Polymer-supported Cobalt(II) Tetraaza Macrocyclic Complexes and their Reaction with Dioxygen†

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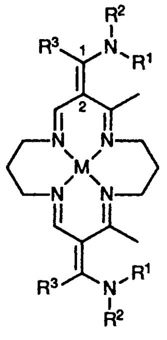
Four cobalt(II) tetraaza macrocyclic complexes of the 'lacunar cyclidene' type have been prepared, including two new, unbridged, examples. The reactions of these complexes with oxygen have been investigated, either in solution, in a mixture of acetonitrile–pyridine (4:1 v/v), or when dispersed in the matrix of a copolymer containing 4-vinylpyridine (vpy), dissolved in dichloromethane. Three different copolymers have been used as supporting matrices (vpy content in parentheses); vpy–styrene (6.2), –methyl methacrylate (5.2) and –butyl methacrylate (15.2%). The oxygenation reactions have been studied both by ESR spectroscopy of frozen solutions and by electronic spectroscopy at or near room temperature. The presence of the polymeric supports has a marked influence on both the formation of Co–O_2 adducts and their stability with respect to autoxidation. The polymer-supported 'copoly complex' oxygen adducts have much greater lifetimes than those of the O_2 dioxygen adducts of the same complexes 'free' in solution. The results are discussed in terms of the complex structure, polymer type and the temperature of the reaction.

One of the principal themes of bioinorganic chemistry is the synthesis of metal complexes which have the ability to mimic the function of metalloproteins.[1] In recent years a great deal of effort has been directed toward the study of complexes which mimic the function of the naturally occurring dioxygen-transporting proteins. Currently a large number of complexes containing Fe^{II}, Co^{II}, Mn^{II} or Cu^{I} are known to undergo reversible co-ordination of the dioxygen ligand in the solution phase.[2,3]

In general, however, solution-based carriers of dioxygen display limited lifetimes as a result of two well understood decomposition processes: (*a*) oxidative dimerization of metal centres *via* a μ-peroxo bridge, and (*b*) proton-promoted oxidation of the metal centre.[4] A number of strategies have been developed to inhibit these processes. (*i*) Model complexes have been designed with a sterically protected cavity around one co-ordination site of the metal. The O_2 can enter the cavity and bind to the metal ion but the steric bulk of the groups defining the cavity prevents the close approach of two metal centres, inhibiting formation of the μ-peroxo-bridged species. Classic examples of this approach are the 'picket fence'[5] and 'capped'[6] porphyrin and the 'lacunar cyclidene' tetraaza macrocyclic complexes.[7] (*ii*) Use of anhydrous media. This limits the availability of a proton source to the bound O_2. (*iii*) Studies at low temperature, reducing the rate of the decomposition processes.[8] By utilizing one or more of these strategies it has proved possible to demonstrate the reversible interaction of dioxygen with a large number of synthetic complexes and significant progress continues to be reported.[9]

Particularly noteworthy is the family of cobalt(II) 'lacunar cyclidene' tetraaza macrocyclic complexes reported by Stevens and Busch.[10] In the presence of an excess of a co-ordinating ligand such as pyridine or 1-methylimidazole, which binds to the unprotected co-ordination site of the metal ion, these complexes (Structure I) form remarkably stable dioxygen adducts, in the solution phase. The synthetic routes to these species allow for a wide variation in the type of group that can be introduced into the superstructure of the molecule and the effect of such structural variation on the dioxygen binding ability of the cobalt(II) ion has been well documented in an elegant series of papers.[11]



I

M				
Ni^{2+}	Co^{2+}	R^1	R^2	R^3
1	**7**	$\frac{1}{2}(CH_2)_6$	Me	Me
2	**8**	Me	Me	Me
3	**9**	CH_2Ph	Me	Me
4	**10**	CH_2Ph	Me	Ph
5		CH_2Ph	H	Me
6		CH_2Ph	H	Ph

Incorporation of dioxygen-reactive complexes within the matrices of synthetic polymers has also been shown to inhibit the decomposition pathways.[12] With a relatively low concentration of complex, the bulk of the polymer chains keeps the metal centres far enough apart to prevent dimerization and, by selecting a relatively hydrophobic polymer support, the concentration of water at the dioxygen binding site is limited, inhibiting the proton-promoted oxidation route. Indeed Wang[13] used a synthetic polymer support when he was the first to demonstrate the *in vitro* reversible binding of O_2 to an iron(II) complex. He embedded the complex of the dimethyl ester of protoporphyrin IX (3,7,12,17-tetramethyl-8,13-divinylporphyrin-2,18-dipropanoic acid) in a polystyrene matrix which contained 1-phenylethylimidazole, and showed that it could be reversibly oxygenated.

Four methods have been studied for the incorporation of

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† *Non-SI unit employed:* G = 10^{-4} T.

