^2 mol^{-1} in MeCN), and it is assumed that pz^- acts as a bridging ligand.

Characterization.—The infrared spectra of all the complexes exhibit bands characteristic of the macrocyclic ligand [ν(NH) 3260–3240 cm^{-1}] and ionic perchlorates (1100 and 630 cm^{-1}). An additional ν(NH) at 3350 cm^{-1} is observed for complex **5** due to the co-ordinated ammonia molecules. Complexes **6**–**8** are also characterized by the out-of-plane deformation vibrations of the corresponding heterocyclic rings[19] (755, 660, **6**; 760, 700, **7**; 805 cm^{-1}, **8**).

The room-temperature magnetic moments of the complexes (Table 1), which vary between 2.7 and 3.1 per Ni^{II}, provide indications of spin-exchange interactions between two $S = 1$ states. Magnetic susceptibility measurements over the temperature range 5–300 K have been carried out. A detailed analysis of the coupling interactions is underway and will be reported separately.[20]

According to their electronic spectral characteristics (Table 1), the complexes can be divided into three groups, *viz.* **4**, **5**–**8** and **9** and **10**. As already mentioned, the absorption spectrum of the species $[Ni_2L(MeOH)_4]^{2+}$ is typical of tetragonal nickel(II) complexes of D_{4h} symmetry. The five d–d bands observed at 8620, 12 350, 13 300, 20 200 and 26 600 cm^{-1} can be related to the spin-allowed transitions from $^3B_{1g}$ to ^3E_g, $^3B_{2g}$, $^3A_{2g}$, ^3E_g and $^3A_{2g}$ and/or $^3E_g(P)$, respectively. The spectrochemical parameters of this complex, *viz.* Dq^{xy} = 1235 cm^{-1}, Dq^z = 490 cm^{-1} and Dt = 425 cm^{-1}, show that the N_2O_2 donors provide a strong in-plane ligand field. The magnitude of Dq^{xy} is comparable to those of [15]aneN_4 nickel(II) complexes (average 1240 cm^{-1}), which are stronger than [16]aneN_4 (average 1100 cm^{-1}) but weaker than [14]aneN_4 (average 1460 cm^{-1}) systems.[3,4,*]

Complexes **5**–**8** also exhibit five d–d bands, but they differ significantly from the spectrum of **4** in that the lowest-energy band is shifted almost to the near-IR region with pronounced increase in intensity. For high-spin nickel(II) complexes with C_{4v} symmetry the orbitally non-degenerate $^3B_1$ ground state usually gives rise to transitions to $^3E(F)$, $^3B_2(F)$, $^3A_2(F)$, $^3E(F)$, $^3E(P)$ and $^3A_2(P)$ levels in ascending order of energies. Although the bands observed for complexes **5**–**8** at about 6800, 11 800, 12 700, 16 000 and 26 500 cm^{-1} have energies similar to those of some well characterized square-pyramidal nickel(II) complexes,[21] in the absence of polarized spectra no definite band assignment can be made.

Three d–d bands observed for complexes **9** and **10** at 10 500, 16 800 and 27 800 cm^{-1} can be attributed in an octahedral model to the transitions $^3A_{2g} \longrightarrow {}^3T_{2g}$, $^3A_{2g} \longrightarrow {}^3T_{1g}$ and $^3A_{2g} \longrightarrow {}^3T_{1g}(P)$, respectively. However, the intensity of the lowest-energy band (ε = 28 dm^3 mol^{-1} cm^{-1}) is unusually strong for octahedral complexes and is probably due to a highly asymmetric ligand field. The bridging pyrazolate in these two compounds is bound to distort severely the co-ordination environment of the metal centres.

