Nickel(II) and Cobalt(II) Complexes of Potentially Quinquedentate Macrobicyclic Ligands. Reversible Binding of Dioxygen to a Cobalt(II) Complex

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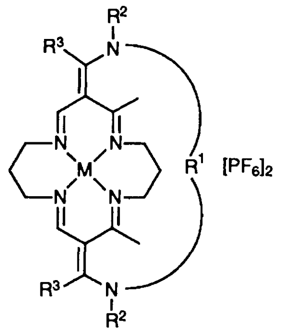
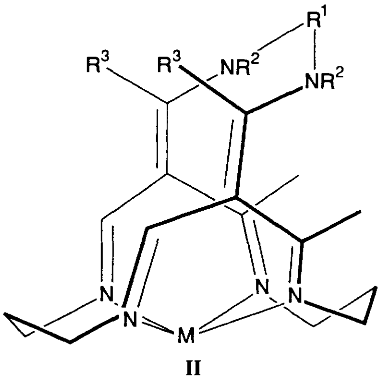
Two new macrobicyclic ligands which are potentially quinquedentate have been prepared and characterised. Variable-temperature NMR studies show that the nickel(II) complex of one of these ligands exists as a mixture of two conformers at low temperature which take part in two independent exchange processes as the temperature is raised. In the first, one conformer undergoes a form of self exchange and in the second, the two conformers interconvert. The ESR spectrum of the cobalt(II) complex of one of the new ligands indicates that it exists as a mixture of four- and five-co-ordinate species, with the five-co-ordinate material arising from intermolecular binding of the ligand secondary amine group to the cobalt(II) ion. This complex binds dioxygen reversibly and the O_2 adduct has reasonable stability with respect to autoxidation.

The chemistry of tetraaza macrocyclic ligands has proven to be a topic of continual and growing interest to co-ordination chemists, following the early work of the groups led by Curtis and Busch on the metal controlled template syntheses of macrocyclic species.[1] The interesting kinetic and thermodynamic stability imparted to metal complexes by the presence of the cyclic ligands has been well documented.[2] A large number of workers are currently engaged in the syntheses of macrocycles having a variety of structural features included as side chains to the main macrocyclic ring. These peripheral groups have been termed the 'ligand superstructure', by analogy with the superstructure of ships. Recent examples include work by Kida and co-workers[3] on cobalt(II) complexes of tetra-functionalised derivatives of cyclam (1,4,8,11-tetraazacyclotetradecane), where the macrocyclic nitrogen atoms bear primary amine or pyridyl functions, and studies by Korybut-Daskiewicz and co-workers[4] on a nickel(II) complex of a diimine macrocycle, functionalised by the anion of nitromethane. This complex has a pH-dependent equilibrium between four- and six-co-ordinate nickel(II) species, the latter being polymeric with bridging superstructure derived from alkyl nitro groups.



I



II

Of particular interest is the body of work reported by Busch and co-workers[5] concerning the chemistry of a large family of nickel(II) complexes of type **I**. Although conventionally drawn as flat molecules, these complexes have a well defined three-dimensional geometry, arising from the conformations adopted by the saturated chelate rings of the parent macrocycle (structure **II**). These ligands have been given the generic name of 'cyclidenes'. Using some parent macrocycles originally reported by Jager,[6] Busch's group has ably demonstrated the wide range of structural flexibility that can be induced into their systems by relatively simple modifications of general synthetic routes. Recently we have reported upon the preparation of some new members of the cyclidene family and discussed the interesting fluxional dynamics of these species, as evidenced by the appearance of their variable-temperature NMR spectra.[7]

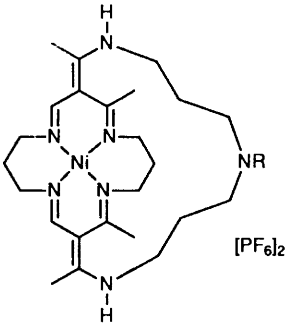
One of the most impressive features of complexes containing Busch's bridged cyclidene ligands is their ability to provide a sterically protected cavity around one co-ordination site of the metal ion.[8] This was exploited to good effect by Busch's group in the preparation of both cobalt- and iron-(II) complexes which are capable of reversible interaction with dioxygen.[9] A large number of complexes displaying this behaviour are now known and they provide a striking example of the relationship between ligand structure and resultant physical properties. Recently we have studied the behaviour of some polymer-bound cobalt(II) cyclidene complexes and their reaction with dioxygen and have established that the O_2 adducts have substantially longer lifetimes in the polymer-bound state than the corresponding complexes in the solution phase.[10]

In this paper, we report on the chemistry of new members of the cyclidene family which contain a nitrogen atom at the centre of the bridging group (structure **III**). This nitrogen atom is potentially capable of acting either as a ligand to a metal centre or as a nucleophile to a suitable electrophilic reagent.