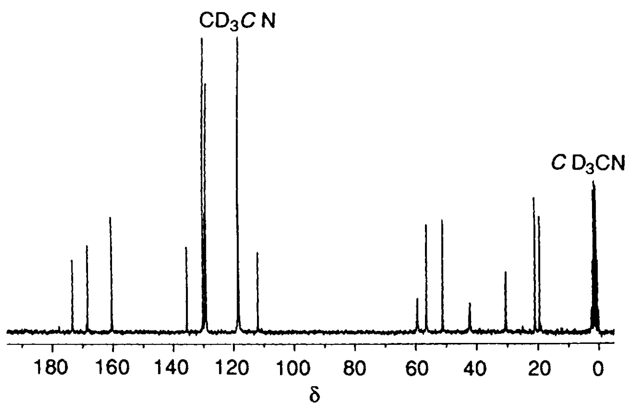

Fig. 1 The ^{13}C NMR spectrum of complex **3**

complexes into polymer supports: (1) simple dispersion of the complex; (2) binding of the complex *via* a co-ordinate bond from a polymer bound ligand; (3) covalent attachment by reaction of a functionalized complex with a functionalized copolymer and (4) copolymerization of a complex bearing a polymerizable group with selected comonomers.[14]

There has been substantial recent interest in the study of cobalt(II) complex–polymer systems from the point of view of producing a permselective membrane for the separation of O_2 from the atmosphere, under ambient conditions. These studies have involved the incorporation methods (1)–(3) and have shown that the resultant polymer–complex systems do react with O_2 in a reversible manner and produce enhanced O_2/N_2 selectivity for the membranes.[15–17]

We are interested in general in the incorporation of macrocyclic complexes within the matrices of polymers and have recently reported the inclusion of some nickel(II) complexes into styrene and methyl methacrylate polymers, utilizing both the copolymerization method[18] and the reaction of functionalized macrocycles with preformed functionalized polymers.[19] In this paper we report on the binding of cobalt(II) complexes, of the 'lacunar cyclidene' type, into polymer matrices *via* co-ordinate bond formation to a polymer-bound ligand. The polymers are copolymers of 4-vinylpyridine with either styrene, methyl methacrylate or butyl methacrylate. The pyridine function serves not only to bind the complex into the polymer but also to provide the necessary axial ligand to allow dioxygen adduct formation to take place.[20] We report on both the formation of the five-co-ordinate cobalt(II) 'copoly complexes' and upon their reaction with dioxygen.

Results and Discussion

Preparation and Characterization of the Cobalt Complexes.—The lacunar cyclidene ligands were prepared as nickel(II) complexes by modifications of the literature procedures of Busch and co-workers.[21] Complexes **1**–**4** were selected for study to provide a comparison between the behaviour of polymer-supported bridged and unbridged species, of varying steric bulk.

It was decided to study complexes containing tertiary substituted amine groups as literature work suggests that cobalt(II) complexes of the cyclidene type, substituted with secondary amino groups, may exhibit internal chelation of the amine nitrogen atom to the metal ion and this would compete with the co-ordination of the polymer-bound ligand to the metal centre, thereby inhibiting the binding of the cobalt(II) complex to the polymer support.[22] Two of the chosen species, **1** and **2**, have previously been reported. The new complexes, **3** and **4**, were prepared readily by deprotonation of the known complexes **5** and **6**, followed by methylation using the potent reagent methyl trifluoromethanesulfonate. The ligands were formed initially as nickel(II) complexes for two reasons. First, the nickel(II) complexes do not react with dioxygen and are thus more easily handled and secondly the products are diamagnetic and are readily characterized by NMR spectroscopy.

The ^{13}C NMR spectroscopic data for complexes **1** and **2** were in close agreement with those published in the literature. The spectrum of complex **3** is shown in Fig. 1. It was readily assigned with the aid of the results from a DEPT (distortionless enhancement by polarization transfer) NMR experiment and by comparison with data for the literature compounds. In common with other compounds of this type, the NMR spectrum indicated that the molecule is fluxional. The resonances due to the N–CH_3 and N–CH_2– carbon atoms were broadened and this was ascribed to rotation of the –NMe(CH_2Ph) group about the bond connecting the amine nitrogen atom to carbon atom 1. It is noteworthy that the immediate precursor to complex **3**, the species **5**, displayed even more pronounced effects of fluxionality in its NMR spectrum, with several resonances being broadened. In this case the pattern of broadening implied that a second rotation was occurring, about the bond C(1)–C(2). We have recently reported the same type of behaviour for a family of similar complexes containing the secondary amine functional grouping.[18] The ^{1}H NMR spectra of the complexes also provide a useful method of characterization, although absolute assignment of the spectra is more difficult due to overlapping and broadening of individual resonances.

The infrared spectra of the nickel(II) complexes were unremarkable but indicated that the expected functional groups were present. Of particular interest were bands in the region 1500–1600 cm^{-1}, assigned to ν(C=N) and ν(C=C). For example, complex **3** had bands at 1601, 1550 and 1535 cm^{-1}.

The electronic spectra of the yellow-orange nickel(II) complexes displayed two bands at λ_{max} *ca.* 395 and 365 nm. This is in keeping with the results for other complexes containing square-planar nickel(II) N_4 co-ordination.[23]

The cobalt(II) complexes, **7**–**10**, were prepared readily using the literature procedure.[10] They were characterized initially by their infrared spectra. As expected these were very similar to those of the corresponding nickel(II) complexes. For example, complex **9** had bands at 1610 and 1548 cm^{-1}, assigned to ν(C=N) or ν(C=C). The presence of the cobalt(II) ion was confirmed by both ESR and electronic spectroscopies and this is further discussed below.

