Chemistry of Polydentate Ligands. Part 6.[1] Synthesis, Characterisation, and Properties of Group 2B Cation Complexes with Novel Quinquedentate Macrocyclic Ligands

By **Jack Lewis** * and **Timothy D. O'Donoghue**, University Chemical Laboratories, Lensfield Road, Cambridge CB2 1EW

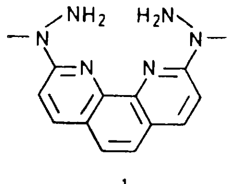
Complexes of quinquedentate macrocyclic ligands with Group 2B cations have been prepared by condensation of 2,6-diformylpyridine and 2,6-diacetylpyridine with 2,9-di(1-methylhydrazino)-1,10-phenanthroline monohydrochloride in the presence of metal-ion templates. Electrical conductivity measurements, i.r. and ^{1}H n.m.r. spectral data are reported and evaluated to show that ring closure rather than polymer formation has occurred. Evidence is presented for some metal ions in the macrocyclic complexes having pentagonal-pyramidal co-ordination geometries. The n.m.r. data are interpreted as indicating the presence of ring currents in the ligands. Hydrogenation of the hydrazone bonds produces two new ligands: the n.m.r. spectra of the zinc(II) complexes demonstrate that these macrocycles are folded. Relative yields of optical isomers of the complex with one of these reduced macrocycles are reported.

THE presence of macrocyclic rings in natural products [2,3] like haemoglobin, vitamin B$_{12}$, and chlorophyll has been the inspiration of, and motivation behind, studies of complexes containing synthetic macrocyclic ligands. The aim is to develop simple, totally synthetic systems where certain features of the biologically important molecules are reproduced.[3,4] This paper reports the synthesis and chemistry of complexes with novel quinquedentate macrocyclic ligands that bear some similarity to porphyrins. Both types of compound are planar, relatively rigid, and have π-electron delocalisation around the macrocyclic rings.

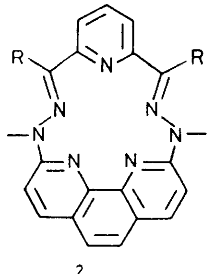
The majority of cyclisation reactions to yield quinquedentate macrocyclic ligands have involved ring closure by 2,6-diacetylpyridine.[5–7] Included in the small number of metal ions capable of directing this reaction are zinc(II), cadmium(II), and mercury(II). The template condensations of 2,9-di(1-methylhydrazino)-1,10-phenanthroline monohydrochloride (L^1·HCl) with 2,6-diformylpyridine and 2,6-diacetylpyridine in the presence of bivalent Group 2B cations are the subjects of this paper.

RESULTS AND DISCUSSION

Zinc(II) *Complexes*.—The preparation of L^1·HCl and some zinc(II) derivatives of this ligand have been reported.[1] The complex Zn(L^1)Cl(O$_2$CMe) is generated *in situ* in the formation of zinc(II) complexes of L^2 and L^3. These ligands result from the addition of the respective 2,6-diketo-derivatives of pyridine to hot aqueous methanolic solutions of the above intermediate, in the presence of several drops of dilute hydrochloric acid. The reaction occurs over 4 h of refluxing and is accompanied by a deepening of the yellow colour of the solution. Precipitation of the complexes, in 60% yields, was induced by addition of [NH$_4$][PF$_6$]. The complexes appear to be indefinitely stable. Ligand L^2 is formed more rapidly than L^3 and complexes of the former are more soluble in polar solvents, details that hold for complexes of these ligands with other metal ions. Incorporation of the substituted pyridine units in L^2 and L^3 is demonstrated by the ^{1}H n.m.r. spectra of the zinc(II) complexes (see below). The analytical data in Table 1 indicate that for the above pair of complexes, rather than the charge on the bivalent zinc being balanced by two PF$_6^-$ groups, only one is included in the products along with one chloride ion. The complex Zn(L^3)Cl(PF$_6$)·0.5dmso was recrystallised from dimethyl sulphoxide (dmso).



L^1



L^2: R = H

L^3: R = Me

Infrared spectroscopy provides valuable information as to whether or not condensation to form hydrazone bonds has occurred. The terminal NH$_2$ groups of the hydrazines give N–H stretching vibrations [8] at 3 300 and 3 200 cm^{-1} and the N–H bending mode is at 1 640 cm^{-1}, while the carbonyl signal from the diketones occurs close to 1 700 cm^{-1}. The hydrazone signal, at *ca.* 1 600 cm^{-1}, does not overlap with the above bands, and simple observation of the 1 600—1 750 cm^{-1} region indicates the success or failure of a reaction. A strong band, the C–H deformation,[9] is always seen at *ca.* 850 cm^{-1}. The spectra of the zinc(II) complexes do not contain any bands above 1 600 cm^{-1}, other than ν(C=N) signals of the appropriate compound. However, the i.r. evidence by itself is not proof of ring closure as it does not distinguish between the products being monomeric macrocyclic complexes or long polymeric chains. If the products are polymeric then the i.r. and n.m.r. data specify that the chains must be of sufficient length that signals from the terminal units are of the same order of magnitude as the noise in the spectra. A comparison of the i.r. data with that obtained from a manganese(II) complex of L^3, the crystal structure of which proves conclusively that a macrocycle is present,[10,11] provides strong support for the presence of the monomeric products with zinc(II). The conductivity measurements in Table 1, taken in conjunction with the i.r. spectra and the analytical data, enable the products to be uniquely defined as complexes of the macrocycles L^2 and L^3. The complexes prepared as the bromide salts serve to illustrate this reasoning.

