Intramolecular Ligand Rearrangement in the Isomerisation of a Seven-co-ordinate to a Six-co-ordinate Nickel(II) Complex of a Multidentate Schiff Base. The Crystal and Molecular Structures of the Six-co-ordinate Product

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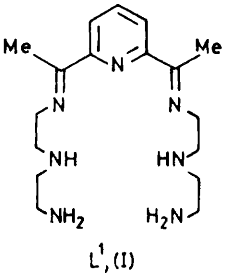
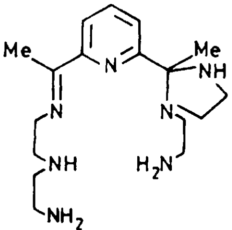
The pentagonal-bipyramidal nickel(II) complex $[NiL^1][BPh_4]_2$, containing the heptadentate ligand L^1 derived from the condensation of one molecule of 2,6-diacetylpyridine with two molecules of diethylenetriamine, isomerises in acetonitrile solution to the distorted octahedral complex $[NiL^2][BPh_4]_2\cdot MeCN$ of an isomeric hexadentate ligand L^2. Crystals of $[NiL^2][BPh_4]_2\cdot MeCN$ are triclinic with a = 11.738(10), b = 14.219(12), c = 18.865(14) Å, α = 83.0(1), β = 109.7(1), γ = 89.2(1)°, Z = 2, space group $P\bar{1}$. 2 362 Reflections above background were measured by diffractometer and refined by full-matrix least squares to R 0.093. The Ni^{II} ion is bound to six nitrogen atoms of the rearranged ligand L^2, derived from L^1 by nucleophilic addition of one secondary amine group across the neighbouring azomethine bond with concomitant formation of a five-membered imidazolidine ring. The co-ordination geometry of the Ni^{II} ion is approximately octahedral with the Ni–N bonds 2.003(20)—2.319(18) Å. The thermodynamic driving force for the ligand isomerisation is attributed to the stereochemical preference of Ni^{II} for O_h over D_{5h} symmetry. The results are discussed in relation to the structures and reactions of complexes of related multidentate ligands.

In the preceding paper[1] a series of first row transition-metal complexes $[ML^1]X_2$ (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}; X = ClO_4^- or BPh_4^-) of the heptadentate Schiff-base ligand L^1 [structure (I)] were reported. On the basis of a single-crystal *X*-ray structure determination of $[CuL^1][ClO_4]_2$, of comparisons of *X*-ray powder patterns of the tetraphenylborate salts, and of various physical properties it was shown that all the complexes have a pentagonal-bipyramidal geometry in which the trimethine group together with the two secondary amine nitrogens make up the pentagonal plane, the two primary amine nitrogens occupying the axial positions. In the preparation of the nickel(II) complex it was found that two products were generally obtained. In addition to the green seven-co-ordinate complex $[NiL^1][BPh_4]_2$ a brown crystalline product $[NiL^2][BPh_4]_2\cdot MeCN$ was isolated from acetonitrile solution, the two complexes being separated by fractional crystallisation. A brown perchlorate salt $[NiL^2][ClO_4]_2$ was also isolated but the green form could not be obtained as the perchlorate in a pure state. In this paper we show that the brown form is a six-co-ordinate complex of nickel(II) in which the heptadentate ligand L^1 has isomerised to the potentially hexadentate ligand L^2 [structure (II)].



L^1,(I)



L^2,(II)

RESULTS

During attempts to optimise the preparative conditions for the green and brown complexes in the metal-ion exchange reaction from alkaline-earth metal ion complexes of L^1, it became apparent that the brown complex ion is an isomerisation product of the green one. Whereas both forms could be isolated from reaction mixtures containing high concentrations of reactants, only the brown form could be isolated from aged solutions. Moreover, solutions of the green complex $[NiL^1][BPh_4]_2$ yielded only the brown complex $[NiL^2][BPh_4]_2\cdot MeCN$ on 'recrystallisation' from acetonitrile. Indeed, the only reason that the green complex $[NiL^1][BPh_4]_2$ could be separated in a pure form is that it is considerably less soluble than brown $[NiL^2][BPh_4]_2\cdot MeCN$ in this solvent. Conversion of the green to the brown complex was complete in *ca.* 1 h in refluxing MeCN. Under these conditions the isomerisation was accompanied by some decomposition, the yield of brown isomer being *ca.* 60%. The decomposition by-products were not isolated or identified. At ambient temperature, and in dilute solution, however, the conversion was virtually quantitative and could be followed spectrophotometrically over a period of 2 days. The solid-state spectra of the green and brown forms are compared in Figure 1. A major difference in the spectra is the replacement of the low energy band at 6 500 cm^{-1} in the green form by one at 10 500 cm^{-1} in the brown complex. The spectrum of the brown complex is characteristic of Ni^{II} in a pseudo-octahedral ligand field,[2] the three bands at 10 500, *ca.* 18 000, and *ca.* 23 000 cm^{-1} being assigned to the transitions $^3A_{2g}\rightarrow{}^3T_{2g}$, $^3A_{2g}\rightarrow{}^3T_{1g}(F)$, and $^3A_{2g}\rightarrow{}^3T_{1g}(P)$ respectively; in O_h symmetry, the two high energy transitions occurring as shoulders on the side of a charge-transfer and/or co-ordinated ligand band at 28 000 cm^{-1}.

