Nickel(II) Complexes of Quinquedentate Macrocyclic Ligands and the Crystal and Molecular Structure of the Ring-opened Hydrolysis Product [11-(6-Acetyl-2-pyridyl)-3,7,10-triazadodec-10-enylamine-*NN′N″N‴-N⁗*]-aquanickel(II) Diperchlorate

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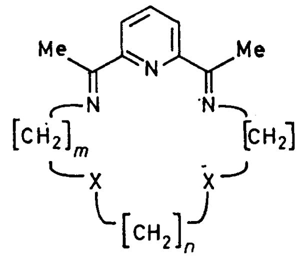
In contrast to several other first-row transition-metal (and non-transition-metal) ions, Ni^{II} is ineffective as a template for the cyclic condensation of 2,6-diacetylpyridine with 4,7-diazadecane-1,10-diamine and related tetra-amines to yield quinquedentate macrocyclic ligands. However, nickel(II) complexes of the 17-membered macrocycle L^3 may be prepared by replacement of Ag^I from the complex $[AgL^3][ClO_4]$. On the basis of electronic spectra and other physical measurements, these complexes $[NiL^3(X)][ClO_4]$ ($X = ClO_4$, NCS, or N_3) are shown to have six-co-ordinate structures in which L^3 adopts a new conformation, *i.e.* one in which it occupies five sites of a distorted octahedron. Replacement of Ag^I from the cavity of the less flexible 16-membered macrocycle L^2 in dry ROH (R = Me or Et) yields distorted octahedral complexes of the new, more flexible, macrocycles L^9 or L^{10} formed by addition of ROH across one azomethine bond of L^2. The driving force for these reactions, which do not occur with (pentagonal) complexes of L^2 with other metal ions, is believed to arise from a strong preference for the d^8 ion for an orthogonal disposition of donor atoms. If the metal exchange is carried out in the presence of water, or if the L^9 and L^{10} complexes are treated with water, a ready hydrolysis occurs to yield octahedral complexes of the ring-opened ligand L^{11}. Crystals of the title complex $[NiL^{11}(OH_2)][ClO_4]_2$ are monoclinic, with $a = 15.292(12)$, $b = 19.807(15)$, $c = 8.432(8)$ Å, $\beta = 106.54(8)°$, $Z = 4$, space group $P2_1/a$. 1 514 Reflections above background have been measured by diffractometer and refined by full-matrix least squares to R 0.076. The ligand occupies five sites of a distorted octahedron around the metal ion [Ni–N 2.099(12), 1.999(14), 2.312(13), 2.084(11), and 2.085(12) Å]. A water molecule at 2.126(8) Å completes the co-ordination sphere.

IN recent publications [1-3] we have described the properties and structures of a number of metal complexes of the quinquedentate macrocyclic ligands L^1—L^7. The complexes were prepared by the Schiff-base condensation of 2,6-diacetylpyridine with the appropriate diaza-, dioxa-, dithia-, or diphosphino-diprimary amine in the presence of a salt of the metal ion which acts as a template for the ring closure and which stabilises the product macrocycle. In all the cases so far examined the macrocycles L^1—L^4 function as quinquedentate ligands. In complexes of the 15- and 16-membered rings L^1, L^4, and L^2, the five donors define an approximate pentagonal plane which also contains the metal ion; in complexes of the 17-membered ring L^3 the macrocycle, while still functioning in a pentagonal manner, is sometimes appreciably folded. Co-ordination numbers are five, six, or seven, depending on the occupancy of the two axial sites.



	X		X
L^1 $m = n = 2$	NH	L^5 $m = 3$, $n = 2$	S
L^2 $m = 2$, $n = 3$	NH	L^6 $m = 3$, $n = 2$	PPh
L^3 $m = 3$, $n = 2$	NH	L^7 $m = n = 3$	PPh
L^4 $m = n = 2$	O		

The isolation of these complexes of unusual structure has so far been restricted to complexes of those metal ions which are effective in the template synthesis. This is because, in the absence of template ion, the products are oils or gums having an oligomeric constitution, and because attempts to liberate the free macrocycle from the metal have yielded only macrocycle decomposition products.† Metal ions found effective as templates, for at least one of the macrocycles, include both transition metals (Mn^{II}, Fe^{III}, Fe^{II}, and Co^{II}) and non-transition metals (Mg^{II}, Zn^{II}, Cd^{II}, Hg^{II}, Ag^{I}, Sn^{IV}, and Pb^{II}).[1-3] Conspicuous absences from the former group are Ni^{II} and Cu^{II}. This contrasts with the special effectiveness of these two ions as templates for the synthesis of the more common quadridentate 'N_4' macrocycles.[5] Among the first-row transition-metal ions, Ni^{II} has a particularly strong preference for geometries in which the metal–ligand bonds are in orthogonal relationship, *i.e.* for the octahedron, the square pyramid, and the square plane. Thus, it seemed possible that our failure to prepare nickel(II) and copper(II) complexes of quinquedentate macrocycles *via* the template method might be due to a disinclination of the metal ion to accommodate a pentagonal disposition of donor atoms. Such a disinclination could be reflected in a thermodynamic instability of the product macrocyclic complex or in some kinetic barrier to ring closure in the template synthesis for which an intermediate having a pentagonal-planar array of donors may be advantageous. However,

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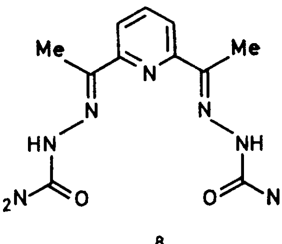
† Evidence for a non-template synthesis of a 15-membered macrocyclic Schiff base closely related to L^4 has recently been obtained;[4] however, this macrocycle adds two molecules of alcohol to yield a macrocycle related to L^9 and L^{10}.

it should be noted that pentagonal-bipyramidal nickel(II) and copper(II) complexes have been prepared[6] by the reaction of the metal nitrates with the pre-formed, open-chain, planar quinquedentate ligand L^8.



L^8

In order to investigate further the possibility of preparing nickel(II) complexes of ' pentagonal ' macrocycles, and, if successful, to elucidate their structures, we have used a new synthetic method (transmetallation) found successful in trial experiments in other systems.[7] This is to synthesise the macrocycle using as template one of the metal ions known to be effective and then by a metal-exchange process in solution replace the co-ordinated template ion by Ni^{II}. This paper reports the preparation and properties of some nickel(II) complexes of the 17-membered macrocycle L^3 and of two new macrocycles derived from L^2 by addition of a molecule of MeOH or EtOH across one azomethine linkage. It is shown that these complexes have distorted octahedral structures. The crystal and molecular structure of a complex of a ring-opened hydrolysis product of L^2 is also described.