TABLE 1

Analytical and conductivity data for zinc(II) complexes

Compound	Analysis (%) [a] C	H	N	Λ [b] S cm^2 mol^{-1}
$Zn(L^2)Cl(PF_6)\cdot 0.5H_2O$	40.5	2.9	16.0	39
	(40.5)	(3.0)	(15.8)	
$Zn(L^2)Br_2\cdot 3H_2O$	39.0	3.3	15.2	54
	(39.0)	(3.6)	(14.9)	
$Zn(L^2)(NCS)_2$ [c]	50.3	3.4	22.8	66
	(50.3)	(3.1)	(23.0)	
$Zn(L^3)Cl(PF_6)\cdot 0.5$dmso	42.3	3.5	14.2	43
	(42.4)	(3.6)	(14.4)	
$Zn(L^3)Cl(BF_4)$	47.5	3.7	17.2	
	(47.8)	(3.7)	(17.0)	
$Zn(L^3)Br_2$	44.3	3.7	15.5	59 [d]
	(44.5)	(3.4)	(15.8)	
(1)	25.3	2.5	10.0	97
	(25.6)	(3.0)	(9.9)	
$Zn(L^4)Cl(PF_6)\cdot H_2O$	40.2	3.7	15.6	29
	(40.4)	(3.7)	(15.7)	
$Zn(L^5)(NCS)_2$ [e]	50.3	4.5	20.6	47
	(50.1)	(4.5)	(21.6)	

[a] Calculated values are given in parentheses. [b] Measured at room temperature on solutions 10^{-3} mol dm^{-3} in dmso. [c] $\nu(C\equiv N)$ at 2 080 and 2 055 cm^{-1}. [d] 148 S cm^2 mol^{-1} when 10^{-3} mol dm^{-3} in methanol. [e] $\nu(C\equiv N)$ at 2 080 and 2 055 cm^{-1}.

Thus, a polymer consisting of n units will have $2n + 1$ ions present ($2n$ bromide ions and one large cation) and a molar conductivity corresponding to a $2:1/n$ electrolyte. As n has to be large, the conductivity of a polymeric species should be noticeably lower than that anticipated for the macrocyclic species. The experimental values, measured at room temperature on 10^{-3} mol dm^{-3} solutions in dmso, fall in the range for 2 : 1 electrolytes,[12] thereby demonstrating the presence of cyclic ligands. The complex $Zn(L^2)(NCS)_2$ is also a 2 : 1 electrolyte and its preparation, by metathesis with a solution of the chloride complex, shows that macrocycles are present in the complexes $Zn(L^2)Cl(PF_6)$ and $Zn(L^3)Cl(PF_6)$ even though they are 1 : 1 electrolytes in dmso.

Both the retention of a single chloride ion per molecule in the above complexes and the conductivity data provide strong evidence for the zinc(II) cations being six-co-ordinate, each with a chloro-ligand in an axial position. As the macrocycles are quinquedentate, there should be some differentiation between the axial sites such that one position is occupied and the other empty. This inequivalence arises from either the metal ion sitting out of the donor plane, or folding of the macrocycles which results in one site being more sterically crowded than the other. Molecular models show that the quinquedentate ligands are approximately planar and favour the former geometry. The covalent radius of six-co-ordinate zinc(II), 1.4 Å,[13] is of comparable magnitude to that of high-spin manganese(II), 1.5 Å, which is known to sit out of the donor-atom plane. The above evidence implies that the unusual co-ordination geometry of a pentagonal pyramid, that was reported for $Mn(L^3)Cl(BF_4)$,[10] also exists in zinc(II) complexes of L^2 and L^3. Small hole size and a rigid quinquedentate ligand, the constraints that lead to this geometry with Mn^{II}, are still present here. It is interesting to note that the zinc(II) complex of the 2,2′-bipyridyl analogue of L^2 has pentagonal-bipyramidal co-ordination geometry about the metal ion.[7] The additional flexibility introduced by the bipyridyl fragment allows the macrocyclic cavity to encompass the zinc(II).

There is less certainty about the co-ordination environment of Zn^{II} when Br$^-$ and NCS$^-$ are the counter ions. Complexes with mixed anions are not isolated when these ions are present. Further, these complexes are 2 : 1 electrolytes in dmso. Hence it is quite feasible that the Zn^{II} is seven-co-ordinate, with the ligands at the vertices of a pentagonal bipyramid. Some evidence for six-co-ordinate Zn^{II} with the NCS$^-$ ions is provided by the $\nu(C\equiv N)$ signals in the i.r. spectrum of $Zn(L^2)(NCS)_2$. Two bands are observed, at 2 080 and 2 055 cm^{-1}, the former being the broader of the two signals. The resonance at 2 080 cm^{-1} is typical of an isothiocyanato-ligand,[14] while the other band is assigned to an ionic NCS$^-$ as the frequency is close to the value of 2 053 cm^{-1} found with K[NCS].* Various fingerprint bands close to 800 cm^{-1} prevent confirmation of these assignments being obtained.