Equilibrium Constants.—The equilibrium constants for reaction (1) have been determined for a number of Lewis bases B = py, 2-methylpyridine (2Me-py), 3Me-py, 4Me-py, pyz and Him) in methanol. Typical changes in the visible spectrum of a methanol solution of complex **4** with varying amounts of 4Me-py are shown in Fig. 1. The successive absorption curves pass through two isosbestic points at 455 and 588 nm. The peak at 500 nm due to $[Ni_2L(MeOH)_4]^{2+}$ becomes depleted and eventually

---

* [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane; [15]aneN_4 = 1,4,8,12-tetraazacyclopentadecane; [16]aneN_4 = 1,5,9,13-tetraazacyclohexadecane.

Table 2 Equilibrium constants for the reaction $[Ni_2L(MeOH)_4]^{2+} + 2B \rightleftharpoons [Ni_2L(B)_2]^{2+} + 4MeOH$ in MeOH solutions

B	$K_1{}^a$/dm^3 mol^{-1}	log (β_2/dm^6 mol^{-2})^b	p$K_H{}^c$	$q_N{}^d$
py	11.0 ± 0.2	1.78 ± 0.02	5.23	1.274
2Me-py	0.3 ± 0.1	−1.40 ± 0.04	5.95	1.494
3Me-py	15.4 ± 0.2	2.07 ± 0.02	5.68	1.368
4Me-py	19.5 ± 0.2	2.28 ± 0.02	6.03	1.521
pyz	4.7 ± 0.2	1.04 ± 0.04		
Him	115 ± 5	3.82 ± 0.04		

[a] Refers to 1 : 1 binding of B to a single metal ion. [b] Overall equilibrium constant. Units dm^6 mol^{-2} assuming [MeOH] fixed. [c] Value at zero ionic strength; ref. 25. [d] Ref. 26.

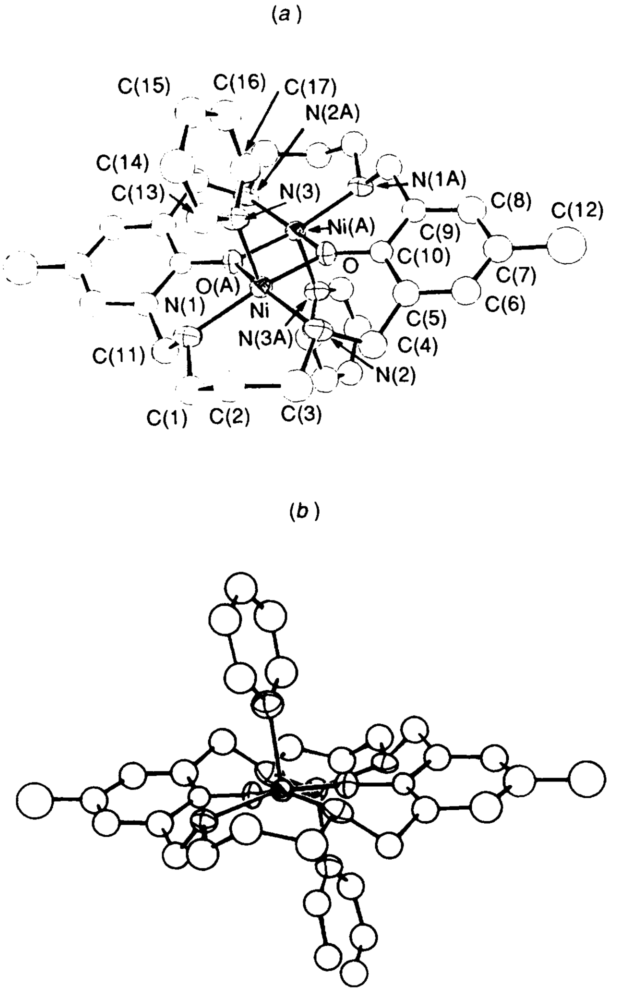


Fig. 2 Two perspective views of the $[Ni_2L(py)_2]^{2+}$ cation showing 30% probability thermal ellipsoids and labels for non-H atoms