TABLE 1

Analytical, electrical-conductance, and magnetic data for the complexes

Complex	Analysis (%) Found C	H	N	Calc. C	H	N	Λ^a/S cm^2 mol^{-1} MeCN	H_2O	$\mu_{eff.}{}^b$/B.M.	θ^c/K
$[NiL^3(ClO_4)][ClO_4]\cdot 3\ H_2O$	33.3	5.0	11.1	33.3	5.4	11.4	302	265	3.26	
$[NiL^3(NCS)][ClO_4]$	41.6	5.3	16.3	41.7	5.3	16.2	184			
$[NiL^3(N_3)][ClO_4]$	40.5	5.5	22.2	40.7	5.4	22.3	153		3.13	
$[NiL^9(NCS)][ClO_4]$	40.3	5.5	15.5	40.4	5.5	15.7	153		3.09	15
$[NiL^9(NCS)][BPh_4]$	66.4	6.6	11.3	66.7	6.5	11.1	135			
$[NiL^{10}(NCS)][ClO_4]$	41.5	5.8	15.2	41.5	5.7	15.3	168			
$[NiL^{11}(OH_2)][ClO_4]_2$	32.8	5.0	12.0	33.1	5.0	12.0	298	239	3.19	
$[NiL^{11}(NCS)][ClO_4]$	39.3	5.2	16.3	39.1	5.2	16.1	163	232	3.31	

[a] For 10^{-3} mol dm^{-3} solutions at 25 °C. [b] At 20 °C, corrected for diamagnetism of ligands. [c] Weiss constant in $\mu_{eff.} = 2.84[\chi_m(T - \theta)]^{\frac{1}{2}}$.

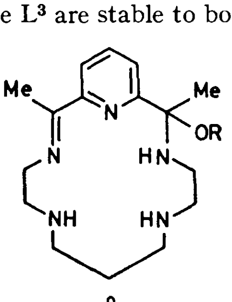
RESULTS AND DISCUSSION

Attempted Template Synthesis of the Nickel(II) *Complexes*.—The reaction conditions employed were similar to those found to be effective for the template synthesis of complexes of quinquedentate macrocyclic ligands of other metal ions.[1-3] These consisted in mixing equimolar proportions of 2,6-diacetylpyridine and the appropriate tetrafunctional diprimary amine in the presence of an equimolar quantity of nickel(II) salt, usually $Ni[ClO_4]_2$, in methanol or ethanol. Reaction times varied from *ca.* 30 min to several days and reaction temperature from ambient to the solvent reflux temperature. Anhydrous solvent was used in most experiments and solutions of hydrated nickel(II) salts were pre-dried.

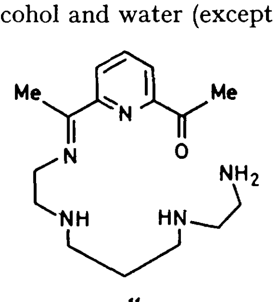
The nature of the reaction products varied somewhat with the reaction conditions but in no case was a product having properties consistent with a macrocyclic complex isolated. Generally, the initial reaction products were tars or amorphous solids which gave broad, poorly resolved, i.r. spectra with bands at both *ca.* 1 700 and *ca.* 1 650 cm^{-1}, due to carbonyl and imine functions, respectively. Repeated ' recrystallisation ' using a variety of solvents failed to remove the band at 1 700 cm^{-1} or to yield materials of consistent analysis or of substantially improved physical properties. In some experiments, small quantities of unchanged 2,6-diacetylpyridine were recovered together with some nickel(II) complex of the diprimary amine.

Transmetallation Reactions.—Preliminary experiments involving the complexes $[AgL^2]_2[ClO_4]_2$ and $[AgL^3][ClO_4]$, of known structure,[1,8] indicated a high degree of lability of the co-ordinated silver(I) ion. Thus, attempts to form neutral six-co-ordinate complexes of the type [AgL(X)] by treatment with MX (M = alkali metal, X = halide or thiocyanate ion) yielded only precipitated AgX together with macrocycle decomposition products.[7] These observations suggested that if the reaction with MX were carried out in the presence of a second metal ion the liberated macrocycle might be ' captured ' and stabilised by co-ordination to the new metal ion before decomposition. The method was tested by treating $[AgL^2]_2[ClO_4]_2$ with Na[NCS] in the presence of $Mn[ClO_4]_2$, or $Mg[ClO_4]_2$, in dry methanol. After separation of the precipitated Ag[SCN] the filtrates yielded, respectively, the known complexes, $[MnL^2(NCS)_2]$ and $[MgL^2(NCS)_2]$. A similar test starting with $[AgL^3][ClO_4]$ yielded the known complex $[MnL^3(NCS)_2]$.[1] Having established the utility of the transmetallation route to known complexes, the method was then applied to the preparation of the previously inaccessible nickel(II) complexes (see Experimental section for details).

Properties and Structures of the Nickel(II) *Complexes*.—The complexes listed in Table 1 were prepared. The ligands L^9, L^{10}, and L^{11} are derived from L^2 by addition of MeOH or EtOH across one of the azomethine linkages (to yield L^9 and L^{10}, respectively) and by hydrolysis of this linkage (to yield L^{11}). Evidence in support of the structures of L^9—L^{11}, and of their co-ordination geometries, is considered below. Whether a complex of L^9, L^{10}, or L^{11} is obtained on the transmetallation of $[AgL^2]_2[ClO_4]_2$ is determined by the reaction conditions. If the reaction is carried out in undried MeOH or EtOH a complex of the ring-opened ligand L^{11} is obtained. On the other hand, if the reaction is carried out under anhydrous conditions a complex of the new macrocycle L^9 or L^{10}, depending on which alcohol is employed, is obtained. Treatment of $[NiL^9(NCS)]^+$ or $[NiL^{10}(NCS)]^+$ with water yields $[NiL^{11}(NCS)]^+$ which does not undergo further hydrolysis in the cold. In contrast to the behaviour of L^2, complexes of the 17-membered macrocycle L^3 are stable to both alcohol and water (except on boiling in water) and these could be prepared from $[AgL^3][ClO_4]$ in methanol in the presence of water.