Preparation and Characterization of the 4-Vinylpyridine Copolymers.—There have been a number of reports of the use of 4-vinylpyridine as a comonomer in polymerization reactions and the reactivity of the vinyl group has been well established. In this work, comonomers were selected such that the resulting copolymers would be in the form of amorphous glasses at room temperature. The comonomers which were selected were styrene, methyl methacrylate and butyl methacrylate and free-radical polymerization reactions were carried out using comonomer mixtures containing 10% molar ratios of 4-vinylpyridine. The resulting copolymers were characterized by infrared and NMR spectroscopies. Quantitative experiments using the latter technique allowed determination of the 4-vinylpyridine (vpy) content of the copolymers: for vpy–styrene, 6.2; vpy–methyl methacrylate, 5.2; vpy–butyl methacrylate, 15.2%. Typical molecular-weight distribution data and glass-transition temperatures for the three copolymers are listed in Table 1.

Polymer-supported Cobalt(II) *Complexes and their Reaction with Dioxygen.*—The solubility properties of the copolymers and the complexes were incompatible and the 'copoly complexes' were prepared by mixing an acetone solution of the complex and a dichloromethane solution of the copolymer and then removing all of the volatile material under high vacuum. In a typical experiment, 1 g of the copolymer and 0.35 g of complex **8** were used, giving a pyridine:Co^{II} of *ca.* 3:2. Although the concentration of pyridine groups was not greatly in excess of that of the cobalt(II) ions, results from ESR spectroscopy (see

Table 1 Molecular-weight distribution and glass-transition data for copolymers

Copolymer	vpy[a] (%)	T_g[b]/°C	Molecular-weight distribution[c] M_N	M_W	M_Z	P_{D_i}[d]
vpy–styrene	6.2	113	71 400	193 000	400 000	2.7
vpy–methyl methacrylate	5.2	96	78 000	120 000	156 000	1.5
vpy–butyl methacrylate	15.2	48	*e*	*e*	*e*	

M_N = Number average molecular weight, M_W = weight average molecular weight and M_Z = *z*-average molecular weight.

[a] Determined by NMR spectroscopy. [b] Determined by differential scanning calorimetry. [c] Determined by gel phase chromatography. [d] Polydispersity index. [e] Very-high-molecular-weight sample.

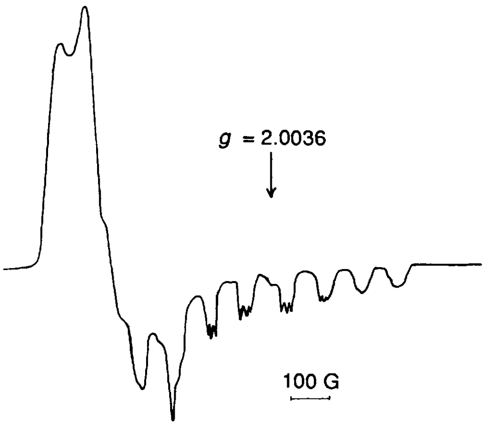

Fig. 2 The ESR spectrum of complex **8** in vpy–styrene copolymer, in frozen dichloromethane solution at 77 K

Fig. 3 The ESR spectrum of the oxygen adduct of complex **8** in vpy–styrene copolymer, in frozen dichloromethane solution at 77 K

below) suggested that all of the Co^{II} was present as the five-co-ordinate, monopyridine complex, there being no evidence for the signal due to the four-co-ordinate complex which has been observed in other work.[14] The resulting orange-brown polymers were soluble in dichloromethane. Reprecipitation of the 'copoly complexes' from methanol resulted in isolation of a white solid (the unchanged copolymer) with the complexes remaining in the methanol solution.

The effect of the copolymers on the behaviour of the cobalt(II) complexes can be determined by contrasting the properties of the same complexes in solution (termed here the 'free' complexes) in acetone–pyridine (4:1 v/v) with the properties of the 'copoly complexes' in dichloromethane solution. The difference in polarity of the solvent media is likely to affect the systems is two ways: (*a*) since it is widely accepted that $Co–O_2$ adducts can be formulated as $Co^{III}–O_2^-$ species, adduct formation will be favoured in the more polar medium, so the 'free' complexes will have higher dioxygen binding constants than the 'copoly complexes'; (*b*) decomposition of the dioxygen adducts produces cobalt species of higher charge, so it is likely that the rate of decomposition will be somewhat reduced in the less-polar medium. Since the 'lacunar cyclidene' complexes are generally insoluble in media of low polarity, it has not proved possible to examine this possibility directly.

ESR Results.—The ESR spectra of the unoxygenated complexes **7–10**, in a frozen solution of acetone containing 20% by volume of pyridine (the 'free' complexes), were very similar to those reported in the literature for similar complexes where 1-methylimidazole was the axially co-ordinated ligand. They were characteristic of tetragonal pyramidal, low-spin Co^{II}, with $g_\perp$ *ca.* 2.3 and $g_\parallel$ *ca.* 2.0 (Table 2).[2] The signal in the parallel direction showed hyperfine splitting to both the cobalt ion (^{59}Co, $I = \frac{7}{2}$) and the nitrogen atom of the axial pyridine ligand (^{14}N, $I = 1$). The presence of the superhyperfine splitting to the nitrogen atom has been interpreted as indicating that the unpaired electron resides in the d_{z^2} orbital of the cobalt ion. This has been reported as a prerequisite to formation of the cobalt(II)–dioxygen bond.[20]

The ESR spectra of the polymer–complex mixtures (the 'copoly complexes') were determined using frozen dichloromethane solutions. The data are listed in Table 2 and a representative spectrum, of complex **8**, supported in the 4-vinylpyridine–styrene copolymer, is shown in Fig. 2. The results clearly showed that the complexes were five-co-ordinate and the presence of superhyperfine coupling to a single nitrogen atom indicated that the complexes were indeed supported within the copolymer structure *via* co-ordination to a pyridine nitrogen atom from the copolymer backbone as this was the only nitrogen atom with which the cobalt(II) complexes came into contact. In fact the ESR results for the 'copoly complexes' were remarkably similar to the results obtained for the 'free' complexes which implied that there was nothing unusual about the nature of the Co^{II}–N(pyridine) bonds in the polymeric media.