Cadmium(II) *and Mercury*(II) *Complexes*.—The ring-closure reaction was readily extended to preparing cadmium(II) and mercury(II) complexes of L^2 and L^3, by using these ions as templates. The solvent was changed to water because of the poor solubility of the intermediates in aqueous methanol. A mineral acid catalyst was still necessary for the cyclisation to occur. Analytical and conductivity data for the complexes prepared are given in Table 2. Following like reasoning to that employed for the zinc(II) compounds indicates that the ligands in the cadmium(II) complexes are monomeric macrocycles. The co-ordination geometry about some cadmium ions is pentagonal pyramidal; complexes containing chloride ions are 1 : 1 electrolytes in dmso, the chloro-ligand remaining bound in solution. However,

---

* We are grateful to a referee who has pointed out that the observation of two $\nu(C\equiv N)$ bands, even when one occurs close to 2 053 cm^{-1}, is not definite proof of one NCS$^-$ being unco-ordinated: see for example M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J.C.S. Dalton*, 1977, 438.

solvent molecules present in several complexes could occupy axial sites, and therefore some uncertainty exists as to the co-ordination environments in these instances. The Cd^{II} and Hg^{II} ions, being larger than Zn^{II}, are expected to sit away from the equatorial planes of the macrocycles. Two ν(C≡N) bands, at 2 070 and 2 055 cm^{-1}, in the i.r. spectrum of $Cd(L^2)(NCS)_2$ again provide evidence for differing axial environments.

The mercury(II) complexes are highly insoluble and have two ligand molecules for every three Hg^{II} ions. Bearing in mind the possibility of forming $[HgCl_4]^{2-}$ ions,[2,6] the complexes are formulated as $[\{Hg(L)Cl\}_2]$-$[HgCl_4]$ where L = L^2 or L^3.

The compound $Cd(L^3)(ClO_4)_2$, which was prepared by using $HClO_4$ as the acid catalyst, does not have a strongly co-ordinating anion present. While the i.r. spectrum contains a broad band at 1 090 cm^{-1}, characteristic of ionic perchlorate,[14] it is still possible that one $[ClO_4]^-$ ion is co-ordinated and that the splitting of this band is obscured by the intense ionic $[ClO_4]^-$ signal. The complex is a 2 : 1 electrolyte in dmso.

TABLE 2

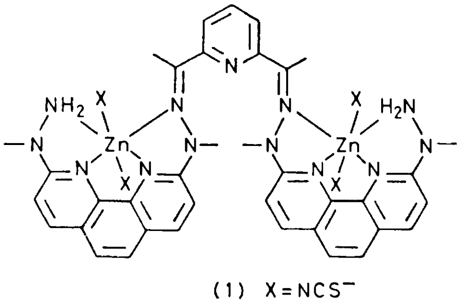
Analytical and conductivity data for cadmium(II) and mercury(II) complexes

Compound	Analysis (%) [a] C	H	N	Λ [b] S cm^2 mol^{-1}
$Cd(L^2)Cl_2 \cdot 1.5H_2O$	43.8	3.3	16.9	29
	(43.7)	(3.5)	(17.0)	
$Cd(L^2)(NCS)_2 \cdot 0.25EtOH$ [c]	46.9	3.1	20.9	34
	(46.4)	(3.1)	(20.7)	
$Cd(L^2)Cl(PF_6) \cdot 0.5H_2O$	37.5	2.8	14.2	33
	(37.7)	(2.7)	(14.6)	
$Cd(L^3)Cl_2 \cdot H_2O$	46.3	3.9	16.5	28
	(46.3)	(3.9)	(16.4)	
$Cd(L^3)(ClO_4)_2 \cdot 0.5H_2O$	38.5	3.0	14.1	52
	(38.6)	(3.1)	(13.7)	
$Hg_3(L^2)_2Cl_6 \cdot MeOH$	32.7	2.8	12.6	*d*
	(32.7)	(2.4)	(12.4)	
$Hg_3(L^3)_2Cl_6$	34.2	2.9	12.5	32
	(34.4)	(2.6)	(12.2)	

[a] Calculated values are given in parentheses. [b] Measured at room temperature on solutions 10^{-3} mol dm^{-3} in dmso. [c] ν(C≡N) at 2 070 and 2 055 cm^{-1}. [d] Insoluble in dmso.

A template ion is necessary for cyclisation to occur, since reaction in the absence of a template yields an orange solid, the i.r. spectrum of which indicates it to be polymeric. Isolation of similar solids from attempts at ring closure around magnesium(II) demonstrates that this ion does not act as a template for L^2 or L^3.[15] The acid catalyst is also vital to the cyclisation process when Group 2B cations are the templates. Addition of $[NH_4][NCS]$ to a neutral refluxing reaction mixture containing zinc(II) as the template yields a pale yellow solid which analyses (Table 1) as $C_{41}N_{17}S_4Zn_2$. The i.r. spectrum of this solid contains N–H bands but no ν(C=O) resonances. The information is consistent with structure (1), the zinc(II) having failed to direct the cyclisation. It seems that ring closure only occurs when the Schiff-base formation is rapid. This condensation is acid catalysed [16] and should be faster with 2,6-diformylpyridine than with 2,6-diacetylpyridine, the carbonyl carbons being more electrophilic in the former. The role of the template ion appears to lie in being complexed by the quadridentate ligand and then forming a bond to the pyridine nitrogen, thereby holding the carbonyl groups in suitable positions for attack by hydrazine nitrogen atoms. The template also prevents polymer formation.