L^9 R = Me
L^{10} R = Et



L^{11}

Analytical and other data pertaining to the complexes are in Table 1. The conclusion that in the formation of $[NiL^3(ClO_4)][ClO_4]\cdot3H_2O$ and $[NiL^3(NCS)][ClO_4]$ from the silver(I) precursor the L^3 macrocycle has remained intact rests primarily on the analytical and i.r. evidence. In neither complex was there any absorption at *ca.* 1 700 cm^{-1} which would be expected if any hydrolysis of the azomethine groups had occurred. Both complexes showed the expected ν(N–H), ν(C=N), and pyridine ring vibrations (Table 2) and in these and other respects the i.r. spectra showed a close similarity to those of complexes of other metals known to contain L^3. In $[NiL^3(NCS)][ClO_4]$ the position and high intensity of the NCS asymmetric stretch is as expected for terminal co-ordination *via* the nitrogen atom, while the ν_3 and ν_4 vibrations of the $[ClO_4]^-$ group occur as unsplit bands at 1 090 and 620 cm^{-1}, respectively, having bandwidths no greater than those in reference complexes known to contain ionic $[ClO_4]^-$. In the i.r. spectra of $[NiL^3(ClO_4)][ClO_4]\cdot3H_2O$, however, both the ν_3 and ν_4 bands, while unsplit, are distinctly broader suggesting that at least one of the $[ClO_4]^-$ ions is co-ordinated. The profile of the ν_3 band is consistent with overlapping absorptions due to ionic $[ClO_4]^-$ ($\nu_{max.}$ at *ca.* 1 090 cm^{-1}) and unidentate $[ClO_4]^-$ [$\nu_{max.}$ at *ca.* 1 120, 1 060, and 980(sh) cm^{-1}].[9] It is concluded, therefore, that these complexes are perchlorate salts of the complex cation $[NiL^3(X)]^+$ (X = NCS or ClO_4). Electrical conductance values (Table 1) in 10^{-3} mol dm^{-3} MeCN solutions fall in the ranges expected for 1 : 1 (X = NCS) and 1 : 2 electrolytes (X = ClO_4) and conform to the predicted behaviour

TABLE 2

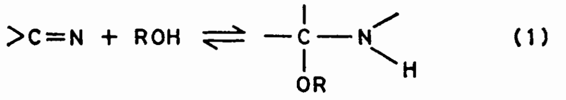
Infrared (cm^{-1}) and electronic spectral data for the complexes

					Electronic spectra [a]		
Complex	ν(N–H)	ν(C=N)	ν_{asym} $[NCS]^-$	$[ClO_4]^-$	Solid [b]	MeCN [c]	H_2O [c]
$[NiL^3(ClO_4)][ClO_4]\cdot3H_2O$	3 290	1 633		*ca.* 1 100br 620br	*ca.* 24.0 (sh) 16.6 11.7	*ca.* 31.7 (sh) *ca.* 28.0 (sh) 17.0 (30) 11.7 (19)	
$[NiL^3(NCS)][ClO_4]$	3 298	1 630	2 070	1 090 622	*ca.* 27.0 (sh) *ca.* 23.0 (sh) 16.8 11.2	*ca.* 31.7 (sh) *ca.* 28.0 (sh) 16.8 (31) 10.9 (25)	
$[NiL^3(N_3)][ClO_4]$	3 292	1 630	2 032 [d]	1 090 620	*ca.* 28.0 (sh) 21.0 16.8 (sh) 11.0	*ca.* 31.0 (sh) *ca.* 28.0 (sh) 20.7 (230)	
$[NiL^9(NCS)][ClO_4]$	3 315	1 642	2 076	1 090	*ca.* 24.0 (sh) 16.6 9.2	*ca.* 31.0 (sh) 17.3 (24) 9.6 (30)	
$[NiL^9(NCS)][BPh_4]$	3 292 3 265	1 640	2 068		*ca.* 24.0 (sh) 16.0 9.0	*ca.* 31.0 (sh) *ca.* 17.4 (sh) 9.6 (25)	
$[NiL^{10}(NCS)][ClO_4]$	3 315 3 295 3 270	1 645	2 078	1 085 622	*ca.* 24.0 (sh) 16.6 9.2	*ca.* 31.0 (sh) 17.3 (25) 9.6 (30)	
$[NiL^{11}(OH_2)][ClO_4]_2$	3 340 3 300 3 275	1 665		1 090 620	*ca.* 28.4 (sh) *ca.* 23.0 (sh) 17.5 10.7	*ca.* 28.7 (2h) *ca.* 23.5 (sh) 18.0br 10.1 (24)	*ca.* 28.6 (sh) *ca.* 23.5 (sh) 18.2 (14) 10.9 (18)
$[NiL^{11}(NCS)][ClO_4]$	3 342 3 320 3 292 3 275	1 665	2 075	1 090 620	*ca.* 27.8 (sh) *ca.* 21.7 (sh) 16.8 (sh) 9.9	*ca.* 28.6 (sh) *ca.* 22.2 (sh) *ca.* 17.0 (sh) 10.4 (23)	*ca.* 28.5 (sh) *ca.* 23.0 (sh) 17.8 (14) 10.7 (20)

[a] In 10^3 cm^{-1}; ε/dm^3 mol^{-1} cm^{-1} in parentheses for solutions. [b] Measured in the range 5 000—30 000 cm^{-1}. [c] Measured in the range 5 000—33 000 cm^{-1}. [d] Azide absorption.

for these two complexes in this solvent, the weakly co-ordinating $[ClO_4]^-$ being replaced by solvent but the NCS group remaining bonded to the metal.

A number of lines of evidence lead us to the conclusion that in the replacement of Ag^I by Ni^{II} in the complex $[AgL^2]_2[ClO_4]_2$ a molecule of solvent alcohol has added across one of the C=N bonds to yield nickel(II) complexes of the new macrocycles L^9 or L^{10}. First, there is the evidence of the analytical data (Table 1). Secondly, in the i.r. spectra the intensity of the N–H stretching modes, occurring as two or three bands at 3 260—3 320 cm^{-1}, is substantially greater than in authentic complexes of L^2 with other metals; in $[MnL^2(NCS)]_n[ClO_4]_n$, for example, ν(N–H) occurs as a single sharp band at 3 285 cm^{-1}. Also, the intensity of the ν(C–H) multiplet is somewhat increased. Confirmation of the occurrence of reaction (1), and for its reversibility, was obtained by ' recrystallisation ' of $[NiL^{10}(NCS)][ClO_4]$ from CD_3OD. The product obtained was identical to $[NiL^9(NCS)][ClO_4]$ except for the virtual disappearance of ν(N–H) bands at *ca.* 3 300 cm^{-1} and the appearance of new bands at 2 465 and 2 440 cm^{-1}, assigned to ν(N–D), and at 2 215 cm^{-1} assigned to ν(C–D). The ratios ν(N–H) : ν(N–D) and ν(C–H) : ν(C–D) are *ca.* 1.34 : 1. It is noteworthy, also, that the relative intensities of the ν(C=N) band at *ca.* 1 645 cm^{-1} and the highest-frequency pyridine-ring deformation at *ca.* 1 595 cm^{-1} are reversed in the complexes of L^9 and L^{10} relative to the situation in, for example, $[MnL^2(NCS)]_n[ClO_4]_n$.[1] In the nickel(II) complexes ν(C=N) is weaker than the pyridine band whereas in the manganese(II) complex, and all other complexes of L^2 so far prepared, the pyridine deformation is the less-intense absorption. Indeed, the intensity ratio of the two bands in $[NiL^9(NCS)][ClO_4]$ is almost exactly the same as in $[NiL^{11}(NCS)][ClO_4]$ in which L^{11}, as will be shown, contains only one azomethine linkage. It is probably significant, also, that there are a number of distinct differences, in the spectra of the nickel(II) complex and those of corresponding complexes of L^2 in the range 600—1 400 cm^{-1}. Particularly noteworthy is the occurrence of a medium-intensity absorption at *ca.* 1 135 cm^{-1} in the spectrum of $[NiL^9(NCS)][BPh_4]$ which we assign to the ν(C–O) mode. (The band is largely obscured by ν_3 of $[ClO_4]^-$ in complexes containing this anion.)