The ESR spectra of the oxygenated 'free' cobalt(II) complexes, oxygenated at −45 °C, and the spectra measured using frozen solutions showed the dramatic change expected for the formation of the dioxygen adducts, with large changes in both the shape of the signals and the value of the ^{59}Co hyperfine coupling constant. The data are included in Table 2. As expected the results were again virtually identical to literature reports with similar complexes where 1-methylimidazole was the axial base. Oxygenation of dichloromethane solutions of the 'copoly complexes' at −60 °C and measurement of the ESR spectra of the frozen solutions clearly indicated that six-co-ordinate oxygen adducts were formed within the matrices of the polymers. The data for the oxygen adducts of the 'copoly complexes' are included in Table 2 and a representative spectrum, for the O_2 adduct of complex **8**, supported on the 4-vinylpyridine–styrene copolymer, is shown in Fig. 3. The $Co–O_2$ adducts have spectra with $g_\perp$ *ca.* 2.0 and $g_\parallel$ *ca.* 2.08. The substantial reduction in the size of the hyperfine coupling constant to the ^{59}Co atom (from *ca.* 100 to *ca.* 20 G) has been interpreted in terms of the transfer of the unpaired electron from

Table 2 ESR data for the cobalt(II) complexes[a]

	Acetone–pyridine[b]		vpy–styrene[c]		vpy–methyl methacrylate[c]		vpy–butyl methacrylate[c]	
Complex	$g_\perp(A_\perp^{Co})$[d]	$g_\parallel(A_\parallel^{Co})$[e]	$g_\perp(A_\perp^{Co})$	$g_\parallel(A_\parallel^{Co})$	$g_\perp(A_\perp^{Co})$	$g_\parallel(A_\parallel^{Co})$	$g_\perp(A_\perp^{Co})$	$g_\parallel(A_\parallel^{Co})$
7	2.303 (15)	2.003 (101)	2.301 (15)	2.006(103)	2.299(15)	2.005(103)	2.292 (16)	2.002 (104)
	[1.999 (10)]	[2.088(20)]	[2.014 (10)]	[2.086 (18)]	[2.013 (10)]	[2.082(19)]	[1.996 (8)]	[2.079 (16)]
8	2.300 (15)	2.009 (100)	2.298 (16)	2.004 (104)	2.296(16)	2.001 (102)	2.290 (15)	2.002 (106)
	[2.018 (9)]	[2.076 (17)]	[2.020 (10)]	[2.081 (19)]	[2.018 (9)]	[2.079 (18)]	[1.994 (9)]	[2.074 (18)]
9	2.306 (15)	2.017 (102)	2.296(15)	2.002 (104)	2.296(16)	2.004 (102)	2.294 (16)	1.997 (102)
	[2.024 (10)]	[2.094 (17)]	[2.009 (10)]	[2.072 (18)]	[2.017 (10)]	[2.081 (16)]	[1.996 (10)]	[2.080 (18)]
10	2.304(15)	2.011 (101)	2.299 (15)	2.006 (105)	2.299 (16)	2.007 (105)	2.301 (15)	2.004 (104)
	[2.021 (10)]	[2.091 (18)]	[2.016 (10)]	[2.082 (18)]	[2.016 (9)]	[2.078 (17)]	[1.997 (10)]	[2.083 (20)]

[a] Using frozen solutions, at 77 K; values for oxygenated samples are given in square brackets. [b] 20% Pyridine by volume. [c] Dichloromethane as solvent. [d] Nuclear hyperfine coupling constant, in Gauss. [e] $g_\parallel$ Signals of unoxygenated samples also display nuclear superhyperfine coupling constants of *ca.* 14 G ($A_\parallel^N$).

Table 3 Estimated lifetimes of the cobalt–oxygen adducts, from ESR spectra[a]

Complex	Acetone–pyridine[b]	vpy–styrene[c]	vpy–methyl methacrylate[c]	vpy–butyl methacrylate
7	*ca.* 2 d	—	—	—
8	*ca.* 10 min	*ca.* 36 h	*ca.* 36 h	*ca.* 48 h
9	*ca.* 90 min	*ca.* 48 h	*ca.* 48 h	*ca.* 72 h
10	*ca.* 6 h	*ca.* 72 h	*ca.* 96 h	*ca.* 4 d

[a] Determined from decay of ESR signal; lifetime represents time to decay to *ca.* 10% of original intensity. [b] 20% Pyridine by volume. [c] Dichloromethane solutions.

the cobalt(II) ion to the O_2 molecule, supporting the $Co^{III}–O_2^-$ formalism for the adduct[24] although this has been challenged by Corden and Drago.[25]

In this work, the close similarity between the spectra of the solution-based complexes and the polymer-supported complexes provides clear evidence that the 'copoly complexes' can form stable dioxygen adducts, albeit at reduced temperatures. Attempts to record ESR spectra at higher temperatures, using liquid-phase samples, were unsuccessful.

