Non-symmetrical Tetraaza Macrocyclic Complexes of Nickel(II) and their Binding to Synthetic Polymer Supports

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The synthesis and characterisation of a family of new tetraaza macrocyclic complexes of nickel(II) have been performed, *via* reaction of a nucleophilic macrocycle with various acid chlorides, or *via* peripheral functionalisation of suitable macrocycles. The new complexes have an asymmetric distribution of the peripheral groups on the macrocyclic rings and this is reflected in the appearance of their NMR spectra. Some of the new complexes have been incorporated into the structure of synthetic polymers, either *via* copolymerisation with a chosen comonomer, in this case styrene, or *via* reaction with a suitably functionalised, preformed polymer.

There has been considerable interest recently in the preparation of macrocyclic complexes of the transition metals which have a variety of functional groups on the periphery of the macrocyclic ring.[1] These functional groups have been termed the 'ligand superstructure' to indicate that, while not necessarily directly involved in binding to the metal ion, they are important in determining both the physical and chemical properties of the resulting complex.[2] A number of papers have described the preparation of non-symmetrical systems where the superstructure groups are asymmetrically placed on the macrocycle and/or there is only one group of each particular functional type. Many examples are now known, and in some the peripheral group can participate in intramolecular binding to the metal centre. Of particular interest to the present work are the following: Costes *et al.*[3] reported the preparation of a fourteen-membered tetraaza macrocycle containing a unique position which is likely to be nucleophilic in nature; Hay *et al.*[4] studied another tetraaza system which has a pendant primary amine function, able to co-ordinate to the metal centre; Kanda *et al.*[5] discussed the preparation and reactions of a tetradentate Schiff-base ligand having a pendant thioether function; Moore and co-workers[6] reported a tetraaza macrocycle having a pendant 2-pyridylmethyl substituent; Stephenson *et al.*[7] produced a fifteen-membered macrocycle bearing a hydroxyl group and investigated its reactivity. Recently Busch and co-workers[8] studied a macrocycle with a pendant pyridyl function which is sterically restricted in its binding to the metal centre and Wade and Hancock[9] reported the preparation of 'reinforced macrocycles', one example of which has a primary amine function capable of undergoing further reaction.

The topic of polymer-supported complexes has received a great deal of attention recently and such systems have been proposed for an extensive variety of purposes.[10] For example, Tsuchida and co-workers[11] have produced a succession of papers on gas-transporting membranes utilising various transition-metal complexes while Drago and co-workers[12] used a similar idea in the study of facilitated oxygen transport and a number of other workers have recently reported on the same topic.[13] Polymer-supported complexes have also been proposed as catalysts, for example, a rhodium(I) complex has been used in the carbonylation of methanol.[14] The *in situ* formation of such complexes has been studied in the development of separation methods for particular metal ions[15] and photo-induced charge separation using a polymer pendant ruthenium complex has also been reported.[16] The subject of 'macromolecular complexes' has recently been extensively reviewed.[17]

In our earlier work, involving suitably functionalised acyclic complexes, methods were established for the production of polymer-bound transition-metal complexes.[18] However in some cases it was found that successful inclusion of the complex into the structure of the polymer was followed by undesired secondary reactions leading to extensive cross-linking of the polymer chains. This caused the polymer–complex mixtures to be insoluble in all solvents with, at best, solvent-swollen gels being produced. To ease the processing of the polymer-supported complexes it is highly desirable that the materials be soluble and the work described in this paper was carried out in an effort to produce materials with suitable solubility properties.

Although the exact nature of the cross-linking reaction observed for the acyclic systems was not identified, it was proposed that it arose from the relative lability of the multidentate acyclic ligand which is able partly to dissociate from one metal ion and then bind to another metal ion in a separate polymer chain. To eliminate this possibility it was decided to take advantage of the well established enhanced kinetic and thermodynamic stability of the complexes of macrocyclic ligands, relative to the analogous open-chain forms. In this paper, we report both the synthesis of a family of suitably functionalised macrocyclic complexes and the inclusion of two members of this family into the structure of synthetic polymers *via* a copolymerisation route or *via* reaction with a functionalised polymer.