$$>C{=}N + ROH \rightleftharpoons -\overset{|}{\underset{OR}{C}}-N\overset{\diagup}{\underset{H}{\diagdown}} \qquad (1)$$

The ν_{asym} vibration of $[NCS]^-$ occurs at 2 068—2 078 cm^{-1}, consistent with a terminal *N*-bonded co-ordination mode. The molar conductances (Table 1) in 10^{-3} mol dm^{-3} solutions in MeCN support the formulation of these complexes as salts of the $[NiL^9(NCS)]^+$ and $[NiL^{10}(NCS)]^+$ complex cations.

The i.r. spectra of the hydrolysis products $[NiL^{11}(OH_2)][ClO_4]_2$ and $[NiL^{11}(NCS)][ClO_4]$ both exhibit, in addition to ν(C=N) at *ca.* 1 665 cm^{-1}, a strong band at *ca.* 1 710 cm^{-1} attributable to ν(C=O) of a carbonyl function. Its position at a slightly higher frequency than in free 2,6-diacetylpyridine (1 704 cm^{-1}) suggests that the oxygen atom is not co-ordinated to the metal. The occurrence of ν(N–H) as a strong four-peaked multiplet (Table 2) is interpreted as evidence for the presence of not only secondary amine groups but also a primary amine group. In the aqua-complex the O–H stretch appears as a sharper band, and at a somewhat lower frequency, than usually observed for lattice water, consistent with its formulation as bonded to the nickel(II) ion. The i.r. bands due to the anions are characteristic of *N*-bonded $[NCS]^-$ and ionic $[ClO_4]^-$. Once again, electrical-conductance measurements (Table 1) support the conclusions reached on the basis of i.r. spectra. Thus, the thiocyanato-complex is a 1 : 1 electrolyte and the aqua-complex a 2 : 1 electrolyte in MeCN; both complexes exhibit 2 : 1 electrolyte behaviour in water.

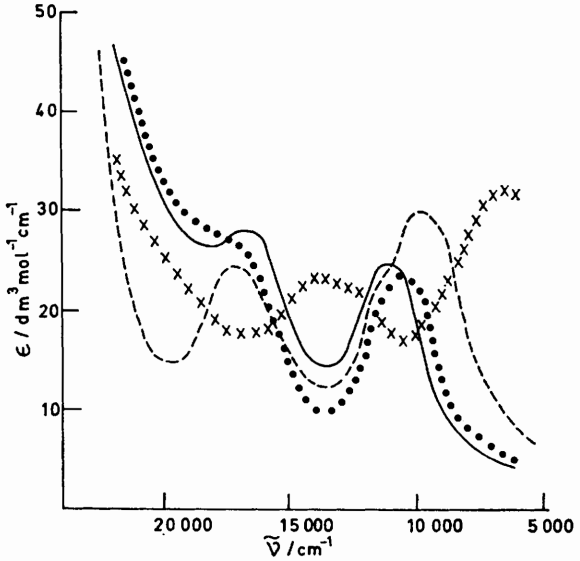


FIGURE 1 Electronic spectra in MeCN solution of $[NiL^3(NCS)][ClO_4]$ (——), $[NiL^9(NCS)][ClO_4]$ (– – – –), and $[NiL^{11}(NCS)][ClO_4]$ (· · · ·). The crosses represent the solid-state spectrum of $[NiL^8(OH_2)_2][NO_3]_2 \cdot H_2O$

We have shown that all the complexes discussed are salts of the singly charged cations $[NiL(X)]^+$ (L = a quinquedentate ligand and X = unidentate anion or H_2O). It remains to establish the co-ordination geometries.

Electronic spectra of the solid complexes and of their solutions in dry MeCN were recorded in the range 5 000—33 000 cm^{-1} (Table 2 and Figure 1). All the complexes show a similar pattern in that there are three absorption regions. The two low-energy bands have low molar absorption coefficients (ε 15—30 dm^3 mol^{-1} cm^{-1}) and are almost certainly due to *d–d* transitions. The much more intense higher-energy absorption in the 20 000—33 000 cm^{-1} region is assigned mainly to a transition of the co-ordinated macrocycle together with charge-transfer transitions. In all cases there is a fair correspondence between solid-state spectra and those obtained in MeCN solution. These observations, coupled with the electrical-conductance data for MeCN solutions, indicate that in the case of the thiocyanato-complexes we are dealing with the same absorbing species, namely $[NiL(NCS)]^+$, in the solid and in solution. For the remaining complexes we conclude that on dissolution a molecule of MeCN replaces the unidentate ligand (H_2O or $[ClO_4]^-$) but without gross change in the stereochemistry around the metal.

The spectral pattern in all cases is precisely that expected for an approximately octahedral co-ordination of the nickel(II) ion. Thus, we assign the lowest-energy band occurring at *ca.* 9 000—12 000 cm^{-1} to the transition ${}^3A_{2g}\rightarrow{}^3T_{2g}$, and the band at 16 000—18 000 cm^{-1} to the transition ${}^3A_{2g}\rightarrow{}^3T_{1g}(F)$ (in O_h symmetry). The third spin-allowed transition ${}^3A_{2g}\rightarrow{}^3T_{1g}(P)$ is obscured by the much more intense absorption of the co-ordinated ligand but may be detected as a shoulder at 24 000—28 000 cm^{-1} in some of the spectra.