Table 3 Summary of crystal data and data collection details for complex 7

Formula	$C_{34}H_{44}Cl_2N_6Ni_2O_{10}$
M	885.06
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	9.2514(15)
b/Å	11.4575(16)
c/Å	18.5548(24)
β/°	100.21(1)
U/Å^3	1935.6(5)
Z	2
D_c/g cm^{-3}	1.512
F(000)	959.8
μ(Mo-Kα)/cm^{-1}	11.8
Crystal size/mm	0.30 × 0.20 × 0.10
Scan type	θ–2θ
No. of parameters refined	160

Table 4 Atomic coordinates with estimated standard deviations (e.s.d.s) in parentheses for $[Ni_2L(py)_2][ClO_4]_2$

Atom	x	y	z
Ni	0.964 21(10)	0.514 01(8)	0.080 99(5)
Cl	0.537 27(25)	0.421 25(20)	0.246 24(12)
O	1.053 2(4)	0.597 2(4)	0.004 00(25)
O(1)	0.562 3(8)	0.542 9(5)	0.250 4(4)
O(2)	0.627 8(6)	0.371 1(7)	0.201 8(3)
O(3)	0.573 0(9)	0.372 9(6)	0.317 6(3)
O(4)	0.387 7(6)	0.395 0(6)	0.216 4(4)
N(1)	0.928 7(6)	0.378 0(5)	0.151 3(3)
N(2)	1.057 8(6)	0.631 9(5)	0.161 7(3)
N(3)	0.760 8(6)	0.587 7(5)	0.057 6(3)
C(1)	0.982 4(8)	0.391 4(7)	0.231 8(4)
C(2)	0.972 9(8)	0.513 5(7)	0.261 0(4)
C(3)	1.088 1(8)	0.592 9(7)	0.239 5(4)
C(4)	1.192 9(8)	0.684 0(7)	0.143 5(4)
C(5)	1.166 5(7)	0.756 9(6)	0.076 1(4)
C(6)	1.211 8(8)	0.873 4(7)	0.079 0(4)
C(7)	1.200 8(8)	0.938 9(7)	0.016 1(4)
C(8)	1.139 5(8)	0.891 7(7)	−0.050 4(4)
C(9)	1.088 2(8)	0.776 9(6)	−0.056 0(4)
C(10)	1.102 7(7)	0.709 3(6)	0.007 8(4)
C(11)	0.993 1(8)	0.266 1(7)	0.128 6(4)
C(12)	1.254 6(10)	1.069 9(8)	0.024 4(5)
C(13)	0.689 8(8)	0.637 9(7)	0.105 2(4)
C(14)	0.558 5(8)	0.697 7(7)	0.086 1(4)
C(15)	0.495 2(9)	0.704 2(7)	0.014 2(4)
C(16)	0.563 9(8)	0.651 3(7)	−0.035 8(4)
C(17)	0.696 6(8)	0.596 7(7)	−0.012 7(4)

vanished at the expense of a peak at 630 nm due to the formation of $[Ni_2L(B)_2]^{2+}$. Similar spectral behaviour has been observed for the other systems. The presence of only two light-absorbing species in solution was further verified by a graphical treatment[22] of the spectrophotometric titration curves.

Inasmuch as the two metal centres in $[Ni_2L(MeOH)_4]^{2+}$ are equivalent, experimentally only the equilibrium constant (K_1) involving the binding of a molecule of B to a single metal centre can be determined. The overall equilibrium constant (β_2) for reaction (1) may be obtained from the relation $\beta_2 = K_1{}^2/2$.