Table 1 Spectroscopic data for the new complexes

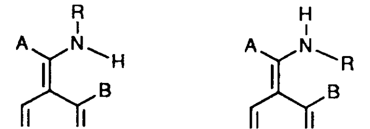
	IR (cm^{-1})				
Complex	ν(N–H)	ν(C=N)	ν(C=C)	ν(PF$_6^-$)	λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})*
1	3 363, 3 300	1 611	1 570, 1 533	840 557	435 (400), 370 (16 000)
2	3 387	1 616	1 573	840 557	435 (400), 370 (15 000)
3	3 369	1 617	1 585, 1 541	840 557	435 (450), 370 (18 500)
4	3 372	1 615	1 585, 1 545	840 557	435 (400), 370 (15 000)

* In acetone.



R
1 H
2 Me
3 4-$CH_2CHC_6H_4CO$
4 4-ClC_6H_4CO

III



'Lid-on' 'Lid-off'

IV

Results and Discussion

Nickel(II) *Complexes*.—The new nickel(II) cyclidene complexes, [NiL^1][PF$_6$]$_2$ **1** and [NiL^2][PF$_6$]$_2$ **2** (structure **III**) were prepared by coupling of a difunctional vinyl ether containing complex[11] with either 1,7-diamino-4-azaheptane or *N,N*-bis(3-aminopropyl)methylamine, under high-dilution conditions, using acetonitrile as solvent. The yellow products were characterised by a combination of spectroscopy (Table 1) and microanalysis. The electronic spectra of the complexes have two shoulders, at λ_{max} *ca.* 435 and 370 nm, which is similar to other square-planar complexes of this general type. The IR spectra of **1** and **2** are unremarkable (Table 1) but contain bands at *ca.* 1613 and 1570 cm^{-1}, assignable to the imine and C=C stretches of the macrocycle and also bands at 840 and 557 cm^{-1}, indicative of the PF$_6^-$ anion. Complex **1** has a band at 3363 cm^{-1}, assigned to the N–H stretch of the secondary amine groups at the bridgehead sites. A broader band at *ca.* 3300 cm^{-1} was assigned to the N–H stretch of the secondary amine group. A band at 3387 cm^{-1} for complex **2** was assigned to the bridgehead N–H groups in that species.

It should be noted that during the preparation of **1** there was a possibility that a dimeric species could be formed by intermolecular coupling of the bridging units. Complex **1** was shown to be solely the monomeric species by carrying out cation-exchange chromatography using the bromide salt. The elution properties of the product were entirely consistent with the monomeric structure, there being no evidence for cations of higher charge.[12] The basic nature of the secondary amine group in the centre of the bridge was observed during metathesis of the Br$^-$ salt by PF$_6^-$, following the ion-exchange experiment. This was carried out using NH$_4$PF$_6$, and yielded as product the corresponding dialkylammonium salt of **1**, showing that the amine is a stronger base than ammonia [equation (1)].

$$[NiL^1][PF_6]_2 + NH_4PF_6 \longrightarrow [Ni(HL^1)][PF_6]_3 + NH_3 \quad (1)$$

Formation of the ammonium salt was indicated by a shift in the position of the band ascribed to the N–H stretch of the secondary amine group, from 3300 to 3393 cm^{-1}.

The ^{1}H NMR spectrum of **2** was far too broad to allow meaningful interpretation and the origin of this broadening is discussed below in greater detail. Likewise the ^{1}H NMR spectrum of **1** at 200 MHz was also rather broad, with many overlapping resonances, but with the aid of a spectrum at 400 MHz, allied to the ^{13}C NMR spectrum at 100 MHz and the results of a COSY (correlation spectroscopy) experiment, it proved possible to assign the observed peaks to the predicted structure. It is noteworthy that a number of the CH$_2$ groups give rise to two well separated signals, showing that the two protons exist in magnetically distinct environments. This behaviour has been seen before with bridged 'cyclidene' complexes. The ^{13}C NMR spectrum of **1** in (CD$_3$)$_2$SO solution is unusual, appearing to contain a group of strong peaks as well as a second set of weaker peaks. Although at first sight this appeared to suggest that complex **1** was impure, on warming the sample to 373 K the two sets of signals were replaced by a single set of sharp peaks whose number and position were in good agreement with those expected for complex **1**. Similarly, the ^{1}H NMR spectrum of **1** sharpened considerably when the sample was heated to 373 K. Clearly **1** exists as a mixture of conformers which do not undergo rapid exchange until the sample is heated well above room temperature.

Previous work by Busch *et al.*[13] has shown that macrocycles of the cyclidene type can adopt two different orientational isomers, the 'lid-on' and the 'lid-off' (structure **IV**). This arises because the nitrogen atoms at the bridgehead positions are planar in nature, as confirmed by X-ray crystal structures of several examples. Where R is part of a bridging group, the 'lid-on' isomer has the bridge lying almost directly over the metal ion, leading to a taller, narrower cavity, while the 'lid-off' form has the bridge displaced to one side, giving a shorter, wider cavity.