Although a pentagonal-bipyramidal complex of Ni^{II} has been described previously [6] its electronic spectrum has not been reported. We therefore re-prepared this complex and measured its electronic spectrum in the solid state. This is compared in Figure 1 with the spectra of the present complexes. As expected, the seven-co-ordinate complex has a quite different spectrum; particularly noteworthy is the occurrence of a band of moderate intensity at *ca.* 6 500 cm^{-1} which may correspond to a ${}^3E\rightarrow{}^3A$ transition.

Magnetic moments of the complexes are in the range 3.0—3.4 B.M.† as expected for spin-free d^8 systems. One of the complexes was investigated over the temperature range 95—293 K. The Curie–Weiss law was obeyed with only a small decrease in $\mu_{eff.}$ with decreasing temperature (Weiss constant $\theta = -15°$).

We conclude, therefore, that none of the four quinquedentate ligands, L^3, L^9, L^{10}, or L^{11}, whether macrocyclic or open-chain, is co-ordinated to the nickel(II) ion in a pentagonal-planar fashion as found previously [1] for complexes of other metal ions with L^1—L^5, and probably also with L^6 and L^7.[2] It is noteworthy that despite several attempts we were unable to isolate a dithiocyanato-complex, $[NiL(NCS)_2]$, in any case. This contrasts with the behaviour of L^1—L^4 complexes of other metals, *e.g.* Mg^{II}, Mn^{II}, Fe^{III}, Fe^{II}, Zn^{II}, and Cd^{II}, where pentagonal-bipyramidal complexes of this type are readily prepared.[1] Thus, the accumulated evidence is that all the nickel(II) complexes described have a basically common six-co-ordinate geometry in which the nitrogen atoms of the ligands (L^3, L^9, L^{10}, or L^{11}) occupy five positions of a distorted octahedron, the sixth being filled by a unidentate anion or solvent molecule. This was verified for one of the complexes of the ring-opened ligand L^{11} by a single-crystal *X*-ray structure determination described below.

Crystal and Molecular Structure Determination of $[NiL^{11}(OH_2)][ClO_4]_2$.—*Crystal data.* $C_{18}H_{29}Cl_2N_5NiO_{10}$, $M = 574.8$, Monoclinic, $a = 15.292(12)$, $b = 19.807(15)$, $c = 8.432(8)$ Å, $\beta = 106.54(8)°$, $U = 2\,448.3$ Å^3, $F(000) = 1\,104$, $D_m = 1.59$ g cm^{-3}, $Z = 4$, $D_c = 1.56$ g cm^{-3}, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, $\mu = 10.7$ cm^{-1}, space group $P2_1/a$ from systematic absences $h0l$, for $h = 2n + 1$, $0k0$ for $k = 2n + 1$.

A crystal with dimensions *ca.* 0.5 × 0.3 × 0.6 mm was mounted with the c^* axis parallel to the instrument axis of a General Electric XRD 5 diffractometer which was equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum *X*-radiation was used. The stationary-crystal–stationary-counter method was employed with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background against 2θ. 2 259 Independent reflections were measured with $2\theta < 40°$ of which 1 514 with $I > 2\sigma(I)$ were used in subsequent calculations. Neither an absorption nor an extinction correction was applied.

The positions of the nickel atoms were obtained from the Patterson map and subsequent Fourier maps gave all the remaining positions. One of the perchlorate ions was disordered. Eight oxygen atoms were located around the chlorine atom making up two distorted tetrahedra and these were given occupancy factors of $\frac{1}{2}$. The structure was refined using anisotropic thermal parameters for all atoms except for the oxygen atoms in the anions and the hydrogen atoms, which were given isotropic thermal parameters. Those hydrogen atoms were fixed in trigonal or tetrahedral positions and their parameters not refined. The structure was refined using full-matrix least squares with a weighting scheme that gave similar values of $w\Delta^2$ with ranges of F_o and $(\sin\theta)/\lambda$, *viz.* $w^{\frac{1}{2}} = 1$ for $F_o < 70$ and $w^{\frac{1}{2}} = 70/F_o$ for $F_o > 70$. The final R value was 0.076. Calculations were made using the ' *X*-Ray '72 ' system [10] on the C.D.C. 7600 at the University of London Computer Centre. Scattering factors and dispersion corrections were taken from ref. 11. The final list of positions is given in Table 3, bond lengths and angles in Table 4. The final difference-Fourier map showed no peaks with heights greater than 0.2 times that of a carbon atom. The zero-weighted reflections gave no large discrepancies. Lists of structure factors and thermal parameters are given in Supplementary Publication No. SUP 22396 (11 pp.).‡

Discussion of the structure. The cation $[NiL^{11}(OH_2)]^{2+}$ is shown in Figure 2 together with the numbering scheme. The nickel atom is in a distorted octahedral environment, being bonded to five nitrogens from the quinquedentate ligand and a water molecule. The geometry of L^{11} in this cation can be contrasted with that of the closed macrocyclic ligands L^1 and L^2 in seven-co-ordinate pentagonal-bipyramidal MLX_2 complexes. In these latter complexes (*e.g.* M = Mg, Fe^{II}, or Fe^{III}) [1] the five nitrogen atoms are coplanar with the metal to within 0.25 Å. In the present cation, however, while

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† Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

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

atoms Ni, N(3), N(6), N(9), and N(15) are planar to within 0.12 Å, the terminal NH_2 group N(12) is twisted

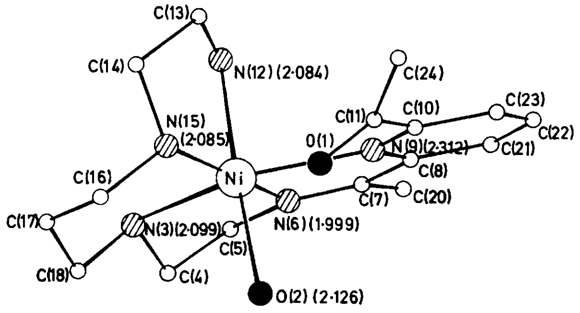


FIGURE 2 The structure of $[NiL^{11}(OH_2)][ClO_4]_2$ together with the atom-numbering scheme. The standard deviations for the bond lengths shown are *ca.* 0.01 Å

way out of the plane to occupy an axial position. As a result there are several changes in the conformation of L^{11} compared to that of L^2. For example, the N(6)–Ni–N(3), N(3)–Ni–N(15), and N(15)–Ni–N(12) angles, at 82.7(5), 90.2(5), and 82.7(5)°, respectively, are considerably larger than the 72° found in ML^2X_2 complexes.[1] The 90.2(5)° angle in the six-membered ring in the open-chain ligand L^{11} reflects the strain involved in restricting this angle to 72° in the complexes of the planar, pentagonal, macrocycle L^2.