For those cases (py, 3Me-py, 4Me-py or Him) where the maximum change in absorbance with the addition of B was obtainable, the equilibrium constants (K_1) were evaluated by linear regression analysis of the absorbance values near the maxima by the method due to Brown.[23] On the other hand, for pyz and 2Me-py, where equilibrium (1) could not be shifted completely to the right-hand side, the K_1 values were evaluated by the Benesi-Hildebrand method.[24]

The K_1 and β_2 values are given in Table 2 along with the proton association constants (pK_H) and charge density on the nitrogen centre (q_N) of the heterocyclic bases. It may be noted that the equilibrium constant for 2Me-py is extremely small, which of course is expected on steric grounds. The structure of $[Ni_2L(py)_2][ClO_4]_2$ (see later) indicates that the approach of 2Me-py towards a metal centre will be strongly inhibited due to the steric interaction between the methyl substituent and equatorial plane of the macrocycle. When the heterocyclic bases offer no steric hindrance (py, 3Me-py, 4Me-py or Him) the equilibrium constants exhibit the trend expected on the basis of q_N and pK_H. The dependence of K_1 on K_H for the pyridine derivatives is precisely as in equation (2). This cannot, however,

$$pK_H = 2.40 + 1.59 \log \beta_2 \qquad (2)$$

Table 5 Selected bond distances (Å) and angles (°) for $[Ni_2L(py)_2][ClO_4]_2$

Ni–O	2.011(4)	N(1)–C(1)	1.496(9)
Ni–O(A)	2.012(5)	N(1)–C(11)	1.505(10)
Ni–N(1)	2.095(6)	N(2)–C(3)	1.489(9)
Ni–N(2)	2.088(6)	N(2)–C(4)	1.477(9)
Ni–N(3)	2.038(5)	O–C(10)	1.361(8)
Ni • • • Ni(A)	3.206(5)	Cl–O(1)	1.412(7)
O–Ni–O(A)	74.3(2)	Ni–N(1)–C(1)	119.0(5)
O–Ni–N(2)	91.9(2)	Ni–N(2)–C(3)	119.0(4)
O–Ni–N(1)	157.5(2)	Ni–N(2)–C(4)	110.9(4)
O(A)–Ni–N(1)	91.0(2)	Ni–N(1)–C(11)	110.2(4)
O(A)–Ni–N(2)	159.7(2)	N(1)–C(1)–C(2)	115.1(6)
N(1)–Ni–N(2)	97.2(2)	N(2)–C(3)–C(2)	114.6(6)
N(3)–Ni–O	97.5(2)	N(2)–C(4)–C(5)	113.6(6)
N(3)–Ni–O(A)	98.8(2)	C(1)–C(2)–C(3)	112.1(6)
N(3)–Ni–N(1)	101.6(2)	C(11)–N(1)–C(1)	106.8(5)
N(3)–Ni–N(2)	97.7(2)	C(4)–N(2)–C(3)	108.7(5)
Ni–O–Ni(A)	105.7(2)	O(1)–Cl–O(2)	109.1(4)

be extended to the imidazole system. The equilibrium constant in this case is appreciably greater than expected on the basis of the pK_H value. This indicates that a stronger Ni–N bond is formed with sp^3 than sp^2 nitrogen.

It may also be noted that pyrazine forms a significantly weaker complex than pyridine; the difference between their log β_2 values is 0.74. The pK_H for pyrazine is not available in the literature. However, a comparison of the log K_1 values[25] for pyrazine complexes of Ni^{2+} (1.01) and Ag^+ (1.38) with the corresponding pyridine complexes (1.87, 2.06) shows a quite similar trend.