Hydrogen-1 *N.M.R. Spectra of the Complexes.* The ^1H n.m.r. spectra of the diamagnetic complexes of L^2 and L^3 were run at 80 MHz in $[^2H_6]$dmso solutions. Analysis of the spectra was undertaken to demonstrate the incorporation of the pyridine rings and to investigate any π-electron delocalisation in the macrocycles.



(1) X = NCS$^-$

The aromatic regions were treated as second-order spectra, a 2,6-disubstituted pyridine being the classic AB_2 spin system.[17] The phenanthroline hydrogens H^3 and H^4 form an AB spin system, as is evident in Figure 1.

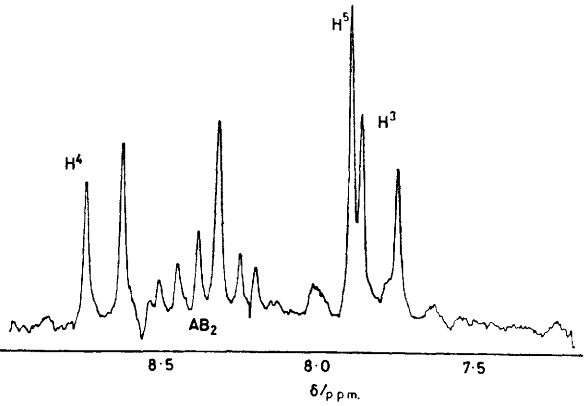


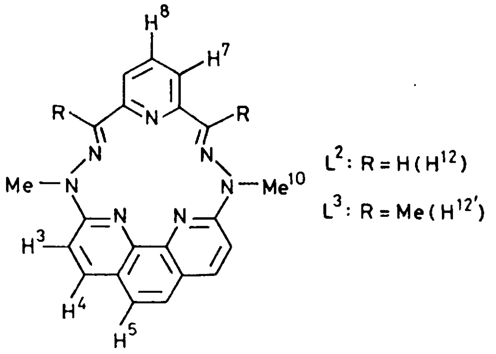
FIGURE 1 The aromatic region of the ^1H n.m.r. spectrum of $Zn(L^3)Cl(PF_6)$. The AB_2 section is labelled and the other signals are from the phenanthroline hydrogens

Assignment of the AB_2 patterns and calculation of chemical shifts and coupling constants were performed using published methods.[18] The values show good agreement with those obtained by iterative least-squares procedures using the program NUMARIT.[19] Table 3 contains details of the spectral parameters, the numbering scheme adopted being that given in the accompanying diagram. The spectra establish that pyridine residues are present.

A comparison of the chemical shifts of the phenanthroline hydrogens and the *N*-methyl groups in Table 3 with the values [1] for a zinc(II) complex of the open-chain ligand L^1 is presented in Table 4. Positive values represent downfield shifts. The average movement for the aromatic hydrogens in $Zn(L^3)Cl(PF_6)$ relative to $Zn(L^1)Cl(O_2CMe)$ is 0.43 p.p.m. and 0.44 p.p.m. for $Cd(L^3)Cl_2$ relative to the same standard. It is unlikely that these shifts are attributable to purely inductive effects, particularly as the phenanthroline hydrogens are up to seven bonds away from the positions of substitution. Ring closure allows the π-electron delocalisation to extend around the complete macrocycles, as long as the lone pair on each unco-ordinated nitrogen occupies a *p* orbital, that is the nitrogen is sp^2 hybridised. This alteration in the ring currents [20] should cause changes in the chemical shifts of the aromatic hydrogens. The values in Table 4 also show that the downfield shifts are greater for L^2 than for L^3. The mean value of this difference is 0.16 p.p.m. for both the zinc(II) and cadmium(II) complexes. Severe steric interaction between adjacent methyl groups, which is evident in the crystal structure of $[Mn(L^3)Cl][BF_4]$,[11] leads to some buckling of the ligand. This strain is absent in L^2 so the macrocycle should adopt a more planar configuration which will increase the conjugation present and thereby lower the resonance frequencies of the aromatic hydrogen atoms.

TABLE 3

Hydrogen-1 n.m.r. data [a] for diamagnetic complexes of L^2 and L^3, and for 2,6-diacetylpyridine

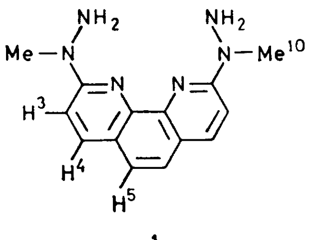


Compound	H^3	H^4	H^5	H^7	H^8	H^{10}	$H^{12'}$	H^{12}	$J(H^3H^4)$	$J(H^7H^8)$
2,6-Diacetylpyridine [b]				8.21	8.01		2.79			7.3
$Zn(L^2)Cl(PF_6)$	8.05	8.79	8.01	8.00	8.38	3.93		8.47	9.2	7.9
$Zn(L^3)Cl(PF_6)$	7.81	8.66	7.89	8.28	8.44	3.93	2.83		9.1	7.4
$Cd(L^2)Cl_2$ [c]	8.08	8.79	8.01			3.92			9.1	
$Cd(L^3)Cl_2$	7.84	8.66	7.89	8.42	8.55	3.94	2.83		9.1	7.8
$Hg_3(L^3)_2Cl_6$ [c]	7.92	8.68	7.93			3.97	2.83		9.1	

[a] Values of chemical shifts are in p.p.m. relative to $SiMe_4$. Coupling constants in Hz. [b] Run in $CDCl_3$ at 60 MHz. [c] Unable to interpret the AB_2 spectrum.