Since the products of decomposition of the cobalt(II)–oxygen adducts are diamagnetic, a qualitative idea of the increased lifetime of the dioxygen adducts of the 'copoly complexes' relative to their 'free' counterparts can be gained by study of the decay of their respective ESR resonances as a function of time. The decomposition of the oxygen adducts in solution has been the subject of an intensive and detailed study, using electronic spectroscopy to monitor the reactions, and this has highlighted the extremely complex nature of the processes involved.[26] Consequently a detailed kinetic analysis was not attempted in this work, nevertheless a comparative study gives insight into the effects of varying both the structure of the complex and the nature of the copolymer.

The oxygenated ESR samples were allowed to stand at room temperature with the ESR spectra being determined at intervals, after cooling the samples to 77 K. The quoted lifetimes represent the time required for the amount of $Co–O_2$ adduct to decay to < 10% of the original concentration, as judged by the intensity of the ESR signal. In the absence of a polymeric support, the lifetime of the 'free' $Co–O_2$ adducts, as predicted from literature results, varied as a function of the structure of the complex: the bridged complex had the longest lifetime, while the unbridged complexes had lifetimes which increased as the steric bulk around the dioxygen binding site increased (Table 3). It should be noted that this steric factor may not be the only important variable in determining the autoxidative stability of the complexes. The longest-lived unbridged complex, **10**, with R^3 = Ph, by analogy with other lacunar cyclidene complexes, will have a positive shift in the position of the $Co^{II}–Co^{III}$ redox couple of *ca.* 100 mV relative to the complex with R^3 = Me, **9**. This not only reduces the affinity of the complex for O_2 but also reduces the rate of any electron-transfer contribution to the decomposition of the cobalt(II) complex.

The influence of the polymer support was clearly seen from the results of similar experiments, determined using dichloromethane solutions of the 'copoly complexes', The lifetime of the unbridged bis(NMe_2) complex, **8**, increased from *ca.* 10 min in acetone–pyridine solution to between 36 and 48 h, depending on the nature of the polymeric support. The other complexes also displayed enhanced stability with respect to autoxidation (Table 3), again with the more sterically encumbered complexes displaying longer lifetimes.

The copolymer containing butyl methacrylate produced the largest enhancement in stability with respect to decomposition of the three systems which were studied. This is ascribed to the higher pyridine content of this copolymer which ensures that essentially all of the complex is bound to the polymer as the five-co-ordinate species, limiting the amount of any mobile, four-co-ordinate complex, which would be capable of irreversibly forming a dimer when in contact with the oxygen adduct.

Electronic Spectroscopic Studies.—While the ESR spectra were very useful in characterizing the co-ordination number and redox state of the cobalt complexes at low temperature, the behaviour of the complexes at elevated temperatures was of more immediate interest. For this reason the electronic spectra of the 'copoly complexes' in dichloromethane solution, using the vpy–methyl methacrylate copolymer as the support, were determined and the results compared with those for the 'free' complexes dissolved in acetonitrile–pyridine (4:1 v/v) solution. The systems were studied both in the absence and presence of O_2 at two temperatures, 25 and 4 °C.

All four cobalt(II) complexes exhibited very similar spectra, with each complex displaying two bands in the near-UV region of the spectrum, at *ca.* 315 and 370 nm. This is in good agreement with literature data for complex **7** in aqueous solution containing 1-methylimidazole, at 6 °C.[10] The unoxygenated 'copoly complexes' displayed the same general pattern in their electronic spectra as did the 'free' complexes, except that the band at *ca.* 315 nm was reduced in intensity slightly relative to that at 370 nm [Fig. 4(——)]. The five-co-ordinate nature of the deoxy 'copoly complexes' has been confirmed by work on similar systems involving measuring ESR spectra of the polymer-supported complexes at room temperature using solid-state samples.[27]

Some significant differences in behaviour were noted for the reaction of O_2 with the 'free' and 'copoly complexes', as a function of complex structure and reaction temperature. At 25 °C exposure of the 'free' bridged complex **7** to O_2 gas brought about rapid formation of a peak in the electronic spectrum at *ca.* 350 nm, with a shoulder on the low-energy side [Fig. 4 (– – –)].

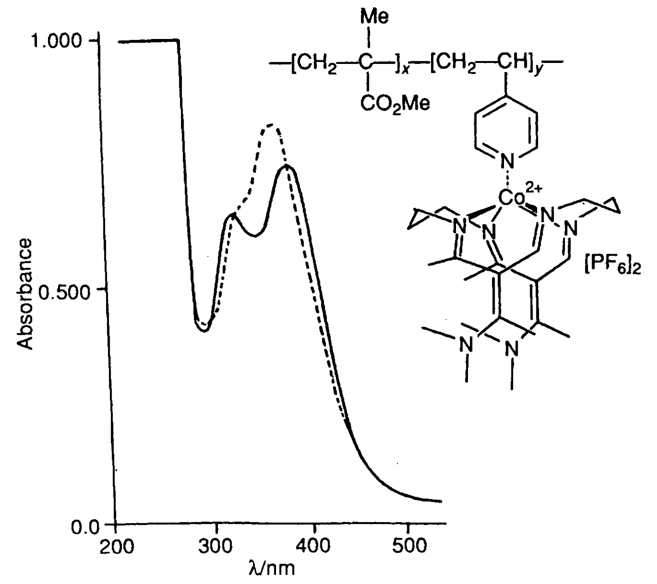

Fig. 4 Electronic spectra of complex **8** in vpy–methyl methacrylate copolymer, in solution in dichloromethane at 4 °C, in the absence (——) and in the presence (- - -) of oxygen

Table 4 Half-lives of the cobalt-oxygen adducts, from electronic spectroscopy[a]

	$t_{\frac{1}{2}}$	
Complex	Acetone–pyridine[b]	vpy–methyl methacrylate[c]
7	>6 h	>48 h
8	*ca.* 20 min	*ca.* 6 h
9	*ca.* 30 min	—
10	*ca.* 60 min	—

[a] Measured from the decay of the electronic spectrum of the dioxygen adduct at 4 °C. [b] 20% Pyridine by volume. [c] In dichloromethane solution.