Several examples of complexes with either 'lid-on' or 'lid-off' orientations of their bridging group have been characterised by X-ray crystallography. In the vast majority of these cases, the conformation of both bridgehead nitrogen atoms is identical, *i.e.* both 'lid-on' or both 'lid-off' but recent work with long polymethylene chain bridged examples resulted in species which contained one bridgehead nitrogen atom in a 'lid-on' orientation while the other was 'lid-off'.[14]

A useful method of distinguishing between the two isomers involves the use of ^{13}C NMR spectroscopy.[15] It has been found that for 'lid-off' species the resonances ascribed to carbon atoms A and B (structure **IV**) appear as sharp singlets at δ *ca.* 20, with a separation of less than 1 ppm. For the corresponding 'lid-on' species, the signal for carbon B remains as a sharp singlet at δ *ca.* 20, but the resonance for carbon A appears at δ *ca.* 15, and is

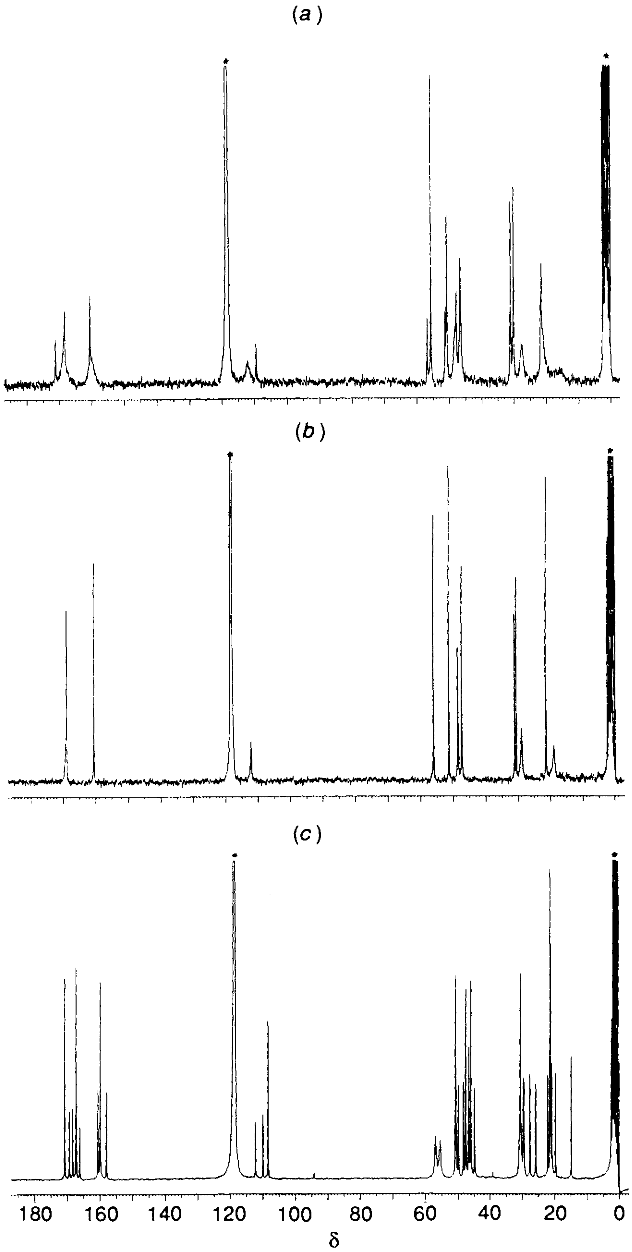


Fig. 1 Carbon-13 NMR spectrum of complex **1** in CD_3CN solution: at 298 (*a*), 353 (*b*) and 238 K (*c*), * indicates solvent peaks

broadened appreciably. This has been ascribed to a steric compression effect, imposed by the R group when in the 'lid-on' position.

Based upon these chemical shift criteria, the stronger peaks observed in the ^{13}C NMR spectrum of complex **1**, in $(CD_3)_2SO$ solution, were completely assignable as belonging to the 'lid-off'/'lid-off' isomer of the complex (*i.e.*, the 'lid-off' conformation is found at both bridgehead nitrogen atoms of the molecule. Similar nomenclature is used in the remainder of this discussion to describe the various conformers). Because of the weak signal at δ 14.5, and because of the loss of the plane of symmetry of the molecule, as evidenced by doubling of the number of peaks, the set of weaker peaks were assigned to the presence of a 'lid-on'/'lid-off' conformer (Table 2). At 373 K, the two conformers readily interconvert by rotation about a C–N bond, leading to the averaged set of signals which is observed.

Analogous behaviour has been reported in the literature for complexes with $(CH_2)_9$ and $(CH_2)_{10}$ bridges.[14] For these molecules, the two bridgehead nitrogen atoms of each molecule behave independently so a mixture of species is observed: for example, with the $(CH_2)_9$ bridge, a mixture of 'lid-off'/'lid-off' and 'lid-off'/'lid-on' species is found, as observed in the present case for **1**.