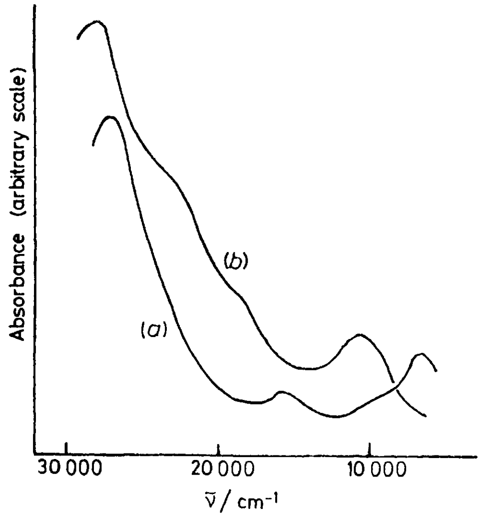


FIGURE 1 The solid-state electronic spectra of (*a*) [NiL^1][BPh$_4$]$_2$ and (*b*) [NiL^2][BPh$_4$]$_2$·MeCN

Analytical data for the brown complexes indicated, at least within the experimental uncertainty of the analyses, that the ligand has the same elemental composition as L^1 in the green complex [NiL^1][BPh$_4$]$_2$ (Table 1). Moreover, the i.r. spectra of the brown complexes while showing some definite differences were similar in important respects to that of green [NiL^1][BPh$_4$]$_2$. In particular they showed multicomponent absorption in the N–H stretching region, a band at 1 655 cm^{-1} characteristic of the imino-group, and the weak to moderate intensity absorption at 1 625 cm^{-1} expected for the NH$_2$ bending vibration, in addition to characteristic features of the pyridine ring. A significant difference however was the reduced intensity of ν(C=N) in the brown complex. The magnetic moments of the brown derivatives are *ca.* 3.05 B.M.* (Table 1) and consistent with a six-co-ordinate structure.

TABLE 1

Analytical, infrared, and magnetic data for the complexes

	Analysis (%)						I.r. bands (cm^{-1})		
	Found			Calc.					
Complex	C	H	N	C	H	N	ν(NH)	ν(C=N)	$\mu_{\text{eff.}}$ [a]/ B.M.
[NiL^1][BPh$_4$]$_2$	75.7	7.0	9.6	75.7	6.9	9.5	3 310, 3 264, 3 160	1 648	3.10
[NiL^2][BPh$_4$]$_2$·MeCN [b]	75.4	6.9	10.2	75.1	6.9	10.4	3 335 (sh), 3 320, 3 270	1 650	3.05
[NiL^2][ClO$_4$]$_2$	34.7	5.3	16.4	34.5	5.3	16.6	3 340, 3 320 (sh), 3 295	1 658, 1 654	3.07

[a] At 293 K, corrected for diamagnetism of ligands. [b] ν(C≡N) of MeCN at 2 260 cm^{-1}.

Considered collectively, the properties of the brown complexes suggested a heptadentate to hexadentate rearrangement of the multidentate ligand. In the light of earlier work,[3,4] in which some macrocyclic Schiff-base ligands were observed to undergo metal-controlled ligand rearrangements involving nucleophilic addition of a secondary amine group across a neighbouring C=N bond, it seemed that L^1 might have isomerised to L^2 [structure (II)]. Proof that this was so was obtained from a single-crystal *X*-ray structure determination of the brown complex [NiL^2][BPh$_4$]$_2$·MeCN.