The position of this peak was in excellent agreement with that reported for the oxygen adducts of cobalt(II) lacunar cyclidene complexes.[10] The complex could be cycled several times between the oxy and deoxy forms by bubbling the solution alternately with O_2 and N_2 gases for several seconds. The oxygen adduct underwent slow decomposition (estimated $t_{\frac{1}{2}}$ *ca.* 90 min). At 4 °C the same behaviour was noted except that decomposition was markedly slower (estimated $t_{\frac{1}{2}}$ *ca.* 6 h). When complex **7** was embedded in a 4-vinylpyridine–methyl methacrylate copolymer matrix it again showed reversible binding of O_2 at both temperatures, but the lifetime of the oxygen adduct was substantially larger (at 4 °C, estimated $t_{\frac{1}{2}}$ *ca.* 48 h).

The polymer support has an even greater effect on the reaction of the unbridged complexes with oxygen. At 25 °C the 'free' unbridged complexes showed no peak in the electronic spectra corresponding to formation of an oxygen adduct, there being instead rapid decomposition of the cobalt(II) complexes. In contrast, at 4 °C, the unbridged complexes did form dioxygen adducts, λ_{max} *ca.* 340 nm, which did not dissociate upon purging the solutions with N_2 gas. The dioxygen adducts of these 'free' unbridged complexes underwent fairly rapid decomposition at 4 °C, and it was observed that the rate of decomposition was inversely related to the steric bulk of the ligand surrounding the dioxygen binding site (estimated $t_{\frac{1}{2}}$ for complexes: **8**, *ca.* 20; **9**, *ca.* 30; **10**, *ca.* 60 min). As was expected from Busch's work, the unbridged materials are much less stable than the corresponding bridged complex.

Only one of the unbridged complexes, **8**, was studied as a 'copoly complex'. As was found for the 'free' complex system, at 25 °C there was no evidence from the electronic spectrum for the formation of an oxygen adduct. Again the cobalt(II) complex underwent rapid decomposition. At 4 °C the 'copoly complex' formed an oxygen adduct and in this case the equilibrium was reversed by purging the solution with N_2, suggesting that the polymer-supported complex has a substantially smaller affinity for O_2 than the same complex 'free' in solution.

Comparing results for the stability to autoxidation of the 'free' and 'copoly' complexes at 4 °C again highlighted the profound influence of the polymer. The 'free' dioxygen adduct of complex **8** has a half-life of *ca.* 20 min but the 'copoly complex' adduct had a half-life of *ca.* 6 h. The data for stability to autoxidation in the various systems are collated in Table 4.

The data from ESR and electronic spectroscopies concerning the stability of the dioxygen adducts to autoxidation do not give results that are directly comparable due to the different criteria used in determining lifetimes and half-lives and also due to the very different experimental conditions which were used, particularly with respect to cobalt(II) concentration and reaction temperature. However both spectroscopic methods give the same trends for the results and clearly show that the introduction of the complexes into a polymer matrix serves to inhibit the well known decomposition processes of dimerization and electron transfer, producing oxygen adducts with substantially greater lifetimes than those found for the same complexes in the absence of the polymer. Our studies are continuing in efforts to produce polymer-supported complexes of even greater stability with respect to autoxidation.

Conclusion

Some cobalt(II) complexes of the lacunar cyclidine type have been prepared and characterized, including some new, unbridged species. The interaction of these complexes with oxygen has been studied, both for the 'free' complexes, in solutions containing pyridine (20% v/v), and for dichloromethane solutions of the complexes supported in various copolymers of 4-vinylpyridine.

The ESR spectra of frozen solutions of both 'free' and 'copoly' complexes show that addition of O_2 to the samples transforms the spectra from those typical of five-co-ordinate, pyramidal, low-spin cobalt(II) to those characteristic of the corresponding six-co-ordinate oxygen adducts.

Under all of the experimental conditions, the bridged complex, **7**, reversibly binds O_2. The unbridged complexes do not bind O_2 at 25 °C, either 'free' or bound to the polymer support, apparently due to rapid decomposition of the cobalt(II) species. At 4 °C, both 'free' and polymer-bound unbridged complexes form dioxygen adducts. In the former case the equilibrium is not reversed by purging with N_2 but, in the latter, oxygen binding is readily reversible.

The presence of the polymer supports has a remarkable effect on the stability of the cobalt(II) complexes with respect to autoxidation. For example, the oxygen adduct of complex **8** in acetonitrile–pyridine solution has a half-life of *ca.* 20 min at 4 °C while at the same temperature the oxygen adduct of the same complex supported in a 4-vinylpyridine–methyl methacrylate copolymer has a half-life of *ca.* 6 h. This enhanced stability to autoxidation is ascribed primarily to the steric effect of the polymer, inhibiting dimerization of the cobalt complexes.