Description of the Structure of $[Ni_2L(py)_2][ClO_4]_2$ 7.—Crystals of complex 7 consist of well separated $[Ni_2L(py)_2]^{2+}$ cations and perchlorate anions, which incidentally are not disordered. Two perspective views of the complex cation are shown in Fig. 2 along with the atom labelling scheme. Atomic coordinates and selected bond lengths and angles are given in Tables 4 and 5, respectively. The structure consists of two square-pyramidal nickel(II) centres bridged by two phenoxide oxygen atoms with two secondary amine nitrogen donors completing the distorted NiN_2O_2 plane. The nickel centre is displaced from the mean plane of the atoms O, N(2), N(1), O(A), towards the pyridine nitrogen atom N(3) by 0.332(3) Å. The two pyridine molecules are bound in a *trans* fashion above and below the dinuclear centres, with Ni–N(3) separations of 2.038(5) Å. The Ni_2O_2 atoms form an exact plane which is required by the crystallographic symmetry. There is a centre of inversion at the middle of this plane. The distortion in the NiN_2O_2 plane involves a compressed O–Ni–O(A) angle of 74.3(2)° and a broadened N(1)–Ni–N(2) angle of 97.2(2)°. The pyridine rings are not exactly over the nickel centres, as is evident from a comparison of the apical angles *viz*. N(3)–Ni–O 97.5, N(3)–Ni–O(A) 98.8, N(3)–Ni–N(2) 97.7, and N(3)–Ni–N(1) 101.6°. The 1,3-diaminopropane bridges on both the sides are puckered and are of neither chair nor boat conformation.

The structure of complex 7 can be compared to that of 4. The Ni–N(amine) distances in 7 (average 2.09 Å) are slightly longer than those of 4 (average 2.06 Å) and lie well within the range reported for a large collection of secondary amine to high-spin nickel(II) bonds (mean 2.11 Å).[27] The Ni–O distances in 7 (2.011 Å) and 4 (2.027 Å) are very close, but they lie on the longer side of the range 1.93–2.01 Å (mean 1.98 Å) reported[28–31] for a selection of high-spin Ni–O(phenolate) bonds. The Ni–N(pyridine) distance in 7 [2.038(5) Å] is normal.[32]

It is relevant to ask why the nickel centres in $[Ni_2L(B)_2][ClO_4]_2$ complexes adopt square-pyramidal in preference to octahedral geometry. Whether this could be due to a mismatch of size between the ligand cavity and the metal ion is considered first. A simple procedure has been described by Henrick *et al.*[2,27] to find the 'bonding cavity' (r_A) available to a metal ion in macrocyclic nickel(II) complexes of square-planar or octahedral geometries from the radius of the ligand hole (r_H). The ratio r_A/r_P (r_P is the Pauling covalent radius of the metal ion, 1.39 Å for high-spin Ni^{2+}) is then used to specify a match or a mismatch of a metal ion for a macrocyclic ligand cavity. A value of unity for r_A/r_P would represent a perfect match. The application of this approach to complex 4 leads to the values of r_H = 2.054 Å and r_A = 1.39 Å, which shows a perfect match. This fact clearly indicates the ring size is not the reason why the metal ions in $[Ni_2L(B)_2][ClO_4]_2$ complexes are squeezed out of the square plane. While one may argue that the presence of two heterocyclic rings on the same side of the basal plane as required for an octahedral configuration will be sterically unfavourable, the same argument will militate against the formation of complex 5 with a less sterically demanding ligand, ammonia. It appears that the axial field of the nitrogen co-ordinating ligands is strong enough to induce greater splitting of each of the orbital triplets of Ni^{2+}, so much so as to confer a square-pyramidal configuration.

The stereochemical behaviours of the unsaturated macrocyclic ligands (H_2L^1, H_2L^2) are in sharp contrast to that exhibited by H_2L. Apparently, the in-plane ligand-field strength of the N_2O_2 donors in H_2L^1 is so strong as to cause spin pairing of the Ni^{2+} ions. On the other hand, the behaviour of H_2L^2 is more complex. While a weak-field ligand like Cl^- leads to square-pyramidal geometry[6] in $[Ni_2L^2Cl_2]$, a strong-field ligand like pyridine produces an octahedral[7] species, $[Ni_2L^2(py)_4]^{2+}$.

Experimental

Materials.—All chemicals were reagent grade and used as received. The ligand H_2L was prepared as reported earlier.[33,34] Its m.p. erroneously reported as 125 °C, is 145 °C. Complex 4 was prepared as reported.[9] Pyridine and monomethylpyridines were dried by refluxing over anhydrous K_2CO_3 and then distilled using an efficient fractionating column.