The appearance of the ^{13}C NMR spectrum of **1** proved to be solvent dependent. When run in CD_3CN solution, the spectrum was basically similar to that in $(CD_3)_2SO$ solution but showed a large increase in intensity and broadness of the set of peaks assigned to the 'lid-on'/'lid-off' isomer. At room temperature, rather than each carbon atom having a separate signal, pairs of carbon atoms gave a single broad signal, strongly indicative of an exchange process involving the 'lid-on'/'lid-off' isomer. In some cases, these broad signals overlapped with the signals of the 'lid-off'/'lid-off' isomer [Fig. 1(*a*)]. Heating of the sample to 353 K resulted in the appearance of a single set of sharp peaks with an averaged value of chemical shift, consistent with rapid exchange between the two conformers at this elevated temperature [Fig. 1(*b*)]. Conversely, cooling the sample to 238 K resulted in the appearance of two sets of sharp signals, assignable to the 'lid-off'/'lid-off' and 'lid-on'/'lid-off' isomers [Fig. 1(*c*)]. The latter displayed separate peaks for almost every carbon atom in the molecule, consistent with the absence of a plane of symmetry in this isomer. The spectrum was in fact very similar to the room-temperature spectrum of **1** in $(CD_3)_2SO$ solution, except that the intensity of the 'lid-on'/'lid-off' species was much greater in CD_3CN solution.

The nature of the two fluxional processes was of interest. The low-temperature process, involving the 'lid-on'/'lid-off' conformer, did not appear to be due to exchange with either the 'lid-on'/'lid-on' conformer, since only one signal is observed at δ *ca.* 15 in the low-temperature spectrum, or with the 'lid-off'/'lid-off' species, the peaks of which remain relatively sharp at 298 K. This low-temperature exchange is ascribed to a process which transforms the 'lid-on'/'lid-off' species into the 'lid-off'/'lid-on'; a kind of self exchange, arising from concerted rotation about the two C–N bonds at the bridgeheads. This leads to the observed averaging of the mixed conformer signals.

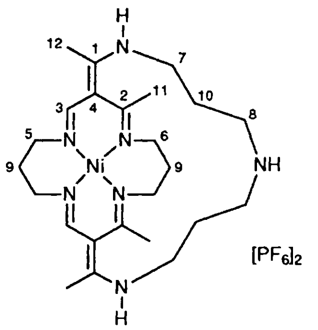
At higher temperatures, the two mixed species are able to interconvert with the 'lid-off'/'lid-off' isomer, resulting in the second averaging effect that is observed in the ^{13}C NMR spectra.

The very severe broadening of the ^{1}H NMR spectrum of **2** in CD_3CN solution is not ascribed to related exchange processes, but rather to the ability of the tertiary nitrogen atom of the bridge to bind to the metal centre. This resulted in the production of some paramagnetic complex in solution. The increase in the relaxation rate of the ^{1}H nuclei, induced by the presence of the paramagnetic ion, resulted in the broadening of the signals.

This difference in behaviour of complexes **1** and **2** arises due to the presence of the electron donating CH_3 group on the bridge nitrogen of **2**, improving its σ-donor properties relative to the N atom of **1**, and therefore leading to a stronger interaction with the metal ion. The presence of a paramagnetic species in a solution of **2** was confirmed from the ESR spectrum in CH_2Cl_2 solution. A broad, ill defined signal was observed with a *g* value *ca.* 2.2. This is similar to literature data for six-co-ordinate Ni^{2+},[16] implying that acetonitrile binds *trans* to the tertiary amine. The paramagnetism of **2** was also shown by measuring the magnetic susceptibility of a solution using Evans method.[17]

The basic properties of the central bridge nitrogen atom of **1** have been noted above and its reactivity as a nucleophile was established by treating a solution of **1** in dichloromethane with 4-vinylbenzoyl chloride or 4-chlorobenzoyl chloride, in the presence of triethylamine. This resulted in the formation of the corresponding tertiary amide derivatives, $[NiL^3][PF_6]_2$ **3** and $[NiL^4][PF_6]_2$ **4**, which were readily characterised from their ^{1}H NMR spectra. Other spectroscopic data are included in Table 1. The ability to functionalise in this position is useful since it gives the potential of binding the complex into a polymer, for example *via* copolymerisation of the vinyl group of **3**.