Experimental

All materials were reagent grade and were used as received. Solvents were purified and dried using standard procedures. 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). Chemical shifts are reported with respect to an external tetramethylsilane reference (positive to low field). Electronic spectra were recorded on a Philips Analytical SP1800 spectrophotometer, equipped with a thermostatted cell holder and appended temperature-control unit. Infrared spectra were recorded as Nujol mulls, using a Perkin-Elmer 580 spectrophotometer, ESR spectra 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 with respect to external diphenylpicrylhydrazyl (dpph).

The synthesis of the cobalt(II) complexes and preparation of solutions for spectroscopic work were carried out under an atmosphere of N_2, using a Miller-Howe inert-atmosphere glovebox, equipped with scavenging trains for both O_2 and H_2O.

Oxygenation of cobalt(II) samples was carried out by bubbling O_2 at atmospheric pressure through solutions of the complex. The samples for electronic spectroscopy were oxygenated at the temperature of the experiment, using a dioxygen stream presaturated in the experimental solvent. The ESR samples were oxygenated at reduced temperatures, controlled by appropriate slush-baths, usually just above the melting-point of the solvent medium.

Preparation of the Complexes.—Nickel(II) *complexes.* The following complexes were prepared according to the literature procedures:[21] (2,3,10,11,13,19-hexamethyl-3,10,14,18,21,25-hexaazabicyclo[10.7.7]hexacosa-1,11,13,18,20,25-hexaene-$\kappa^4N^{14},N^{18},N^{21},N^{25}$)nickel(II) bis(hexafluorophosphate) **1**, [3,11-bis(1-methoxyethylidene)-2,12-dimethyl-1,5,9,13-tetraazaacyclohexadeca-1,4,9,12-tetraene-κ^4N]nickel(II) bis(hexafluorophosphate) **11**, [3,11-bis(1-benzylaminoethylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-$\kappa^4N^1,N^5,N^9,N^{13}$]nickel(II) bis(hexafluorophosphate) **5** and [3,11-bis(α-benzylaminobenzylidene)-2,12-dimethyl-1,5,9,13-tetraazacyclohexadeca-1,4,9,12-tetraene-$\kappa^4N^1,N^5,N^9,N^{13}$]-nickel(II) bis(hexafluorophosphate) **6**.

[2,12-*Dimethyl*-3,11-*bis*(1-*dimethylaminoethylidene*)-1,5,9,13-*tetraazacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N^1,N^5,N^9,N^{13})-*nickel*(II) *bis*(*hexafluorophosphate*) **2**. This complex was prepared by a modification of the literature procedure.[21] To a rapidly stirred solution of complex **11** (2.0 g, 2.82 mmol) and anhydrous dimethylamine hydrochloride (0.49 g, 6 mmol) in dry acetonitrile (40 cm^3) was added triethylamine (0.84 cm^3, 6 mmol). The colour of the solution changed immediately from olive green to deep red. The mixture was stirred for 2 h at room temperature then the solvent was removed by rotary evaporation. Water (25 cm^3) was added to the oily residue and the resulting yellow-orange solid was collected and crystallized from acetonitrile–ethanol (1.5 g, 72%) (Found: C, 35.7; H, 5.1; N, 11.6; Ni, 8.2. $C_{22}H_{38}F_{12}N_6NiP_2$ requires C, 35.9; H, 5.2; N, 11.4; Ni, 8.0%).

[3,11-*Bis*(1-*benzylmethylaminoethylidene*)-2,12-*dimethyl*-1,5,-9,13-*tetraazacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N^1,N^5,N^9,N^{13}]-*nickel*(II)*bis*(*hexafluorophosphate*) **3** *and* [3,11-*bis*(α-*benzylmethylaminobenzylidene*)-2,12-*dimethyl*-1,5,9,13-*tetraazacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N^1,N^5,N^9,N^{13})*nickel*(II) *bis*(*hexafluorophosphate*) **4**. These complexes were prepared by the same procedure and details are given only for **4**. To a solution of complex **6** (2.8 g, 2.85 mmol) in dry MeCN (50 cm^3) was added a solution of KOBu^t (0.65 g, 5.8 mmol) in dry methanol (20 cm^3) whereupon the solution turned deep red. To this was added, dropwise with stirring, under a blanket of N_2, a solution of methyl trifluoromethanesulfonate (0.66 cm^3, 5.8 mmol) in MeCN (20 cm^3). After stirring for 2 h the solution had become golden brown whereupon the solvent volume was reduced by rotary evaporation, the residual solution filtered through a pad of Celite to remove precipitated $KOSO_2CF_3$, and chromatographed on a column of neutral alumina, with acetonitrile as eluent. The fast moving yellow-orange band was collected, the solvent removed *in vacuo* and the resulting solid crystallized from acetonitrile–ethanol (2.25 g, 78%) (Found: C, 52.6; H, 5.1; N, 8.2; Ni, 5.9. $C_{44}H_{50}F_{12}N_6NiP_2$ requires C, 52.2; H, 4.95; N, 8.3; Ni, 5.8%). ^{13}C NMR (CD$_3$CN): δ 173.4 (br), 169.3, 162.9, 135.6, 133.8, 132.9, 131.6, 130.4, 130.2, 130.0, 113.9, 60.6 (br), 56.3, 51.4, 42.5 (br), 30.2 and 21.5. Complex **3** (Found: C, 46.1; H, 5.3; N, 9.2; Ni, 6.8. $C_{34}H_{46}F_{12}N_6NiP_2$ requires C, 45.9; H, 5.2; N, 9.5; Ni, 6.6%). ^{13}C NMR (CD$_3$CN): δ 173.4, 168.4, 160.4, 135.4, 130.1, 129.5, 129.0, 112.0, 59.4 (br), 56.4, 51.3, 42.2 (br), 30.6, 30.4, 21.0 and 19.4.