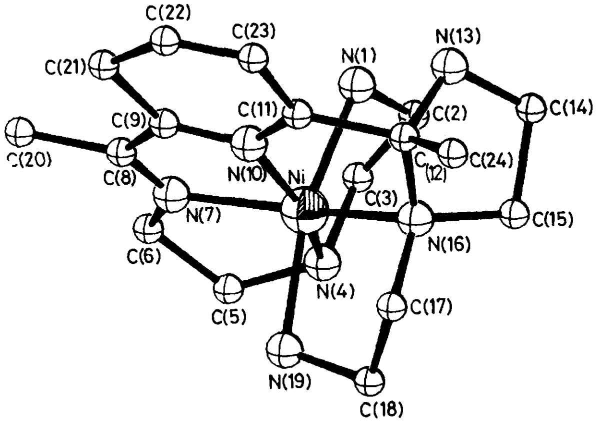


FIGURE 2 The structure of [NiL^2]$^{2+}$ showing the atomic numbering scheme

Discussion of the Structure.—The asymmetric unit consists of discrete [NiL^2]$^{2+}$ cations, two [BPh$_4$]$^-$ anions, and one molecule of solvent acetonitrile. The structure of the complex is shown in Figure 2 together with the atomic numbering scheme. The nickel atom is bonded to six nitrogens of the ligand L^2 in an approximately octahedral array. Data in Table 2 show that the unsaturated segment of the ligand is relatively planar (Plane 1). The Ni–N(7) and Ni–N(10) bonds [2.003(20), 2.026(16) Å] are the shortest of the six Ni–N bonds, probably because of the relative freedom from steric strain of this part of the ligand. Also in this equatorial plane are N(4) and N(16) but at distances of −0.32 and 0.54 Å, respectively, from plane 1. It is to be expected that N(4) will be pulled out of this plane towards N(1) so that this atom can achieve an axial position. This involves a degree of strain as is apparent from the torsion angles in Table 3. In particular, C(2)–C(3)–N(4)–C(5) 145.4° and N(4)–C(5)–C(6)–N(7) −42.8° are distorted from the staggered 120° and −60°. The most highly strained part of the ligand is the segment from N(10) to N(16) which bears the five-membered imidazolidine ring formed by the nucleophilic attack of the N(16)H group (in L^1) at C(12). The atom C(12) is coplanar with the dimethine segment but N(16) is twisted out of this plane such that the N(10)–C(11)–C(12)–N(16) torsion angle is −25.2°. The Ni–N(16) bond is the longest of all at 2.319(19) Å. The five-membered ring C(12), N(13), C(14), C(15), N(16) is puckered as expected, with C(12) and N(16) being furthest from the

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* Throughout this paper: 1 B.M. = 0.927 × 10^{-23} A m^2.

TABLE 2

Least-squares planes †

Plane 1	Ni * 0.03, N(7) −0.02, C(8) 0.01, C(9) 0.04, N(10) 0.07, C(11) 0.02, C(12) −0.05, C(20) −0.06, C(21) 0.02, C(22) −0.00, C(23) −0.05, N(16) * 0.54, C(6) * −0.21, C(5) * 0.18, N(4) * −0.32
Plane 2	Ni −0.03, N(4) −0.09, N(7) 0.17, N(10) −0.16, N(16) 0.12
Plane 3	Ni 0.09, N(1) 0.33, N(7) −0.41, N(16) −0.41, N(19) 0.40
Plane 4	Ni 0.06, N(1) 0.29, N(4) −0.32, N(10) −0.28, N(19) 0.25
Plane 5	C(12) 0.25, N(13) −0.18, C(14) 0.05, C(15) 0.09, N(16) −0.21
Plane 6	Ni 0.00, N(10) 0.00, N(16) 0.00, C(11) * −0.31, C(12) * −0.65
Plane 7	Ni 0.00, N(1) 0.00, N(4) 0.00, C(2) * 0.59, C(3) * −0.09
Plane 8	Ni 0.00, N(4) 0.00, N(7) 0.00, C(5) * 0.57, C(6) * 0.05
Plane 9	Ni 0.00, N(16) 0.00, N(19) 0.00, C(17) * −0.29, C(18) * 0.42

† Distances of atoms from the planes are given in Å. Atoms not contributing to the planes are marked with an asterisk.

TABLE 3

Torsion angles (°). Standard deviations are *ca.* 1°

Ni–N(1)–C(2)–C(3)	50.4
N(1)–C(2)–C(3)–N(4)	−55.2
C(2)–C(3)–N(4)–C(5)	145.4
C(3)–N(4)–C(5)–C(6)	−72.6
N(4)–C(5)–C(6)–N(7)	−42.8
C(5)–C(6)–N(7)–C(8)	−165.4
N(10)–C(11)–C(12)–N(13)	86.4
N(10)–C(11)–C(12)–N(16)	−25.2
N(10)–C(11)–C(12)–C(24)	−149.0
C(11)–C(12)–N(16)–C(17)	−78.0
N(16)–C(17)–C(18)–N(19)	−60.4
C(17)–C(18)–N(19)–Ni	45.6

best ring plane which intersects plane 1 at an angle of 67.1°.