TABLE 4

Chemical shift * data relative to $Zn(L^1)Cl(O_2CMe)$

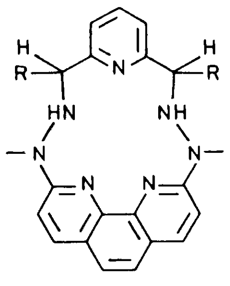


L^1

Compound	H^3	H^4	H^5	H^{10}
$Zn(L^2)Cl(PF_6)$	0.76	0.56	0.47	0.53
$Zn(L^3)Cl(PF_6)$	0.52	0.43	0.35	0.53
$Cd(L^2)Cl_2$	0.79	0.56	0.47	0.52
$Cd(L^3)Cl_2$	0.55	0.43	0.35	0.54
$Zn(L^4)Cl(PF_6)$	0.12	0.19	0.14	0.13
$Zn(L^5)(NCS)_2$	0.15	0.23	0.15	0.16

* Values in p.p.m. Positive figures indicate downfield shifts.

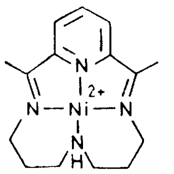
The other entries in Table 4 refer to zinc(II) complexes of L^4 and L^5, details of which are presented below. Reduction of the hydrazone bonds in L^2 and L^3 destroys any π delocalisation that extended completely around the macrocyclic rings. The upfield movement of the phenanthroline-hydrogen chemical shifts in L^4 and L^5 relative to L^2 and L^3 respectively provides additional evidence for extended ring currents in L^2 and L^3. The new values are relatively close to those of the parent quadridentate ligand L^1 in $Zn(L^1)Cl(O_2CMe)$.



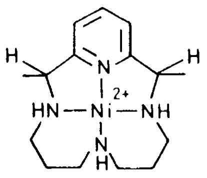
L^4: R = H

L^5: R = Me

Zinc(II) *Complexes of* L^4 *and* L^5.—Hydrogenation of imine bonds in macrocyclic complexes is a well known method of altering the degree of unsaturation present in these ligands.[21–24] The reductions normally produce mixtures of isomers as the hydrogenated co-ordinated nitrogens become asymmetric centres, the isomerism involving the relative positions of the N–H bonds.* Thus, when (3) is formed by reaction of $Na[BH_4]$ with (2), different isomers, with the newly formed N–H bonds *cis* and *trans*, are found.[22] The flexibility of the aliphatic chelate rings allows the planar co-ordination of the ligand to be retained with both types of isomer. The two rigid segments in L^4 and L^5, the aromatic rings, remove this flexibility here and only for one of the configurations, that with *trans* N–H bonds, can planar co-ordination of the ligands be retained. † Molecular models demonstrate that in the configuration with *cis* N–H bonds the macrocycle must be folded, with the fold axis running between the saturated nitrogens. The models also show that the conformation with *trans* N–H bonds is highly strained.



(2)



(3)

Zinc(II) complexes of L^4 and L^5 were prepared by reduction, with sodium tetrahydroborate in aqueous solution, of the hydrazone bonds in complexes of L^2 and L^3 respectively. The reagent was added in roughly a ten-fold excess before the solutions were made acidic. Analytical and electrical-conductance data for the pale yellow solids isolated are contained in Table 1. The ν(N–H) bands at 3 300 and 3 200 cm^{-1}, along with a bending mode at 1 640 cm^{-1}, in the i.r. spectra of these complexes confirm that hydrogenation has occurred. Two ν(C≡N) signals, at 2 080 and 2 055 cm^{-1}, for $Zn(L^5)(NCS)_2$ provide evidence for the zinc(II) being six-co-ordinate, a conclusion that is supported by $Zn(L^4)Cl(PF_6)$ acting as a 1 : 1 electrolyte in dmso. Steric crowding of one axial site by the macrocycle (see below) is proposed as the reason for co-ordination of a sole axial ligand here.

The two asymmetric centres in complexes of L^4, the hydrazine donor atoms, give rise to four possible optical isomers, two with *cis* N–H bonds and the other pair with these bonds *trans*. The axial ligand, by differentiating the two axial sites, enables the relative positions of the N–H bonds in L^4 to be obtained from the n.m.r. spectrum of $Zn(L^4)Cl(PF_6)$. The hydrazine hydrogens in the *trans* isomers will be in different environments and therefore inequivalent and distinguishable, whereas these atoms will be equivalent for the *cis* isomers. The spectrum, Figure 2, contains signals from only one of the isomer pairs and the assignments to the various hydrogens are presented in Table 5: the diagram accompanying the Table gives the numbering scheme employed. Analysis of the spectrum shows that the two hydrazine hydrogens are equivalent, thereby demonstrating that only *cis* isomers are formed, and that hydrogenation results in folding of the macrocycle. The co-ordination geometry around the zinc(II) is between octahedral and pentagonal pyramidal.[6,10]