Cobalt(II) *complexes* **7**–**10**. The corresponding cobalt(II) complexes of nickel complexes **1**–**4** were prepared using the literature procedure described for the known complex **7**.[28]

(2,3,10,11,13,19-*Hexamethyl*-3,10,14,18,21,25-*hexaazabicyclo*-[10.7.7]*hexacosa*-1,11,13,18,20,25-*hexaene*-κ^4N^{14},N^{18},N^{21},-N^{25})*cobalt*(II) *bis*(*hexafluorophosphate*) **7**. Gaseous HCl was bubbled through a solution of complex **1** (1.0 g, 1.3 mmol) in MeCN (25 cm^3) for *ca.* 10 min during which time the colour changed from yellow-orange to blue-green. To this solution was added a solution containing the $[ZnCl_4]^{2-}$ anion in MeCN (25 cm^3), prepared by bubbling HCl through a suspension of Zn metal in MeCN. The resulting white precipitate was collected and washed with MeCN before being dissolved in water. To this aqueous solution was added a solution of NH_4PF_6 in water whereupon the protonated, demetallated ligand precipitated as the hexafluorophosphate salt and this was collected and dried. The product was dissolved in methanol (70 cm^3), along with cobalt(II) acetate tetrahydrate (0.267 g, 1.07 mmol) and anhydrous sodium acetate (0.263 g, 3.25 mmol), and the mixture warmed to *ca.* 50 °C. The resulting orange solution was allowed to cool to room temperature and the orange product crystallized. Recrystallization was effected from hot methanol (0.65 g, 64%) (Found: C, 40.7; H, 6.1; Co, 7.5; N, 10.5. $C_{26}H_{44}CoF_{12}N_6P_2$ requires C, 40.6; H, 6.0; Co, 7.4; N, 10.5%).

[2,12-*Dimethyl*-3,11-*bis*(1-*dimethylaminoethylidene*)-1,5,9,13-*tetraazacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N^1,N^5,N^9,N^{13}]-*cobalt*(II) *bis*(*hexafluorophosphate*) **8**. Yield 65% (Found: C, 35.8; H, 5.2; Co, 8.1; N, 11.5. $C_{22}H_{38}CoF_{12}N_6P_2$ requires C, 35.9; H, 5.2; Co, 8.0; N, 11.4%).

[3,11-*Bis*(1-*benzylmethylaminoethylidene*)-2,12-*dimethyl*-1,5,-9,13-*tetraazacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N^1,N^5,N^9,N^{13}]-*cobalt*(II) *bis*(*hexafluorophosphate*) **9**. Yield 59% (Found: C, 45.7; H, 5.55; Co, 6.4; N, 9.0. $C_{34}H_{46}CoF_{12}N_6P_2\cdot MeOH$ requires C, 45.7; H, 5.4; Co, 6.4; N, 9.1%).

[3,11-*Bis*(α-*benzylmethylaminobenzylidene*)-2,12-*dimethyl*-1,5,9,13-*tetraazacyclohexadeca*-1,4,9,12-*tetraene*-κ^4N^1,N^5,N^9,-N^{13}]*cobalt*(II) *bis*(*hexafluorophosphate*) **10**. Yield 67% (Found: C, 52.3; H, 5.0; Co, 5.9; N, 8.3. $C_{44}H_{50}CoF_{12}N_6P_2$ requires C, 52.2; H, 4.9; Co, 5.8; N, 8.3%).

Copolymerization Reactions.—The copolymers of 4-vinylpyridine were prepared by bulk copolymerization reactions carried out in evacuated, sealed tubes with α,α'-azobis(isobutyronitrile) (aibn) as initiator. The reactions were carried out at 60 °C and the conversion was kept below *ca.* 10% of the total monomer concentration to produce moderate copolymer molecular weights and to reduce the extent of composition drift of the polymer. The reactions were carried out using 4-vinylpyridine with either styrene, methyl methacrylate or butyl methacrylate. The monomers were freshly distilled under vacuum immediately prior to use. The concentrations of the comonomers for a nominal 10% 4-vinylpyridine copolymer were calculated using the free-radical copolymerization equation, using literature values of reactivity ratios for the various comonomers.

For a typical polymerization of 4-vinylpyridine with methyl methacrylate, 4-vinylpyridine (2.4 cm^3), methyl methacrylate (21.4 cm^3) and aibn (0.08 g, 1% w/w) were placed in a polymerization vessel and the reaction mixture was thoroughly degassed by three freeze–pump–thaw cycles. The vessel was sealed under vacuum and warmed to 60 °C for *ca.* 3 h, by which time the solution had become viscous. The copolymer was precipitated into cold methanol and purified by thrice dissolving in chloroform and reprecipitating into methanol. The resulting white copolymer was dried overnight at 50 °C *in vacuo*. Yield 3.2 g. The 4-vinylpyridine content of the copolymers was determined by quantitative ^1H and ^{13}C NMR spectroscopy. The molecular-weight distributions and glass-transition temperatures were determined by gel-phase chromatography (GPC) and differential scanning calorimetry (DSC). The data are listed in Table 1.

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