The least-squares planes calculations (Table 2) show that the three NiN_4 planes of the octahedron are relatively planar with deviations up to 0.41 Å for a contributing atom. Also shown in Table 2 are the distances of the two carbon atoms of a five-membered saturated chelate ring from the NiN_2 plane. These show no unusual conformations except for the ring containing Ni, N(10), N(16) in which C(11) is −0.31 and C(12) is −0.65 Å from the NiN_2 plane.

As might be expected from the ease with which the crystal deteriorates in the absence of solvent, the N(100) atom of the MeCN solvate molecule participates in short contacts with both N(4) and N(19) (3.14 and 3.07 Å, respectively); the estimated N-H · · · N(100) angles are 135° and 133°, respectively. While these distances do not constitute strong hydrogen bonds the interactions are clearly important for the stabilisation of the crystal structure.

There are no contacts between the ions less than the sum of van der Waals radii and, indeed, only five are less than 3.5 Å. This inefficiency in packing is reflected in the very low density.

DISCUSSION

The results described above show that the co-ordinated ligand L^1 [structure (I)] has rearranged to L^2 [structure (II)] as a result of nucleophilic addition of a secondary amine group across an adjacent azomethine bond with concomitant formation of a five-membered imidazolidine ring. The ligand isomerisation has two important consequences for its co-ordinating properties. First, it reduces the maximum denticity (towards a centrally co-ordinated metal ion) from seven to six, and secondly, it alters the conformation, *via* conversion of a double C=N bond to a single C–N bond, so that it can now accommodate to co-ordination on an octahedron.

The isomerised ligand L^2 is the product of intramolecular addition of an NH group to a C=N bond and therefore contains a *gem*-diamine (aminal) moiety. Such addition compounds are not generally isolable although, where primary amines are involved, they are postulated as intermediates in transamination reactions.[5] They are, however, known to be stabilised by co-ordination to a metal ion in a few cases.[6] Two interesting precedents for the metal-ion promoted addition of NH to C=N relevant to the present system have been reported recently.[3,4] In one of these, replacement of alkaline-earth metal ions from their complexes with a planar hexadentate ' N_6 ' Schiff-base macrocycle by the smaller transition metal ions Mn^{II}, Fe^{II}, Co^{II}, or Zn^{II} is accompanied by a contraction of the 18-membered inner large ring to 15 member atoms.[3] In the second example [4] replacement of two Ag^I ions from a 24-membered macrocycle by a single Ba^{II} ion is similarly accompanied by a contraction of the inner large ring to 18 member atoms. In both these cases the ligand rearrangement is in response to the geometrical demands of the metal ion, *i.e.* the relative sizes of the macrocycle cavity and the incoming metal ion. In the present system we observe a variant of the same entatic principle. Here, the isomerisation of the ligand is in response not to the size but to the stereochemical preference of the complexed metal ion; namely, the desire of the Ni^{II} ion to alter its symmetry from D_{5h} to O_h. There is ample evidence that the preferred stereochemistries of Ni^{II} are those in which the metal–ligand bonds are in an orthogonal relationship. On crystal-field considerations alone the stability advantage of O_h over other high-spin stereochemical configurations (T_d, D_{3h}, C_{4v}, D_{5h}) is apparent in a comparison of crystal-field stabilisation energies (c.f.s.e.).[7] Table 4 compares the c.f.s.e. of the high-spin d^5—d^{10} divalent ions, Mn, Fe, Co, Ni, Cu, Zn, in O_h and D_{5h} crystal fields. It can be seen that of the series of ions under consideration only Ni^{II} and Cu^{II} are thermodynamically disadvantaged in D_{5h} compared to O_h symmetry, the effect being considerably greater for Ni^{II}.

TABLE 4

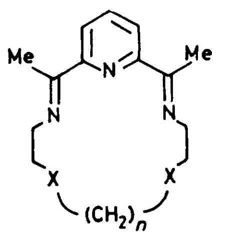
Comparison of crystal-field stabilisation energies * (in *Dq*) in O_h and D_{5h} fields for the ions Mn^{II}—Zn^{II}

Ion	O_h	D_{5h}	c.f.s.e. ($O_h - D_{5h}$)
Mn^{II}	0	0	0
Fe^{II}	4	5.28	−1.28
Co^{II}	8	10.56	−2.56
Ni^{II}	12	7.74	4.26
Cu^{II}	6	4.93	1.07
Zn^{II}	0	0	0

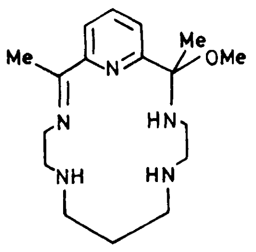
* Values from ref. 7.