Interest in the assignment of the isomers of L^4 focuses attention on the signals from H^{12}, H^{13}, and H^{16}. These hydrogens form an ABX spin system,[18] with each multiplet having an integrated intensity of two atoms. It is the successful refinement of this part of the spectrum, using the program NUMARIT,[19] that demonstrates the formation of only those isomers with *cis* N–H bonds. Analysis of an ABX spectrum does not yield the sign of J_{AB} but as geminal hydrogen coupling constants are usually negative,[8] $J(H^{12}H^{13})$ is entered in Table 5 as −15.8 Hz. A typical value for a five-membered ring is −12 Hz and two opposing factors are responsible for the difference here, the pyridine π-electron cloud and the electronegativity of the α nitrogen atoms. The influence of an α nitrogen, which makes $J(H^{12}H^{13})$ less negative, is more than offset by the π contribution: the latter increment varies with ϕ, the angle between the π orbital and one of the methylene hydrogens.[25] The π contribution is close to the maximum, which occurs for $\phi = 35°$, and a value of $\phi = 25°$ is consistent with a molecular model of the complex. This model shows

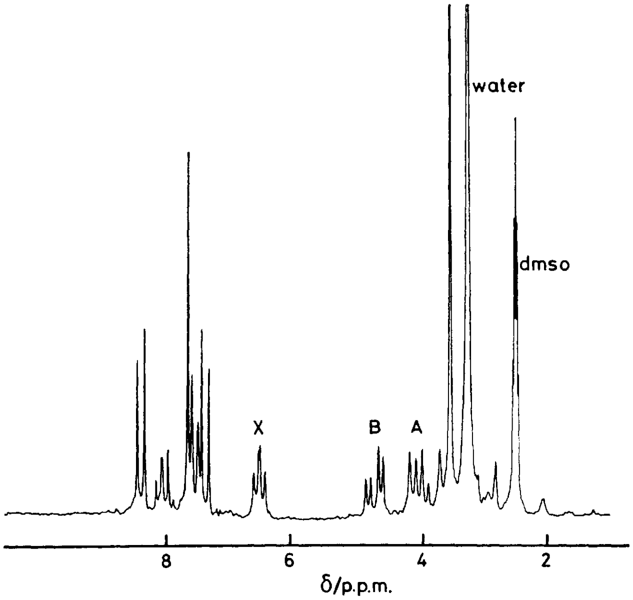


FIGURE 2 The ^1H n.m.r. spectrum of $Zn(L^4)Cl(PF_6)\cdot H_2O$. Multiplets from the ABX spin system are labelled

---

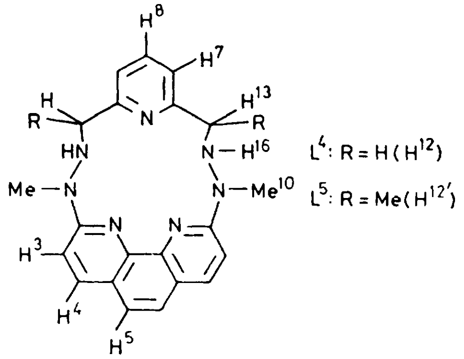
* For ease of writing, the phrase ' *cis* isomer ' refers to the N–H bonds being on the same side of the ring, and ' *trans* isomer ' means that these bonds are on opposite sides of the ring concerned.

† A preliminary report of part of this work has appeared (J. Lewis and T. D. O'Donoghue, *Inorg. Chim. Acta*, 1978, **30**, L21).

that the axial hydrogens are on the less hindered side of the ring. The higher-field multiplet of the AB pair is assigned to the axial hydrogens since they should be less affected by the pyridine ring currents. The chemical-shift difference between δ_A and δ_B, 0.68 p.p.m., is similar to the value of 0.6 p.p.m. found for methylene hydrogens α to a pyrrole ring in a capped porphyrin.[26]

TABLE 5

Chemical shifts [a] and coupling constants [b] for complexes of L^4 and L^5



Compound	H^3	H^4	H^5	H^7	H^8	H^{10}	H^{12}	$H^{12'}$	H^{13}
$Zn(L^4)Cl(PF_6)$	7.41	8.42	7.68	7.51	8.08	3.53	4.05		4.73
$Zn(L^5)(NCS)_2$	7.44	8.46	7.69	7.70	8.20	3.56		1.00	4.92
	H^{16}	$J(H^3H^4)$	$J(H^7H^8)$	$J(H^{12}H^{16})$	$J(H^{13}H^{16})$	$J(H^{12}H^{13})$	$J(H^{12'}H^{13})$		
$Zn(L^4)Cl(PF_6)$	6.56	8.8	7.3	7.8	6.4	−15.8			
$Zn(L^5)(NCS)_2$	6.84	8.8	7.3		4.8		6.9		

[a] Values in p.p.m. relative to $SiMe_4$. [b] Values in Hz.