Synthesis.—$[Ni_2L(NH_3)_2][ClO_4]_2$ **5**. Through a methanol solution (30 cm^3) of complex **4** (1 g) dry NH_3 was bubbled for 2 min. On slow evaporation green crystals of the complex were deposited on the upper part of the flask. These were collected by filtration and washed with small portions of chilled MeOH and Et_2O (Found: C, 38.1; H, 5.4; N, 11.2. $C_{24}H_{40}Cl_2N_6Ni_2O_{10}$ requires C, 37.85; H, 5.25; N, 11.05%).

$[Ni_2L(Him)_2][ClO_4]_2$ **6**.—A methanol solution (20 cm^3) of complex **4** (1.19 g, 1 mmol) and imidazole (0.14 g, 2 mmol) was refluxed for 0.5 h. The bright green crystals which deposited on standing were recrystallized from MeOH. (Found: C, 41.5; H, 4.9; N, 12.8. $C_{30}H_{42}Cl_2N_8Ni_2O_{10}$ requires C, 41.7; H, 4.85; N, 13.0%).

$[Ni_2L(py)_2][ClO_4]_2$ **7**. Complex **4** (1 g) was dissolved in hot MeOH (15 cm^3) and treated with pyridine (5 cm^3). The solution on standing overnight afforded bright green crystals of the complex. Crystals suitable for X-ray diffraction studies were obtained by diffusing Et_2O into a MeOH–py(1:1) solution of the complex (Found: C, 45.8; H, 4.9; N, 9.35. $C_{34}H_{44}Cl_2N_6Ni_2O_{10}$ requires C, 46.15; H, 5.0; N, 9.5%).

$[Ni_2L(pyz)_2][ClO_4]_2$ **8**. Complex **4** (1.19 g, 1 mmol) and pyrazine (1.2 g, 15 mmol) dissolved in MeOH (30 cm^3) was stored over $CaCl_2$ in a desiccator. The green crystals which were deposited on the walls of the beaker were collected on a glass frit and washed with Et_2O (Found: C, 43.8; H, 4.9; N, 12.5. $C_{32}H_{42}Cl_2N_8Ni_2O_{10}$ requires C, 43.3; H, 4.75; N, 12.65%).

$[Ni_2L(\mu\text{-pz})(H_2O)_2][ClO_4]$ **9** *and* $[Ni_2L(\mu\text{-pz})(Hpz)(H_2O)][ClO_4]\cdot H_2O$ **10**. A methanol solution (30 cm^3) of complex **4** (1.19 g, 1 mmol) was treated with pyrazole (0.07 g, 1 mmol) and triethylamine (0.1 g, 1 mmol). The solution was refluxed for 0.5 h and then concentracted (20 cm^3). On cooling in an ice-bath, blue crystals of complex **9** deposited. These were collected by filtration and recrystallized from Me_2CO (Found: C, 44.2; H, 5.5; N, 11.65. $C_{27}H_{41}ClN_6Ni_2O_8$ requires C, 44.4; H, 5.6; N, 11.5%). When the above reaction was carried out with 1 equivalent of complex **4** and 3 equivalents each of pyrazole and triethylamine, complex **10** was obtained as sky-blue crystals (Found: C, 45.5; H, 5.8; N, 13.95. $C_{30}H_{45}ClN_8Ni_2O_8$ requires C, 45.1; H, 5.65; N, 14.05%).

Physical Measurements.—Infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer using KBr discs, electronic spectra on a Hitachi U3400 or JASCO 7850 spectrophotometer in the UV/VIS and near-IR regions. Room-temperature magnetic susceptibilities were measured on a EG & G PAR 155 vibrating-sample magnetometer using $Hg[Co(NCS)_4]$ as the calibrant. Conductivity measurements were carried out using a Philips PR 9500 conductivity bridge. Elemental analyses were performed on a Perkin-Elmer 240C C, H and N analyzer.