The prediction that, among the first row, high-spin

d^5—d^{10} transition metal ions the pentagonal bipyramid is the least stable for d^8 with respect to the octahedral alternative is borne out by the results presented here. Of the series $[ML^1]^{2+}$ only the nickel(II) complex undergoes the $D_{5h} \rightarrow O_h$ configurational change, at least under the mild reaction conditions employed. Again, it is noteworthy that stable pentagonal-bipyramidal complexes of the quinquedentate macrocycles L^3, L^4, and L^5 have been prepared for the ions Mn^{II}, Fe^{II}, Co^{II}, and Zn^{II} [8-10] but not for Ni^{II}. Attempts to prepare an analogous nickel(II) complex of L^4, for example, by replacement of Ag^I from the planar macrocycle in methanol solution yielded six-co-ordinate complexes of the new macrocycle L^6 formed by addition of MeOH across one azomethine bond.[11] Here L^6 has sufficient flexibility to accommodate to five positions of an octahedron, such folding being denied to its precursor ligand L^4.

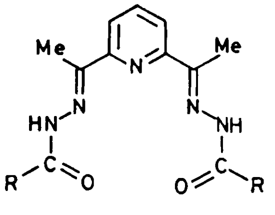


L^3 : X = NH, n = 2
L^4 : X = NH, n = 3
L^5 : X = O, n = 2

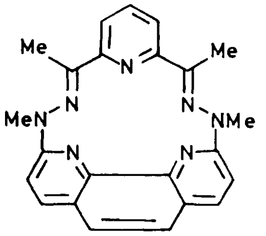


L^6

It is not surprising, therefore, that few seven-co-ordinate nickel(II) complexes have yet been prepared. In addition to the pentagonal-bipyramidal $[NiL^1]^{2+}$ cation described in this and the preceding paper[1] there are three other polydentate ligands known to impose, along with two monodentate axial ligands, a pentagonal-bipyramidal geometry upon Ni^{II}. These are the closely related quinquedentate ligands L^7 (ref. 12) and L^8 (ref. 13) and the macrocyclic ligand L^9 (ref. 14) all of which possess a more rigid ' pentagonal planar ' framework as a result of a more extensive π-electron delocalisation than, for example, L^1 or L^4. The greater rigidity of L^9 over L^4 prevents it from adopting the same device (folding following alcohol addition) to achieve ' octahedral ' co-ordination.



L^7: R = NH_2
L^8: R = Ph



L^9

EXPERIMENTAL

Preparation of the Complexes.—$[NiL^1][BPh_4]_2$ *and* $[NiL^2][BPh_4]_2$. To $[CaL^1][ClO_4]_2 \cdot H_2O$ (1 mmol) in MeCN (60 cm^3) was added $Ni[ClO_4]_2 \cdot 6H_2O$ (1 mmol) followed by $Na[BPh_4]$ (2 mmol). The resulting solution was stirred at ambient temperature for *ca.* 30 min before reducing the volume by rotary evaporation. Small green crystals of $[NiL^1][BPh_4]_2$ separated in 45% yield. If the reaction mixture was heated the yield of green product was much reduced. Further slow evaporation of the solutions gave large brown nuggets of $[NiL^2][BPh_4]_2 \cdot MeCN$.

When the above preparation was carried out in MeOH an immediate beige precipitate separated on addition of $Na[BPh_4]$. This crude material was fractionally crystallised from MeCN solution to give both green and brown forms.

$[NiL^2][ClO_4]_2$. Addition of $Ni[ClO_4]_2 \cdot 6H_2O$ (1 mmol) in a small quantity of MeOH to $[CaL^1][ClO_4]_2 \cdot H_2O$ (1 mmol) in MeOH (200 cm^3), followed by heating to reflux for 30 min, gave a deep brown solution. On cooling, the product separated as small brown needles after several hours. Yield *ca.* 70%.