TABLE 3

Positional parameters ($\times 10^4$) with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Ni	2 232(1)	1 327(1)	2 974(2)
N(3)	1 227(7)	1 962(6)	3 411(13)
C(4)	0 635(10)	1 510(9)	4 103(19)
C(5)	0 441(10)	0 881(9)	3 104(19)
N(6)	1 311(8)	0 611(7)	2 971(14)
C(7)	1 413(11)	−0 010(9)	2 691(17)
C(8)	2 351(11)	−0 192(7)	2 663(14)
N(9)	2 959(8)	0 316(6)	2 820(12)
C(10)	3 817(10)	0 162(7)	2 804(17)
C(11)	4 507(11)	0 728(9)	2 983(19)
N(12)	1 838(9)	1 371(7)	0 397(14)
C(13)	2 521(15)	1 749(10)	−0 095(21)
C(14)	2 756(13)	2 380(8)	3 805(22)
N(15)	3 009(7)	2 167(6)	2 742(15)
C(16)	3 023(11)	2 747(9)	3 805(22)
C(17)	2 121(11)	3 009(8)	3 783(18)
C(18)	1 531(11)	2 563(9)	4 490(18)
C(20)	0 692(11)	−0 571(8)	2 420(24)
C(21)	2 563(12)	−0 864(7)	2 467(18)
C(22)	3 456(15)	−1 012(9)	2 430(22)
C(23)	4 044(12)	−0 504(10)	2 577(22)
C(24)	5 212(14)	0 686(11)	2 102(32)
O(1)	4 462(7)	1 182(5)	3 864(14)
O(2)	2 824(6)	1 249(5)	5 574(11)
Cl(1)	4 724(3)	2 391(2)	8 582(5)
O(3)	4 501(10)	1 745(7)	8 023(17)
O(4)	3 864(12)	2 726(8)	8 096(19)
O(5)	5 372(14)	2 667(10)	7 849(20)
O(6)	5 024(14)	2 362(10)	10 205(27)
Cl(2)	2 112(4)	−0 159(2)	7 764(6)
O(10)	1 493(21)	0 376(16)	7 008(37)
O(11)	2 556(20)	−0 149(14)	6 451(37)
O(12)	1 900(36)	−0 805(27)	8 259(60)
O(13)	2 982(23)	0 153(18)	9 085(46)
O(14)	2 572(25)	−0 798(18)	8 531(42)
O(15)	1 508(15)	−0 067(11)	8 854(26)
O(16)	1 652(18)	−0 468(13)	6 240(33)
O(17)	2 827(27)	0 227(20)	8 007(54)

TABLE 4

Molecular dimensions (distances in Å; angles in °)

Ni–N(3)	2.099(12)	N(3)–Ni–N(6)	82.7(5)
Ni–N(6)	1.999(14)	N(3)–Ni–N(9)	156.4(5)
Ni–N(9)	2.312(13)	N(3)–Ni–N(12)	98.6(5)
Ni–N(12)	2.084(11)	N(3)–Ni–N(15)	90.2(5)
Ni–N(15)	2.085(12)	N(3)–Ni–O(2)	88.9(4)
Ni–O(2)	2.126(8)	N(6)–Ni–N(9)	74.6(5)
N(3)–C(4)	1.503(22)	N(6)–Ni–N(12)	91.9(6)
N(3)–C(18)	1.491(19)	N(6)–Ni–N(15)	170.4(5)
C(4)–C(5)	1.486(24)	N(6)–Ni–O(2)	92.4(4)
C(5)–N(6)	1.467(22)	N(9)–Ni–N(12)	88.8(5)
N(6)–C(7)	1.270(23)	N(9)–Ni–N(15)	113.0(5)
C(7)–C(8)	1.487(24)	N(9)–Ni–O(2)	85.7(4)
C(7)–C(20)	1.535(24)	N(12)–Ni–N(15)	82.7(5)
C(8)–N(9)	1.350(19)	N(12)–Ni–O(2)	171.8(5)
C(8)–C(21)	1.391(21)	N(15)–Ni–O(2)	93.9(4)
N(9)–C(10)	1.351(21)	C(14)–N(15)	1.488(21)
C(10)–C(11)	1.517(23)	N(15)–C(16)	1.453(21)
C(10)–C(23)	1.391(25)	C(16)–C(17)	1.469(25)
C(11)–C(24)	1.475(33)	C(17)–C(18)	1.502(25)
C(11)–O(1)	1.172(21)	C(21)–C(22)	1.405(30)
N(12)–C(13)	1.439(26)	C(22)–C(23)	1.333(28)
C(13)–C(14)	1.524(25)		
Ni–N(3)–C(4)	105.3(9)	Ni–N(6)–C(5)	113.3(11)
Ni–N(3)–C(18)	117.9(9)	Ni–N(6)–C(7)	124.3(12)
C(4)–N(3)–C(18)	110.9(12)	C(5)–N(6)–C(7)	121.9(15)
N(3)–C(4)–C(5)	108.9(14)	N(6)–C(7)–C(8)	114.0(14)
C(4)–C(5)–N(6)	108.0(12)	N(6)–C(7)–C(20)	127.4(16)
		C(8)–C(7)–C(20)	118.5(14)
C(7)–C(8)–N(9)	117.3(13)	Ni–N(12)–C(13)	107.7(9)
C(7)–C(8)–C(21)	119.5(14)	N(12)–C(13)–C(14)	108.9(16)
N(9)–C(8)–C(21)	123.2(15)	C(13)–C(14)–N(15)	108.1(13)
Ni–N(9)–C(8)	108.8(10)	Ni–N(15)–C(14)	109.1(9)
Ni–N(9)–C(10)	132.8(10)	Ni–N(15)–C(16)	118.8(11)
C(8)–N(9)–C(10)	118.3(13)	C(14)–N(15)–C(16)	110.3(12)
N(9)–C(10)–C(11)	118.8(14)	N(15)–C(16)–C(17)	115.0(12)
N(9)–C(10)–C(23)	119.8(15)	C(16)–C(17)–C(18)	117.0(14)
C(11)–C(10)–C(23)	121.4(16)	N(3)–C(18)–C(17)	110.2(13)
C(10)–C(11)–C(24)	119.7(16)	C(8)–C(21)–C(22)	117.5(15)
C(10)–C(11)–O(1)	117.8(17)	C(21)–C(22)–C(23)	118.4(17)
C(24)–C(11)–O(1)	122.4(17)	C(10)–C(23)–(C22)	122.7(19)
Cl(1)–O(3)	1.37(1)	Cl(2)–O(10)	1.44(3)
Cl(1)–O(4)	1.42(2)	Cl(2)–O(11)	1.45(4)
Cl(1)–O(5)	1.42(2)	Cl(2)–O(12)	1.41(5)
Cl(1)–O(6)	1.31(2)	Cl(2)–O(13)	1.60(3)
O(3)–Cl(1)–O(4)	102.5(9)	Cl(2)–O(14)	1.50(3)
O(3)–Cl(1)–O(5)	110.1(11)	Cl(2)–O(15)	1.49(3)
O(3)–Cl(1)–O(6)	107.3(11)	Cl(2)–O(16)	1.42(3)
O(4)–Cl(1)–O(5)	113.4(11)	Cl(2)–O(17)	1.30(4)
O(4)–Cl(1)–O(6)	109.8(12)		
O(5)–Cl(1)–O(6)	113.0(12)		
O(10)–Cl(2)–O(11)	92(2)	O(14)–Cl(2)–O(15)	98(2)
O(10)–Cl(2)–O(12)	128(3)	O(14)–Cl(2)–O(16)	94(2)
O(10)–Cl(2)–O(13)	110(2)	O(14)–Cl(2)–O(17)	99(2)
O(11)–Cl(2)–O(12)	116(3)	O(15)–Cl(2)–O(16)	112(2)
O(11)–Cl(2)–O(13)	93(2)	O(15)–Cl(2)–O(17)	118(2)
O(12)–Cl(2)–O(13)	111(2)	O(16)–Cl(2)–O(17)	125(2)