Table 2 Carbon-13 NMR data for complex **1**



Isomer	Solvent	T/K	C^1	C^2	C^3	C^4	C^5	C^6	C^7	C^8	C^9	C^{10}	C^{11}	C^{12}
Averaged	$(CD_3)_2SO$	403	168.2	166.1	157.7	109.0	53.8	49.2	44.7	44.4	28.6	26.3	19.4	18.1
'Lid-off'/'lid off'	$(CD_3)_2SO$	298	170.2	166.0	159.2	107.7	55.3	49.9	46.3	45.6	29.7	29.2	20.7	20.5
'Lid-off'/'lid on'	$(CD_3)_2SO$	298	168.4	*a*	160.0	111.7	54.1	49.5	47.5	44.0	*a*	27.4	21.5	19.5
			167.0	*a*	157.6	109.4	*a*	*a*	*a*	*a*	*a*	25.3	20.1	14.6
Averaged	CD_3CN	353	*a*	169.0	160.6	112.2	56.2	51.4	48.7	47.5	31.2, 30.7	29.0	21.5	19.1
'Lid-off'/'lid off'	CD_3CN	298	171.1	168.2	160.5	109.5	55.8	50.8	48.0	46.7	31.1, 30.6	27.7	21.7	21.5
'Lid-off'/'lid on'[b]			*a*	168.0	160.0	112.0	56.8	51.3	48.1	*a*	31.4, 30.7	*a*	21.0	17.0
'Lid-off'/'lid off'	CD_3CN	238	170.6	167.2	159.8	108.3	55.4	50.8	46.6	45.9	30.6, 29.6	29.4	21.4	21.2
'Lid-off'/'lid on'			169.2	167.0	160.5	112.1	56.9	50.6	48.3	47.6	*a*, *a*	27.6	20.8	19.7
			168.2	166.0	157.9	109.9	*a*	49.9	47.6	44.8	*a*, *a*	25.8	22.0	14.9

[a] Resonance obscured. [b] Fluxional, all peaks broadened.

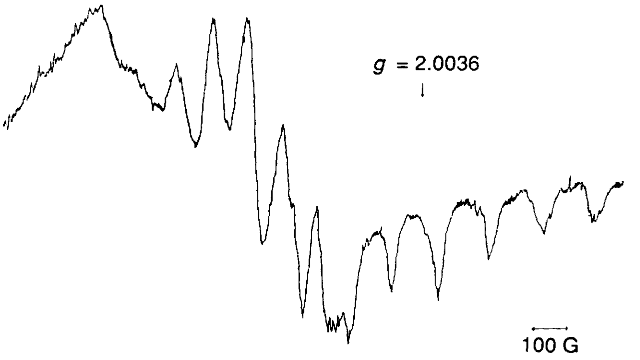


Fig. 2 The ESR spectrum of complex **5** in frozen CH_2Cl_2 solution at 153 K

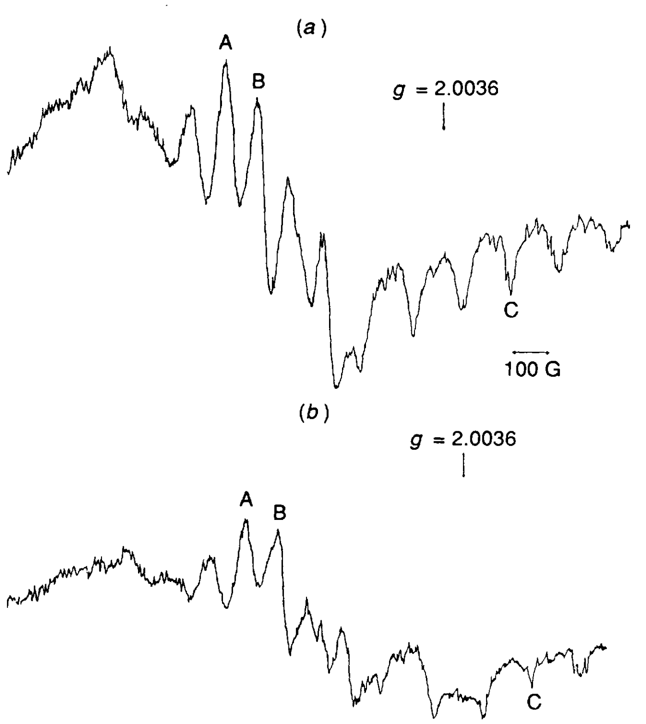


Fig. 3 The ESR spectrum of complex **5** as a function of concentration; (*a*) 5.15×10^{-3} mol dm^{-3}, (*b*) 1.1×10^{-3} mol dm^{-3}, in frozen CH_2Cl_2 solution at 153 K

Cobalt(II) *Complexes*.—The macrocyclic ligand of **1** was liberated from the nickel(II) complex using the literature procedure for ligands of a similar type.[18] The cobalt(II) complex, $[CoL^1][PF_6]_2$ **5**, was prepared by addition of stoichiometric amounts of the metal-free ligand, cobalt(II) acetate tetrahydrate and sodium acetate to a Schlenk tube, evacuation and distillation of a small quantity of dry methanol into the tube. The mixture was stirred at room temperature until an orange solution formed, whereupon the methanol was immediately removed *in vacuo*. This new method of preparation for a cobalt(II) complex was necessary because, if the usual literature procedure[19] was followed, using methanol at reflux as solvent, the reaction solution rapidly turned dark green, indicative of the occurrence of a rearrangement reaction of the ligand, producing the so-called 'half-clathro, half-cyclidene' product. Similar species have been reported previously[20] and arise from deprotonation of a bridgehead nitrogen, followed by its co-ordination to the metal ion, accompanied by oxidation of Co^{II} to Co^{III}. In this work, keeping the solvent at room temperature or below prevented this reaction and the desired product was isolated as an orange solid, similar in properties to other cobalt(II) complexes of cyclidene ligands.