Crystal Data.—$[NiL^2][BPh_4]_2 \cdot MeCN$, $C_{66}H_{74}B_2N_8Ni$, M = 1 059.7, Triclinic, a = 11.738(10), b = 14.219(12), c = 18.865(14) Å, α = 83.0(1), β = 109.7(1), γ = 89.2(1)°, U = 2 936.5 Å^3, $F(000)$ = 2 228, Z = 2, D_c = 1.18 g cm^{-3}, μ(Mo-K_α) 3.8 cm^{-1}, λ(Mo-K_α) = 0.710 7 Å, space group $P\bar{1}$ from the successful structure determination. A crystal of approximate size 0.65 × 0.3 × 0.8 mm was sealed in a capillary which contained several drops of solvent MeCN. In the absence of solvent the crystal rapidly decomposed in the X-ray beam. The crystal was set up with the 1 0 0 planes perpendicular to the instrument axis of a General Electric XRD-5 diffractometer which was used to measure cell dimensions by least-squares refinement of high-angle data and diffraction intensities by the stationary-crystal–stationary-counter method. 3 645 Independent intensities were measured with $2\theta < 35°$ of which 2 362 with $I > 2\sigma(I)$ were used in subsequent calculations. Neither an absorption nor an extinction correction was found to be necessary.

Structure Determination.—The position of the nickel atom was located from the Patterson map. Positions of the

TABLE 5

Atomic co-ordinates (× 10^4) for $[NiL^2][BPh_4]_2 \cdot MeCN$ with estimated standard deviations in parentheses

Atom	*X*	*Y*	*Z*
Ni	583(3)	2 147(2)	2 697(2)
N(1)	1 548(15)	2 481(13)	1 932(10)
C(2)	2 786(21)	2 701(17)	2 395(13)
C(3)	3 285(22)	1 937(18)	3 030(14)
N(4)	2 395(17)	1 798(15)	3 495(12)
C(5)	2 378(24)	798(19)	3 800(15)
C(6)	1 726(23)	199(19)	3 195(15)
N(7)	620(18)	740(14)	2 688(11)
C(8)	−317(25)	417(20)	2 184(16)
C(9)	−1 186(23)	1 111(19)	1 714(14)
N(10)	−983(16)	1 999(14)	1 843(10)
C(11)	−1 669(20)	2 736(17)	1 428(13)
C(12)	−1 238(21)	3 701(17)	1 627(13)
N(13)	−400(17)	4 002(14)	1 228(11)
C(14)	384(27)	4 668(22)	1 665(16)
C(15)	310(24)	4 450(19)	2 491(15)
N(16)	−461(16)	3 617(13)	2 427(11)
C(17)	−1 123(21)	3 540(17)	2 971(13)
C(18)	−378(22)	3 046(18)	3 722(14)
N(19)	−24(16)	2 082(13)	3 642(10)
C(20)	−401(28)	−635(23)	2 094(18)
C(21)	−2 263(25)	930(23)	1 094(16)

TABLE 5 (*continued*)

Atom	X	Y	Z
C(22)	−2 951(28)	1 734(23)	692(18)
C(23)	−2 692(26)	2 578(23)	811(17)
C(24)	−2 294(24)	4 433(20)	1 456(17)
B(1)	2 295(26)	2 486(22)	−226(17)
C(31)	3 200(22)	2 255(19)	−716(14)
C(32)	3 700(20)	1 366(18)	−690(13)
C(33)	4 431(25)	1 177(22)	−1 130(16)
C(34)	4 754(27)	1 877(23)	−1 553(17)
C(35)	4 273(26)	2 771(23)	−1 636(17)
C(36)	3 498(27)	2 988(24)	−1 219(17)
C(41)	814(21)	2 608(17)	−823(14)
C(42)	516(24)	2 829(18)	−1 612(15)
C(43)	−735(27)	2 985(21)	−2 079(18)
C(44)	−1 609(27)	2 949(19)	−1 773(17)
C(45)	−1 345(23)	2 729(17)	−1 002(15)
C(46)	−102(23)	2 584(17)	−529(16)
C(51)	2 379(21)	1 549(17)	402(13)
C(52)	1 628(23)	805(18)	305(15)
C(53)	1 835(27)	−14(21)	865(17)
C(54)	2 804(24)	−75(20)	1 472(16)
C(55)	3 604(24)	618(19)	1 599(16)
C(56)	3 409(22)	1 423(18)	1 084(13)
C(61)	2 699(20)	3 456(16)	155(12)
C(62)	1 816(21)	4 092(16)	225(13)
C(63)	2 167(21)	4 905(17)	559(13)
C(64)	3 370(23)	5 130(19)	811(14)
C(65)	4 224(28)	4 519(21)	750(16)
C(66)	3 903(24)	3 698(19)	398(14)
B(2)	6 854(26)	2 555(21)	4 721(16)
C(71)	5 869(23)	3 396(18)	4 207(15)
C(72)	4 820(24)	3 666(20)	4 356(16)
C(73)	3 979(28)	4 395(22)	3 904(17)
C(74)	4 180(29)	4 859(22)	3 268(18)
C(75)	5 159(32)	4 656(25)	3 118(21)
C(76)	6 027(29)	3 926(22)	3 580(18)
C(81)	6 340(20)	2 012(16)	5 389(13)
C(82)	5 485(22)	1 312(18)	5 197(15)
C(83)	4 916(21)	875(17)	5 695(14)
C(84)	5 215(23)	1 106(19)	6 422(16)
C(85)	6 081(23)	1 803(19)	6 640(16)
C(86)	6 615(21)	2 230(18)	6 103(14)
C(91)	7 116(24)	1 749(19)	4 215(16)
C(92)	6 604(25)	1 846(21)	3 428(16)
C(93)	6 859(28)	1 164(24)	3 000(21)
C(94)	7 512(27)	367(24)	3 389(20)
C(95)	7 984(28)	216(24)	4 121(20)
C(96)	7 853(25)	943(21)	4 548(17)
C(01)	8 106(22)	3 021(19)	5 189(14)
C(02)	9 095(26)	2 510(22)	5 630(16)
C(03)	10 234(31)	2 954(26)	6 085(19)
C(04)	10 196(30)	3 860(24)	6 038(18)
C(05)	9 272(34)	4 407(29)	5 618(21)
C(06)	8 227(29)	3 989(23)	5 190(18)
N(100)	2 212(25)	2 389(20)	5 006(16)
C(101)	2 800(31)	2 874(25)	5 428(21)
C(102)	3 418(31)	3 392(25)	6 061(21)