The effect of the enlarging of the N–Ni–N angles while maintaining four nitrogen donors coplanar with the metal atom is that N(9)–Ni–N(15) is only 113.0(5)° compared to 144° in the pentagonal-bipyramidal complexes. This angle is still much larger, however, than the octahedral angle. The conformations of the saturated rings are relatively unstrained. The two five-membered rings adopt puckered conformations: C(13), C(14) 0.49, −0.20 Å from the Ni, N(12), N(15) plane; C(4), C(5) 0.53, −0.12 Å from the Ni, N(3), N(6) plane. The six-membered ring has the flattened chair conformation with C(16) 0.76, C(17) 0.47, and C(18) 0.86 Å from the Ni, N(3), N(15) plane. In fact, the only major difference from ML^2X_2 complexes is that the positions of C(14) and H(15) are reversed. Thus, in $[NiL^{11}(OH_2)]^{2+}$, the C(17)–C(16)–N(15)–C(14) torsion angle is 73.9° and in $[FeL^2(NCS)_2]$ it is $-157.3°$. Thus, the N(15)–C(14) bond is approximately perpendicular to the NiN_4 plane and hence the terminal N(12) can achieve an axial position.

Another difference between L^2 and L^{11} is seen in the metal–nitrogen bond lengths. In $[NiL^{11}(OH_2)]^{2+}$ the Ni–N(9) bond [2.312(13) Å] is much longer, whereas Ni–N(6) [1.999(14) Å] is slightly shorter than the others [Ni–N(3) 2.099(12), Ni–N(12) 2.084(11), and Ni–N(15) 2.085(12) Å]. This contrasts with the situation found in most complexes of L^2 where the metal–pyridine nitrogen bond is the shortest by up to 0.1 Å. This bond is also the shortest in $[NiL^8(OH_2)_2]^{2+}$.[6] The reason for the relative lengthening of Ni–N(9) and shortening of Ni–N(6) is probably steric in origin since both bond-length changes serve to keep the COMe group well away from the metal [Ni–O(1) 3.29 Å]. This group is twisted by an angle of 33.7° out of the plane of the pyridine ring, a fact which also allows an intramolecular hydrogen bond to be formed to the axially positioned terminal amine group N(12). Least-squares calculations (Table 5) for the equatorial girdle show that the pyridine ring is not appreciably twisted out of the plane.

TABLE 5

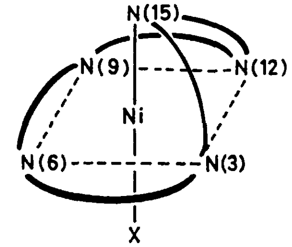
Least-squares planes in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic co-ordinates. Distances (Å) of relevant atoms from the planes are given in square brackets

	A	*B*	*C*	*D*
Plane (1): Ni, N(3), N(6), N(9), N(15)				
	1.91	−0.03	7.71	2.63
[Ni 0.01, N(3) 0.11, N(6) −0.13, N(9) 0.09, N(15) −0.08]				
Plane (2): N(3), N(6), N(9), C(7), C(8), C(10), C(11), C(20), C(21) C(22), C(23)				
	−0.08	−2.86	8.01	2.17
[Ni −0.19, N(3) −0.01, N(6) 0.02, N(9) −0.02, N(15) −0.62, C(5) 0.06, C(7) −0.02, C(8) 0.00, C(10) 0.00, C(11) −0.02, C(20) −0.07, C(21) 0.03, C(22) 0.04, C(23) 0.00, C(24) −0.72, O(1) 0.54]				

The geometry of the ordered perchlorate ion is as expected. We have attempted to explain the disordered perchlorate in terms of two tetrahedra of oxygen atoms each with an occupancy of $\frac{1}{2}$. The dimensions for these tetrahedra are not too unreasonable but it may be that this explanation is over-simplified.

There are an exceptionally large number of intermolecular distances less than 3.4 Å and these are listed in SUP 22396. Two contacts, between O(2) and the disordered perchlorate ion, are less than 3.0 Å and may indicate weak hydrogen bonding.

General Discussion.—Evidence has been presented that all the nickel(II) complexes described have a six-co-ordinate structure in which the nitrogen donor atoms of the quinquedentate ligands occupy five sites of a distorted octahedron. In the complexes of the open-chain ligand L^{11} it has been shown that the terminal primary amine group is positioned axially with respect to an approximate square plane composed of the remaining four nitrogens. It remains to consider the mode of co-ordination of the macrocycles L^3, L^9, and L^{10}. From an inspection of molecular models it is clear that there is only one way in which these cyclic ligands can accommodate, even approximately, five octahedral sites. This is for one of the secondary amine groups to occupy the apical position. For the case of the asymmetric macrocycles L^9 and L^{10} models show that the axial donor must be N(15). {We adopt the same numbering scheme as used for $[NiL^{11}(OH_2)]^{2+}$.} N(3) is excluded from this position by virtue of the trigonal hybridisation of the neighbouring imine group N(6) together with the shortness of the (ethylene) bridge linking N(6) with N(3). For, as can be seen from the structure of $[NiL^{11}(OH_2)]^{2+}$, as well as from the structures of previously investigated[1] $[ML^2X_2]$ complexes, C(5) must remain close to the equatorial plane thereby preventing N(3) from assuming an axial position. However, C(11) and N(12) have tetrahedral geometry so that the same restrictions do not apply to C(13) and N(15).