The ESR spectrum of **5**, run under strictly anaerobic conditions as a frozen dichloromethane glass at 153 K, was not typical of a four-co-ordinate, square-planar cobalt(II) system (Fig. 2). Comparison with ESR spectra reported in the literature indicated that the spectrum of **5** strongly resembled that of [5,10,15,20-tetra(*p*-methoxyphenyl)porphyrinato]cobalt(II) in the presence of the sterically hindered Lewis base, acridine.[21] Thus the ESR spectrum of **5** indicates that the secondary amine of the bridge is capable of binding to Co^{II}, generating, at least in part, a five-co-ordinate complex. This co-ordination could be inter- or intra-molecular in origin. The appearance of the ESR

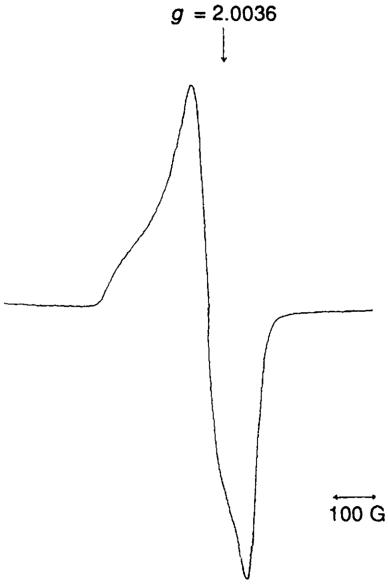


Fig. 4 The ESR spectrum of the dioxygen adduct of complex **5** in frozen CH_2Cl_2 solution at 153 K

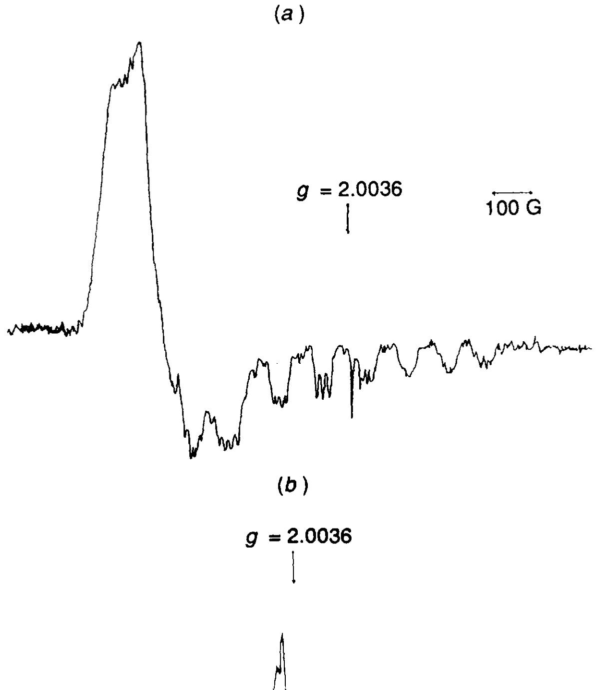


Fig. 5 The ESR spectrum of complex **5** in the presence of pyridine; (*a*) no O_2, (*b*) + O_2. Solvent CH_2Cl_2, 153 K

spectrum of **5** proved to be concentration dependent: reducing the concentration from 5.15×10^{-3} to 1.1×10^{-3} mol dm^{-3} caused a change in the relative areas under certain peaks (Fig. 3). For example, the peaks labelled A, B and C in the more concentrated solution displayed the following relative integrated intensities: A:B = 1:1, A:C = 2.4:1, B:C = 2.4:1. In the more dilute solution the ratios were: A:B = 1.1:1, A:C = 5.3:1, B:C = 4.7:1. Since the ratio of A to B is approximately constant, these peaks are assigned to the same species. Clearly the species responsible for peak C is dramatically reduced in concentration in the more dilute solution.

From this result, the observed ESR spectrum of **5** is assigned as consisting of a mixture of both four- and five-co-ordinate complexes, with the five-co-ordinate species arising from intermolecular association (Table 3). Because of the hindered nature of the Lewis base, this intermolecular association is not complete, even at the higher concentration. Dilution of the sample disfavours intermolecular association and the relative concentation of the four-co-ordinate species increases.

Reaction of complex **5**, in dichloromethane solution, with dioxygen produced a species whose ESR spectrum was typical of a six-co-ordinate dioxygen adduct of Co^{II}, usually formulated as a $Co^{III}{-}O_2^-$ species (Fig. 4).[22] Notably dioxygen adduct formation appeared complete under these conditions. The adduct was relatively stable to autoxidation, since the sample could be stored at 298 K for several minutes without any loss of ESR signal intensity. This is consistent with the O_2 molecule binding *within* the protected cavity of the macrocycle, rather than outside. This observation also favours inter- rather than intra-molecular co-ordination of the secondary nitrogen atom, since intramolecular co-ordination of the amine would block the O_2 binding site inside the cavity.