Equilibrium Constants.—The equilibrium constants for the reaction $[Ni_2L(MeOH)_4]^{2+} + 2B \rightleftharpoons [Ni_2L(B)_2]^{2+} + 4MeOH$ (B = py, 2Me-, 3Me-, 4Me-py, Him or pyz) were determined spectrophotometrically at room temperature (25 ± 0.5 °C) by recording a series of spectra of methanol solutions of complex **4** mixed with varying quantities of the Lewis base (B). A pair of matched quartz cells (path length 1 cm) and appropriate blank solutions were used throughout the measurements. The concentration of complex **4**, fixed for a series of measurements, was kept between 5×10^{-3} and 1×10^{-2} mol dm^{-3}, and that of the base varied over a wide range till no further change in absorbance at the maxima was noted.

Crystal Structure Determination and Refinement.—Diffraction data were collected at 298 K with an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.709 30 Å). Crystal data and details of the data collection are given in Table 3. The unit-cell parameters were obtained by least-squares refinement of the scattering angles of 25 reflections with 2θ = 30–35°. A total of 2512 reflections were measured to $2\theta_{max}$ = 48.8°, of which 2494 were unique and 1713 having $I > 2.5\sigma(I)$ were considered as independent and used in the structure analysis. They were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by direct and Fourier difference methods using the NRCVAX crystal-structure programs[35] and refined by full-matrix least-squares methods to final residuals of R = 0.053 and R' = 0.039, using weights based on counting statistics. The values of f' and f'' used were those given in ref. 36. The positions of the hydrogen atoms were located from difference maps. The highest peak in the final Fourier difference map had an electron density of 0.57 e Å^{-3}.