TABLE 6

Molecular dimensions,* distances (Å) and angles (°), for $[NiL^2][BPh_4]_2 \cdot MeCN$ with estimated standard deviations in parentheses

(*a*) In the cation

Ni–N(1)	2.132(21)	Ni–N(10)	2.028(16)
Ni–N(4)	2.159(17)	Ni–N(16)	2.319(19)
Ni–N(7)	2.003(20)	Ni–N(19)	2.124(22)

N(1)–Ni–N(4)	82.0(7)	N(7)–Ni–N(16)	151.2(7)
N(1)–Ni–N(7)	97.1(8)	N(10)–Ni–N(16)	75.1(7)
N(4)–Ni–N(7)	81.7(7)	N(1)–Ni–N(19)	163.4(6)
N(1)–Ni–N(10)	92.8(7)	N(4)–Ni–N(19)	87.8(7)
N(4)–Ni–N(10)	158.5(8)	N(7)–Ni–N(19)	94.3(8)
N(7)–Ni–N(10)	78.3(7)	N(10)–Ni–N(19)	101.3(7)
N(1)–Ni–N(16)	95.1(7)	N(16)–Ni–N(19)	80.3(7)
N(4)–Ni–N(16)	125.9(7)		

N(1)–C(2)	1.482(27)	C(11)–C(12)	1.52(3)
C(2)–C(3)	1.47(3)	C(11)–C(23)	1.41(3)
C(3)–N(4)	1.58(3)	C(12)–N(13)	1.47(3)
C(3)–N(4)	1.58(3)	C(12)–N(16)	1.465(27)
N(4)–C(5)	1.47(3)	C(12)–C(24)	1.53(3)
C(5)–C(6)	1.51(3)	N(13)–C(14)	1.46(3)
C(6)–N(7)	1.466(28)	C(14)–C(15)	1.58(4)
N(7)–C(8)	1.32(3)	C(15)–N(16)	1.49(3)
C(8)–C(9)	1.40(3)	N(16)–C(17)	1.48(3)
C(8)–C(20)	1.53(4)	C(17)–C(18)	1.47(3)
C(9)–N(10)	1.33(3)	C(18)–N(19)	1.47(3)
C(9)–C(21)	1.46(3)	C(21)–C(22)	1.37(4)
N(10)–C(11)	1.307(27)	C(22)–C(23)	1.27(4)