Addition of pyridine to an anaerobic solution of **5** produced a species with an ESR spectrum typical of a five-co-ordinate cobalt(II) complex (Fig. 5, Table 3). This suggested that the sterically unhindered pyridine competes successfully with the bridge nitrogen atom for the unprotected cobalt(II) binding site, forming exclusively the five-co-ordinate, mono(pyridine) complex. This species also underwent reversible binding of dioxygen, producing adducts of reasonable stability to autoxidation.

Experimental

All materials were reagent grade and were used as received. Solvents were purified and dried using standard methods. The ^1H and ^{13}C NMR spectra were run on a Bruker WP200 spectrometer, operating at 200.133 (^1H) or 50.323 MHz (^{13}C), or a Bruker WH400, operating at 400.150 (^1H) or 100.62 MHz (^{13}C). Chemical shifts are reported with respect to an external tetramethylsilane reference (positive to low field). The ESR spectra were recorded as frozen solutions, using a JEOL JES-PE spectrometer fitted with a variable-temperature unit, operating in the X band at *ca.* 9.22 GHz, with samples referenced to external diphenylpicrylhydrazyl (dpph), infrared spectra, as Nujol mulls, on Perkin Elmer 983 or 580 spectrophotometers, electronic spectra on a Shimadzu UV-160 spectrophotometer.

The solutions of the cobalt(II) complex **5** for spectroscopic analysis were prepared under N_2, using a Miller–Howe inert-atmosphere glove-box, equipped with scavenging trains for both O_2 and H_2O. Oxygenation of the cobalt(II) complex was carried out by bubbling O_2 at atmospheric pressure through solutions of the complex, generally at temperatures below 273 K.

Preparation of the Complexes.—Nickel(II) *complexes.* [3,11-Bis(1-methoxyethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-κ^4*N*]nickel(II) bis(hexafluorophosphate), **6**, was prepared by the literature procedure.[11]

(2,12,14,20-*Tetramethyl*-3,7,11,15,19,22,26-*heptaazabicyclo*[11.7.7]*heptacosa*-1,12,14,19,21,26-*hexaene*-κ^{4}N^{15},N^{19},N^{22},N^{26})*nickel*(II) *bis*(*hexafluorophosphate*) **1** *and* (2,7,12,14,20-*pentamethyl*-3,7,11,15,19,22,26-*heptaazabicyclo*[11.7.7]*heptacosa*-1,12,14,19,21,26-*hexaene*-κ^{4}N^{15},N^{19},N^{22},N^{26})*nickel*(II) *bis*-

Table 3 ESR data for cobalt(II) complex **5** under various conditions[a]

Added ligand	$g_{\perp}(A_{\perp}^{\mathrm{Co}})^{b}$	$g_{\parallel}(A_{\parallel}^{\mathrm{Co}})^{b}$	Assignment
None	2.520	2.016 (124)	Five-co-ordinate
	2.310 (80)	*d*	Four-co-ordinate
O_2	2.003^{c}	2.110^{c}	O_2 Adduct
Pyridine (py)	2.327 (17)	2.009 (108)	Five-co-ordinate py adduct
Pyridine, O_2	1.989 (15)	2.082 (18)	Six-co-ordinate py, O_2 adduct

[a] In CH_2Cl_2 solution, 153 K. [b] Nuclear hyperfine coupling constant, in G (= 10^{-4} T). [c] Coupling not resolved. [d] Signal obscured.

(*hexafluorophosphate*) **2**. These complexes were prepared by the same procedure. Details are given for complex **1**. A solution of complex **6** (1.0 g, 1.42 × 10^{-3} mol) in MeCN (100 cm^3) and a solution of 1,7-diamino-4-azaheptane (0.2 cm^3, 1.43 × 10^{-3} mol) in MeCN (100 cm^3) were added simultaneously and dropwise at the same rate to a stirred volume of MeCN (300 cm^3) at reflux, under a blanket of nitrogen. Addition was complete after 2 h whereupon the volume of the reaction mixture was reduced to approximately 10 cm^3 and the solution was chromatographed on a column of neutral alumina, using MeCN–ethanol (50:50 v/v) as eluent. The fast moving yellow band was collected and the solvent removed to yield the product as a yellow powder (0.72 g, 65%). ^{1}H NMR spectrum [200 MHz, $(CD_3)_2SO$, 403 K]: δ 7.57 (2 H, s), 6.3 (2 H, br s), 3.9 (1 H, q), 3.6–3.1 (11 H, m), 2.95–2.8 (5 H, m), 2.40 (6 H, s), 2.20 (4 H, m), 2.05 (6 H, s) and 1.8–1.4 (4 H, m) (Found: C, 36.9; H, 5.5; N, 12.4. $C_{24}H_{41}F_{12}N_7NiP_2$ requires C, 37.1; H, 5.3; N, 12.6%). $[Ni(HL^1)][PF_6]_3$ (Found: C, 33.15; H, 4.95; N, 10.05. $C_{24}H_{42}F_{18}N_7NiP_3$ requires C, 33.1; H, 4.9; N, 10.0%). Complex **2** (Found: C, 38.0; H, 5.5; N, 12.1. $C_{25}H_{43}F_{12}N_7NiP_2$ requires C, 38.0; H, 5.4; N, 12.4%).