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

References

1 L. F. Lindoy, *The Chemistry of Macrocyclic Ligand Complexes*, Cambridge University Press, Cambridge, 1989.
2 K. Henrick, P. A. Tasker and L. F. Lindoy, *Prog. Inorg. Chem.*, 1985, **33**, 1.
3 *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum, New York, 1979.
4 D. H. Busch, *Acc. Chem. Res.*, 1978, **11**, 392.
5 H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn.*, 1972, **42**, 1959.
6 N. H. Pilkington and R. Robson, *Aust. J. Chem.*, 1970, **23**, 2225.
7 C. L. Spiro, S. L. Lambert, T. J. Smith, E. N. Duesler, R. R. Gagne and D. N. Hendrickson, *Inorg. Chem.*, 1981, **20**, 1229.
8 S. L. Lambert and D. N. Hendrickson, *Inorg. Chem.*, 1979, **18**, 2683.
9 R. Das and K. Nag, *Inorg. Chem.*, 1991, **30**, 2831.
10 E. K. Barefield, *Inorg. Chem.*, 1972, **11**, 2273; E. K. Barefield and F. Wagner, *Inorg. Chem.*, 1973, **12**, 2435; F. Wagner and E. K. Barefield, *Inorg. Chem.*, 1976, **15**, 408.
11 E. K. Barefield, A. Bianchi, E. J. Billo, P. J. Connolly, P. Paoletti, J. S. Summers and D. G. Van Derveer, *Inorg. Chem.*, 1986, **25**, 4197.
12 P. Moore, J. Sachinidis and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1984, 1323; E. H. Curzon, N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1980, 574; N. Herron and P. Moore, *J. Chem. Soc., Dalton Trans.*, 1979, 441.
13 E. J. Billo, *Inorg. Chem.*, 1984, **23**, 236, 2223.
14 M. Ciampolini, M. Micheloni, N. Nardi, P. Paoletti, P. Dapporto and F. Zanobini, *J. Chem. Soc., Dalton Trans.*, 1984, 1357.
15 V. J. Thom and R. D. Hancock, *J. Chem. Soc., Dalton Trans.*, 1985, 1877.
16 M. D. Cassa, L. Fabbrizzi, M. Mariani and B. Seghi, *J. Chem. Soc., Dalton Trans.*, 1990, 55; M. Ciampolini, L. Fabbrizzi, M. Licchelli, A. Perotti, F. Pezzini and A. Poggi, *Inorg. Chem.*, 1986, **25**, 4131; L. Fabbrizzi, M. Micheloni and P. Paoletti, *Inorg. Chem.*, 1980, **19**, 535.
17 E. Iwamoto, T. Yokoyama, S. Yamasaki, T. Yabe, T. Kumamuru and Y. Yamamoto, *J. Chem. Soc., Dalton Trans.*, 1988, 1935.
18 L. P. Battaglia, A. Bianchi, A. B. Corradi, E. Garcia-Espana, M. Julve and M. Micheloni, *Inorg. Chem.*, 1988, **27**, 4174.
19 C. N. R. Rao, *Chemical Applications of Infrared Spectroscopy*, Academic Press, New York, 1963.
20 R. Das, K. K. Nanda, L. K. Thompson, K. Venkatsubramanian, P. Paul and K. Nag, unpublished work.
21 A. B. P. Lever, *Inorganic Electronic Spectroscopy*, 2nd edn. Elsevier, Amsterdam, 1984.
22 J. S. Coleman, L. P. Varga and S. H. Mastin, *Inorg. Chem.*, 1970, **9**, 1015.
23 K. L. Brown, *Inorg. Chim. Acta*, 1979, **37**, L513.
24 H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, 1949, **71**, 2703; R. L. Scott, *Recl. Trav. Chim. Pays-Bas*, 1956, **75**, 787.
25 R. M. Smith and A. E. Martell, *Critical Stability Constants*, Plenum, New York, 1975, vol. 2, pp. 165, 263.
26 D. A. Brown and M. J. S. Dewar, *J. Chem. Soc.*, 1953, 2407.
27 K. Henrick, L. F. Lindoy, M. McPartlin, P. A. Tasker and M. P. Wood, *J. Am. Chem. Soc.*, 1984, **106**, 1641; H. J. Goodwin, K. Henrick, L. F. Lindoy, M. McPartlin and P. A. Tasker, *Inorg. Chem.*, 1982, **21**, 3923.
28 M. Bell, A. J. Edwards, B. F. Hoskins, E. H. Kachab and R. Robson, *J. Am. Chem. Soc.*, 1989, **111**, 3603.
29 R. M. Buchanan, M. S. Mashuta, K. J. Oberhausen, J. F. Richardson, Q. Li and D. N. Hendrickson, *J. Am. Chem. Soc.*, 1989, **111**, 4497.
30 M. Seleborg, S. L. Holt and B. Port, *Inorg. Chem.*, 1971, **10**, 1501.
31 M. Di Vaira, P. L. Orioli and L. Sacconi, *Inorg. Chem.*, 1971, **10**, 553; P. L. Orioli, M. Di Vaira and L. Sacconi, *J. Am. Chem. Soc.*, 1966, **88**, 4383; L. Sacconi, P. L. Orioli and M. Di Vaira, *J. Am. Chem. Soc.*, 1965, **87**, 2059.
32 K. Wieghardt, E. Schoffmann, B. Nuber and J. Weiss, *Inorg. Chem.*, 1986, **25**, 4877.
33 S. K. Mandal and K. Nag, *J. Org. Chem.*, 1986, **51**, 3900.
34 S. K. Mandal, L. K. Thompson, K. Nag, J.-P. Charland and E. J. Gabe, *Inorg. Chem.*, 1987, **26**, 1391.
35 E. Gabe, F. L. Lee and Y. Le Page in *Crystallographic Computing III*, eds. G. M. Sheldrick, C. Kruger and R. Goddard, Clarendon, Oxford, 1985, p. 167.
36 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

Received 16th July 1991; Paper 1/03617C