In L^3, on the other hand, there is an additional carbon atom between the imino- and secondary amino-nitrogen and this propylene bridge does provide sufficient length and flexibility for one of the latter donors to co-ordinate in an apical position without undue strain. The greater flexibility of this 17-membered ring has been noted previously.[1]

The results described lend strong support to the view that the d^8 ion does not accommodate readily a pentagonal-planar disposition of ligand donor atoms. The capacity of a multidentate ligand of particular preferred structure or conformation to impose an unusual or irregular co-ordination geometry on a metal ion is well documented; the pentagonal-bipyramidal and related complexes of a range of metal ions formed with L^1—L^7 are good examples.[1-3] In this paper we see the opposite effect in operation, namely the imposition on the ligand of a new conformation because of the stereochemical preferences of the metal. For the case of the 17-membered macrocycle L^3 the response to the preferred octahedral stereochemistry of the metal is apparently accomplished without undue strain. Other cases of (more flexible) quinquedentate 'N_5' macrocycles co-ordinating in a 'square-pyramidal' mode are known. Thus, the reduced macrocycle derived from L^1 by hydrogenation of the two azomethine groups forms octahedral complexes with Ni^{II} and Co^{III}, while with Fe^{III}, which has a spherical electron distribution, it adopts a planar conformation.[12]

For the case of the 16-membered macrocycles a more interesting situation arises. From models and earlier structural work it appears that the conformation of L^2 in its complexes cannot be other than approximately planar unless a great deal of strain is involved. It is the strong preference of Ni^{II} for octahedral co-ordination which is presumably the driving force for this macrocycle, after replacement of Ag^I by Ni^{II}, to add ROH across one of the two C=N bonds, thereby acquiring the necessary flexibility to allow co-ordination on an octahedron. Addition of ROH to co-ordinated C=N bonds has been noted previously in a few cases and rationalised in terms of relief of steric constraints.[4,13] It is relevant to the present discussion to note that pentagonal-bipyramidal complexes of L^2 with other metal ions,[1] including those of similar size and charge such as Fe^{II}, are relatively stable to this kind of nucleophilic attack by ROH or H_2O.

Despite the strong preference of Ni^{II} for an orthogonal disposition of bonding orbitals, the complex $[NiL^8(OH_2)_2]^{2+}$ has been shown [6] to have approximate D_{5h} symmetry. Here, the quinquedentate ligand is apparently resonance stabilised in the planar arrangement so that the metal ion has no choice but to conform to the stereochemical demands of the ligand. It thus seemed that if our attempted preparation of a Ni^{II}–L^2 macrocyclic complex were carried out in a solvent not capable of reacting with the azomethine bonds it might be possible to isolate a pentagonal-bipyramidal complex. However, experiments carried out in dry MeCN resulted only in macrocycle decomposition products.

EXPERIMENTAL

Preparation of the Complexes.—2,6-Diacetylpyridine (Aldrich) was used as supplied; 3,7-diazanonane-1,9-diamine and 4,7-diazadecane-1,10-diamine were prepared as described by Brubaker and Schaefer.[14] The silver(I) complexes of L^2 and L^3, used as starting materials for the preparation of the nickel(II) complexes, were synthesised by template methods as described previously.[1] The metal-replacement reactions were carried out under a N_2 atmosphere using dried solvents except where otherwise indicated. Solutions of hydrated nickel(II) salts were pre-dried by refluxing with 2,2-dimethoxypropane for 1 h.

$[NiL^9(NCS)][ClO_4]$. A solution of $Ni[ClO_4]_2$ (0.002 mol) in methanol (50 cm^3) was added to a solution of $[AgL^2]_2[ClO_4]_2$ (0.002 mol) in methanol (150 cm^3). The mixture was heated under reflux for 1 h during which time the colour changed from yellow to green. A slight excess of LiBr was added and the precipitated AgBr filtered off to yield an olive-green solution. Addition of Na[NCS] (0.004 mol) gave a brown solution which was refluxed gently for 30 min. Rotary evaporation followed by cooling yielded a light brown powder which was recrystallised from methanol. Yields were within the range 60—70%. The complex $[NiL^9(NCS)][BPh_4]$ was prepared from the above complex in *ca.* 65% yield by treatment of a cold methanol solution with 1 equivalent of $Na[BPh_4]$. A light brown powder separated on standing and this was recrystallised from methanol.

The complex $[NiL^{10}(NCS)][ClO_4]$ was prepared as for the analogous L^9 complex except that dry ethanol was used as solvent. The light brown crystals were obtained in 60—65% yield.

$[NiL^{11}(OH_2)][ClO_4]_2$ *and* $[NiL^{11}(NCS)][ClO_4]$. Equimolar quantities of $[AgL^2]_2[ClO_4]_2$ and $Ni[ClO_4]_2\cdot6H_2O$ (0.002 mol scale) were heated under reflux for 1 h in undried methanol at which stage LiBr (0.002 mol) was added. The filtrate from this reaction was either allowed to concentrate to yield the brown diperchlorate, or treated with an excess of Na[NCS] to yield the brown thiocyanato-perchlorate. The latter complex could also be obtained by 'recrystallisation' of $[NiL^9(NCS)][ClO_4]$ or $[NiL^{10}(NCS)][ClO_4]$ from wet methanol. Yields were in the range 60—85%.

$[NiL^3(ClO_4)][ClO_4]\cdot3H_2O$. A hot solution of $Ni[ClO_4]_2\cdot6H_2O$ (0.002 mol) in methanol (50 cm^3) was mixed with a methanolic solution (150 cm^3) of $[AgL^3][ClO_4]$ (0.002 mol) and heated under reflux gently for 1 h, during which time the colour changed from yellow to brown. On cooling and concentration a brown powder separated. This was recrystallised from methanol. Yield 55—60%.

$[NiL^3(NCS)][ClO_4]$. This complex was prepared in *ca.* 70% yield from the diperchlorate by addition of an excess of Na[NCS] to a methanol solution. The complex $[NiL^3(N_3)][ClO_4]$ was prepared analogously except that $Na[N_3]$ was used. Yield *ca.* 70%.

Physical measurements were carried out as described in earlier papers in this series.

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[8/516 *Received, 20th March,* 1978]

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