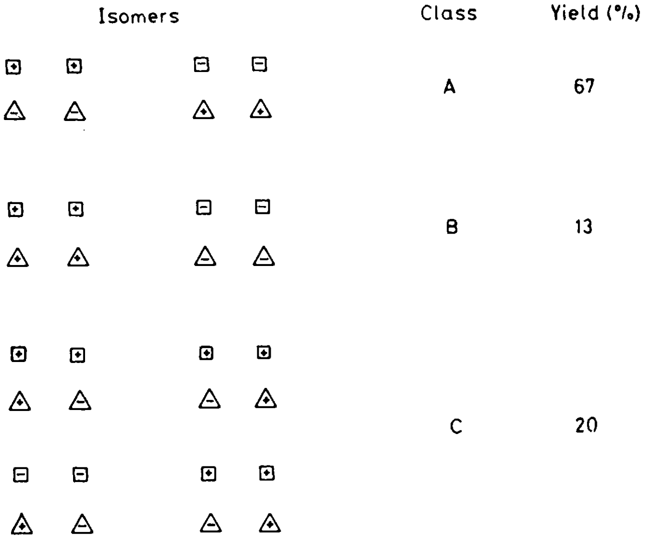


FIGURE 3 Schematic representation of the isomers of $Zn(L^5)(NCS)_2$ formed on hydrogenation of $[Zn(L^3)]^{2+}$. The isomers are arranged in categories that are distinguishable by n.m.r. spectroscopy, and the relative yields of these groups are given. A + sign indicates that the hydrogen attached to an atom is above the plane of the paper, a − sign that it is below. Carbon atoms are represented by triangles and nitrogens by squares

The above analysis is of importance in assigning signals to the various isomers prepared in the synthesis of $Zn(L^5)(NCS)_2$. The four asymmetric centres in the complex give 16 possible isomers but assuming that only isomers with *cis* N–H bonds are formed on hydrogenation halves this number. These eight isomers fall into three categories distinguishable by n.m.r. spectroscopy, as shown schematically in Figure 3. Included in this Figure are the relative yields of the isomer classes. The n.m.r. spectrum is presented in Figure 4 and the spectral parameters for the most abundant isomer class are contained in Table 5. Percentage yields of the classes were measured from the relative areas of the high-field methyl-group doublets. Four, rather than three, doublets are present since one of the isomer categories, C, has one axial and one equatorial methyl group.

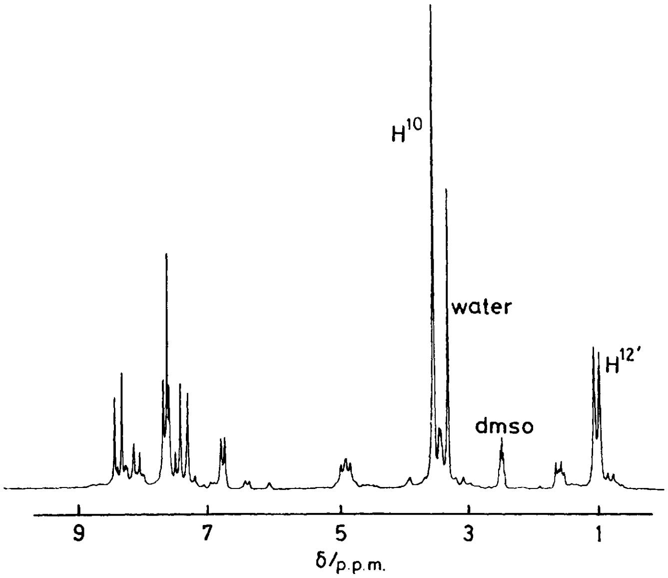


FIGURE 4 The ^1H n.m.r. spectrum of $Zn(L^5)(NCS)_2 \cdot H_2O$

Comparison of the spectra of L^4 and L^5, Figures 2 and 4, shows that the methyl doublet of isomer class A has replaced the multiplet assigned to H^{12} in $Zn(L^4)Cl(PF_6)$. Since H^{12} is the axial hydrogen in L^4 this suggests that the most abundant isomer class has both *C*-methyl groups on the side of the macrocycle with less steric crowding. Class B has these groups on the more hindered side. This interpretation is supported by the methyl doublet of category A isomers occurring at higher field (1.00 p.p.m.) than that of class B (1.60 p.p.m.); the equatorial methyl groups are more affected by the pyridine ring currents than the axial methyls.

EXPERIMENTAL

Infrared spectra of Nujol mulls supported between sodium chloride discs were recorded using Perkin-Elmer 257 and 457 spectrometers, over the range 625—4 000 cm^{-1}. Conductance measurements were made with a Wayne–Kerr Universal bridge. The ^1H n.m.r. spectra were run at 80 MHz on a Varian CFT-20 spectrometer, apart from one example run at 60 MHz on a Perkin-Elmer R12. Microanalyses were performed by the University Chemical Laboratory Microanalytical Department.

Reagents, of analytical grade where possible, were used without further purification, apart from 2,6-diformylpyridine which was recrystallised from chloroform.

Zinc(II) *Complexes of* L^2 *and* L^3.—An example of the general preparative method for these complexes is the synthesis of $Zn(L^3)Cl(PF_6)$. The compound $L^1{\cdot}HCl$ (1 mmol) was dissolved in a hot 50% water–methanol mixture (50 cm^3) to which zinc acetate dihydrate (1 mmol) was added, followed by 2,6-diacetylpyridine (1 mmol). Dilute HCl (1 cm^3) was introduced and the refluxing continued for 4 h, during which time the yellow colour of the solution deepened. An aqueous solution of $[NH_4][PF_6]$ (2 mmol) was then added slowly. After cooling, the solid present was filtered off and washed with ethanol and diethyl ether. Yields were generally close to 60%. The bromide complexes were obtained by using HBr as the mineral acid catalyst.

Cadmium(II) *Complexes of* L^2 *and* L^3.—The method was similar to that used for the zinc(II) complexes. The source of Cd^{II} was generally $CdCl_2$, although $Cd[O_2CMe]_2$ was used occasionally, and water was the solvent. Yields 55%.