{2,12,14,20-*Tetramethyl*-7-(4-*vinylbenzoyl*)-3,7,11,15,19,22,26-*heptaazabicyclo*[11.7.7]*heptacosa*-1,12,14,19,21,26-*hexaene*- κ^4-N^{15},N^{19},N^{22},N^{26}}*nickel*(II)*bis*(*hexafluorophosphate*) **3** *and* {7-(4-*chlorobenzoyl*)-2,12,14,20-*tetramethyl*-3,7,11,15,19,22,26-*heptaazabicyclo*[11.7.7]*heptacosa*-1,12,14,19,21,26-*hexaene*-κ^4-N^{15},N^{19},N^{22},N^{26}}*nickel*(II) *bis*(*hexafluorophosphate*) **4**. These complexes were prepared by the same procedure. Details are given only for **3**. Complex **1** (0.1 g, 1.3 × 10^{-4} mol) was dissolved in the minimum amount of MeCN and CH_2Cl_2 was added to take the total volume of the solution to 50 cm^3 and to this was added a solution of 4-vinylbenzoyl chloride (0.025 g, 1.5 × 10^{-4} mol) and triethylamine (0.09 g, 7.5 × 10^{-4} mol) in CH_2Cl_2 (20 cm^3). After stirring for 90 min, the mixture was washed with water (× 3), the organic layer dried over Na_2SO_4 and the volume reduced *in vacuo*. The residue was chromatographed on a column of neutral alumina using as eluent CH_2Cl_2–acetone (60:40) (Yield, 0.01 g, 8%). ^{1}H NMR spectra (200 MHz, CD_3CN): **3**, δ 7.50 (2 H, s), 7.40 (4 H, AB q), 6.82 (1 H, dd), 5.90 (1 H, d), 5.35 (1 H, d), 3.95 (1 H, q), 3.6–3.0 (16 H, m), 2.90 (2 H, m), 2.20 (14 H, m), 1.80 (1 H, m) and 1.60 (2 H, m); **4**, δ 7.50 (2 H, s), 7.40 (4 H, AB q), 3.95 (1 H, q), 3.55 (2 H, m), 3.5–3.0 (14 H, m), 2.90 (2 H, m), 2.4–2.1 (14 H, m), 1.90 (2 H, m) and 1.60 (1 H, m) (Found: C, 40.8; H, 5.0; N, 8.9. $C_{33}H_{47}F_{12}N_7NiOP_2\cdot(CH_3)_2CO.\ 1.5\,CH_2Cl_2$) **3**$\cdot Me_2CO\cdot 1.5CH_2Cl_2$ requires C, 41.2; H, 5.1; N, 8.9%. Found: H, 4.3; N, 9.2. $C_{31}H_{44}ClF_{12}N_7NiOP_2\cdot 1.25CH_2Cl_2$ **4**$\cdot 1.25CH_2Cl_2$ requires H, 4.6; N, 9.6%).

Cobalt(II) *Complex*.—(2,12,14,20-*Tetramethyl*-3,7,11,15,19,22,26-*heptaazabicyclo*[11.7.7]*heptacosa*-1,12,14,19,21,26-*hexaene*-κ^{4}N^{15},N^{19},N^{22},N^{26})*cobalt*(II) *bis*(*hexafluorophosphate*) **5**. To a Schlenk tube were added $[H_3L^1][PF_6]_3$ (0.1 g, 1.15 × 10^{-4} mol), cobalt(II) acetate tetrahydrate (0.028 g, 1.15 × 10^{-4} mol) and sodium acetate (0.028 g, 3.45 × 10^{-4} mol). The tube was evacuated and methanol (2 cm^3) added by vacuum distillation. The tube was slowly warmed to room temperature, during which time the reactants dissolved and the solution became orange. The solvent was immediately removed by vacuum distillation and the residue dissolved in CH_2Cl_2 and filtered. The product was isolated from the resulting orange solution.

Acknowledgements

We thank Stephen Graham for carrying out some preliminary experiments, Heather Harvey for some useful discussion, Dr. O. Howarth of the SERC NMR Service for the spectra at high field, and Dr. A. S. F. Boyd for help in obtaining the other NMR spectra. We are grateful to the SERC and British Petroleum plc for the provision of a CASE award (to E. L. S.).

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Received 15*th July* 1992; *Paper* 2/03778E