Ni–N(1)–C(2)	106.9(14)	C(12)–C(11)–C(23)	125.3(20)
N(1)–C(2)–C(3)	109.0(19)	C(11)–C(12)–N(13)	109.0(21)
C(2)–C(3)–N(4)	109.5(19)	C(11)–C(12)–N(16)	109.8(17)
Ni–N(4)–C(3)	106.9(12)	N(13)–C(12)–N(16)	102.5(17)
Ni–N(4)–C(5)	104.4(14)	C(11)–C(12)–C(24)	112.0(19)
C(3)–N(4)–C(5)	112.1(21)	N(13)–C(12)–C(24)	112.1(20)
N(4)–C(5)–C(6)	112.9(20)	N(16)–C(12)–C(24)	111.0(22)
C(5)–C(6)–N(7)	107.9(21)	C(12)–N(13)–C(14)	107.0(22)
Ni–N(7)–C(6)	116.4(15)	N(13)–C(14)–C(15)	104.9(23)
Ni–N(7)–C(8)	116.0(16)	C(14)–C(15)–N(16)	102.7(21)
C(6)–N(7)–C(8)	127.4(21)	Ni–N(16)–C(12)	106.0(14)
N(7)–C(8)–C(9)	115.2(24)	Ni–N(16)–C(15)	115.2(14)
N(7)–C(8)–C(20)	122.0(21)	C(12)–N(16)–C(15)	105.8(17)
C(9)–C(8)–C(20)	122.7(22)	Ni–N(16)–C(17)	102.5(12)
C(8)–C(9)–N(10)	116.3(21)	C(12)–N(16)–C(17)	114.5(17)
C(8)–C(9)–C(21)	125.1(25)	C(15)–N(16)–C(17)	112.9(20)
N(10)–C(9)–C(21)	118.6(21)	N(16)–C(17)–C(18)	112.1(20)
Ni–N(10)–C(9)	114.2(13)	C(17)–C(18)–N(19)	109.3(20)
Ni–N(10)–C(11)	121.6(16)	Ni–N(19)–C(18)	108.9(15)
C(9)–N(10)–C(11)	124.0(18)	C(9)–C(21)–C(22)	114.1(27)
N(10)–C(11)–C(12)	116.4(17)	C(21)–C(22)–C(23)	125.3(27)
N(10)–C(11)–C(23)	118.2(23)	C(11)–C(23)–C(22)	119.6(25)

(*b*) In the solvent

N(100)–C(101)	1.17(4)
C(101)–C(102)	1.46(5)
N(100)–C(101)–C(102)	168(4)

* The distances and angles in the anion are listed in the Supplementary Publication.

remaining atoms were located from subsequent Fourier maps. The nickel atom was refined anisotropically and the other atoms isotropically. Hydrogen atoms were placed in the appropriate trigonal or tetrahedral positions but their parameters were not refined. Least-squares refinement was carried out in three large blocks for the ions. The weighting scheme used was $w = 1$ for $F_o < 85$ and $w = 85/F_o$ for $F_o > 85$. The structure converged at R 0.093. In the final cycle of refinement no shift was greater than 0.1σ. A final difference-Fourier showed no significant peaks. The zero weighted reflections showed no serious discrepancies. Calculations were done at the University of Manchester Computer Centre using SHELX-76;[15] scattering factors were taken from International Tables.[16] Table 5 lists the positional parameters and Table 6 the bond distances and angles. Thermal parameters, hydrogen-atom positions, and observed and calculated structure factors are listed in Supplementary Publication No. SUP 23053 (18 pp.).†

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REFERENCES

[1] M. G. B. Drew, J. Nelson, and S. M. Nelson, preceding paper.

[2] A. B. P. Lever, 'Electronic Absorption Spectroscopy,' Elsevier, Amsterdam, 1968.

[3] S. M. Nelson, F. S. Esho, M. G. B. Drew, and P. Bird, *J. Chem. Soc., Chem. Commun.*, 1979, 1035.

[4] M. G. B. Drew, J. Nelson, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1981, 1678.

† For details see Notices to Authors No. 7, *J. Chem. Soc. Dalton Trans.*, 1980, Index issue.

[5] R. W. Layer, *Chem. Rev.*, 1963, **63**, 489.

[6] V. Katovic, L. T. Taylor, and D. H. Busch, *Inorg. Chem.*, 1971, **10**, 458.

[7] F. Basolo and R. G. Pearson, ' Mechanisms of Inorganic Reactions,' Wiley, New York, 1968.

[8] M. G. B. Drew, A. H. bin Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 1173; M. G. B. Drew, A. H. bin Othman, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1976, 1394, and related papers.

[9] M. G. B. Drew and S. M. Nelson, *Acta Crystallogr.*, 1975, **A31**, S140.

[10] C. Cairns and S. M. Nelson, unpublished results.

[11] C. Cairns, S. G. McFall, S. M. Nelson, and M. G. B. Drew, *J. Chem. Soc., Dvlton Trans.*, 1979, 446.

[12] D. Wester and G. J. Palenik, *J. Am. Chem. Soc.*, 1974, **96**, 7565.

[13] T. J. Giordano, G. J. Palenik, R. C. Palenik, and D. A. Sullivan, *Inorg. Chem.*, 1979, **18**, 2445.

[14] C. Ansell, J. Lewis, J. N. Ramsden, P. R. Raithby, and T. D. O'Donoghue, *Abs. First Int. Symp. Macrocyclic Ligands*, Basel, July 1980.

[15] G. M. Sheldrick, personal communication.

[16] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.