$Cd(L^2)(ClO_4)_2{\cdot}0.5\ H_2O$.—The salt $L^1{\cdot}HClO_4$ (0.3 mmol) and cadmium acetate (0.3 mmol) were added to hot ethanol (50 cm^3) and the solution filtered while hot after 20 min stirring. 2,6-Diacetylpyridine (0.3 mmol) was then introduced, followed by 70% aqueous $HClO_4$ (2 cm^3), and the heating continued for 2 h. After cooling, the precipitate was filtered off and washed with ethanol. Yield 40%.

Mercury(II) *Complexes of* L^2 *and* L^3.—The preparative method was the same as for cadmium(II) complexes. Water was used as the solvent and the source of the template ions was $HgCl_2$. The reactions were rapid and produced yellow solids.

Zinc(II) *Complexes of* L^4 *and* L^5.—The example given here is the preparation of $Zn(L^5)(NCS)_2{\cdot}H_2O$. A solution of $Zn(L^3)Cl_2$ in aqueous ethanol was prepared by the method above, using only a few drops of HCl catalyst, and filtered when cold. An excess of sodium tetrahydroborate was then added and the mixture stirred for 15 min. Dilute HCl was used to neutralise the solution. After filtration the addition of an excess of $[NH_4][NCS]$ gave a pale yellow solid which was filtered off and washed with water, ethanol, and diethyl ether. Yield 60%.

Compound (1).—Zinc acetate dihydrate, $L^1{\cdot}HCl$, and 2,6-diacetylpyridine (0.3 mmol of each) were reacted together in hot aqueous ethanol (50 cm^3) for 1 h, after which dropwise addition of an aqueous solution of $[NH_4][NCS]$ gave a pale yellow solid. This was filtered off after cooling and washed with ethanol.

We thank the S.R.C. for support (to T. D. O'D.) and Mr. B. Crysell and Dr. A. Charles for recording the n.m.r. spectra.

[9/501 *Received, 27th March*, 1979]

REFERENCES

[1] Part 5, J. Lewis and T. D. O'Donoghue, preceding paper.

[2] F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, New York, 1972.

[3] D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Adv. Chem. Ser.*, 1971, **100**, 44.

[4] L. F. Lindoy, *Chem. Soc. Rev.*, 1975, **4**, 421.

[5] J. D. Curry and D. H. Busch, *J. Amer. Chem. Soc.*, 1964, **86**, 592.

[6] S. M. Nelson, S. G. McFall, M. G. B. Drew, A. H. Othman, and N. B. Mason, *J.C.S. Chem. Comm.*, 1977, 167.

[7] Z. P. Haque, D. C. Liles, M. McPartlin, and P. A. Tasker, *Inorg. Chim. Acta*, 1977, **23**, L21.

[8] D. H. Williams and I. Fleming, 'Spectroscopic Methods in Organic Chemistry,' 2nd edn., McGraw-Hill, Maidenhead, 1973.

[9] A. A. Schilt and R. C. Taylor, *J. Inorg. Nuclear Chem.*, 1959, **9**, 211.

[10] M. M. Bishop, J. Lewis, T. D. O'Donoghue, and P. R. Raithby, *J.C.S. Chem. Comm.*, 1978, 476.

[11] T. D. O'Donoghue, Ph.D. Thesis, University of Cambridge, 1977.

[12] W. J. Geary, *Co-ordination Chem. Rev.*, 1971, **7**, 81.

[13] M. B. Hursthouse, 'Molecular Structure by Diffraction Methods,' *Specialist Periodical Reports*, The Chemical Society, London, 1976, vol. 4, and refs. therein.

[14] K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds,' 2nd edn., Interscience, New York, 1970.

[15] D. H. Cook, D. E. Fenton, M. G. B. Drew, S. G. McFall, and S. M. Nelson, *J.C.S. Dalton*, 1977, 446.

[16] R. L. Reeves, 'Chemistry of the Carbonyl Group,' ed. S. Patai, Interscience, London, 1966, p. 601.

[17] H. J. Bernstein, J. A. Pople, and W. G. Schneider, *Canad. J. Chem.*, 1957, **35**, 65.

[18] J. A. Pople, W. G. Schneider, and H. J. Bernstein, 'High Resolution Nuclear Magnetic Resonance,' McGraw-Hill, New York, 1959.

[19] J. S. Martin, R. A. Quirt, and K. M. Worvill, 'NUMARIT. High Resolution Spectral Analysis,' Science Research Council Bulletin, No. 9, 1975.

[20] R. Ditchfield, 'Nuclear Magnetic Resonance,' *Specialist Periodical Reports*, The Chemical Society, London, 1976, vol. 5, and refs. therein.

[21] N. F. Curtis, *Co-ordination Chem. Rev.*, 1968, **3**, 3.

[22] J. L. Karn and D. H. Busch, *Inorg. Chem.*, 1969, **8**, 1149.

[23] R. Dewar and E. F. Fleischer, *Nature*, 1969, **222**, 372.

[24] M. Rakowski, M. Rycheck, and D. H. Busch, *Inorg. Chem.*, 1975, **14**, 1194.

[25] M. Barfield and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1899.

[26] M. D. Turnbull, Ph.D. Thesis, University of Cambridge, 1977.