Results and Discussion

Synthesis and Characterisation of Macrocyclic Complexes.—To prevent the occurrence of cross-linking reactions during the preparation of the polymer-supported complexes it was important to use a macrocycle having only a single functional site. The known complex of an asymmetric macrocycle[3] [6-acetyl-7,12,14-trimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,-11,13-tetraenato(2−)]nickel(II) **1** was selected for study in this work because it contains a single methine carbon atom, labelled C^7, which is likely to be reasonably nucleophilic in character and capable of reacting with suitable electrophilic reagents. It is well established from studies with other macrocyclic systems,[19] and indeed with acyclic Schiff-base complexes,[20] that carbon atoms in chemical environments similar to that of C^7 readily undergo such reactions. As a specific example, Busch and co-workers[21] have reported the reaction

Table 1 NMR data for the complexes[a]

(*a*) ^{1}H NMR

Complex	H^5	H^7	H^{8-11}	H^{12-15}	H_c	H_d	X		
1	7.60 (s, 1 H)	4.61 (s, 1 H)	3.10–3.30 (m, 8 H)	2.30, 2.20, 1.90, 1.89 (4 × s, 12 H)					
2	7.70 (s, 1 H)		3.15–3.40 (m, 8 H)	2.44, 2.30, 1.87, 1.86 (4 × s, 12 H)	7.85 (AA′BB′ q, 4 H)	7.40			
3	7.70 (s, 1 H)		3.15–3.40 (m, 8 H)	2.40, 2.30, 1.86, 1.85 (4 × s, 12 H)	7.60 (AA′BB′ q, 4 H)	7.80			
4	7.67 (s, 1 H)		3.15–3.37 (m, 8 H)	2.38, 2.25, 1.81, 1.80 (4 × s, 12 H)	7.96 (AA′BB′ q, 4 H)	8.23			
5	7.70 (s, 1 H)		3.20–3.40 (m, 8 H)	2.43, 2.30, 1.86, 1.84 (4 × s, 12 H)	7.15 (AA′BB′ q, 4 H)	7.92	2.35 (s, 3 H)		
6	7.70 (s, 1 H)		3.20–3.40 (m, 8 H)	2.42, 2.30, 1.84, 1.83 (4 × s, 12 H)	7.90 (AA′BB′ q, 4 H)	7.45	4.62 (s, 2 H)		
7	7.70 (s, 1 H)		3.20–3.40 (m, 8 H)	2.42, 2.30, 1.84, 1.83 (4 × s, 12 H)	7.82 (AA′BB′ q, 4 H)	7.24	2.42 (s, 3 H)		
8	7.70 (s, 1 H)		3.15–3.40 (m, 8 H)	2.40, 2.25, 1.86, 1.84 (4 × s, 12 H)	7.85 (AA′BB′ q, 4 H)	7.44	6.75 (dd, 1 H)	5.85 (d, 1 H)	5.38 (d, 1 H)
9	7.70 (s, 1 H)		3.20–3.40 (m, 8 H)	2.42, 2.30, 1.84, 1.83 (4 × s, 12 H)	7.90 (AA′BB′ q, 4 H)	7.63	6.69 (s, 1 H)		
10	7.70 (s, 1 H)		3.15–3.35 (m, 8 H)	2.40, 2.28, 1.82, 1.81 (4 × s, 12 H)	7.78 (AA′BB′ q, 4 H)	6.52	4.12 (s, 2 H)		
10[b]	7.75 (s, 1 H)		3.10–3.40 (m, 8 H)	2.27, 2.14, 1.66 (2 × s, 6 H) (br s, 6 H)	7.48 (AA′BB′ q, 4 H)	6.52	6.02 (s, 2 H)		
11	7.70 (s, 1 H)		3.20–3.40 (m, 8 H)	2.30, 2.22, 1.82, 1.81 (4 × s, 12 H)	7.60 (AA′BB′ q, 4 H)	7.88	8.12 (br s, 1 H)	2.41 (s, 3 H)	
12[c]	7.86 (s, 1 H)		3.20–3.40 (m, 8 H)	2.34, 2.24, 1.82, 1.81 (4 × s, 12 H)	7.62 (AA′BB′ q, 4 H)	6.51			

(*b*) ^{13}C NMR

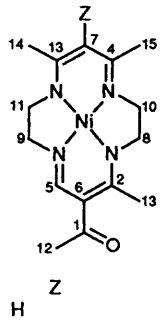
Complex	C^1	C^2	C^3	C^4	C^5	C^6	C^7	$C^{8,9}$	$C^{10,11}$	C^{12-15}	C_a	C_b	C_c	C_d	C_e	X		
1	193.3	166.2	158.8	158.5	156.6	111.6	97.5	60.2, 54.5	52.7, 52.5	28.2, 21.2, 20.9, 20.5								
2	193.7	166.5	159.7	159.2	156.7	111.8	110.3	59.5, 54.1	53.4, 53.1	28.4, 21.0, 20.7, 20.5	198.5	138.7	130.8	128.7	139.9			
4	193.9	166.5	161.5	160.5	156.6	111.8	110.8	59.4, 54.0	53.6, 53.3	28.4, 21.6, 21.2, 20.5	196.9	147.1	130.0	123.7	149.6			
5	193.6	166.4	159.4	158.9	156.6	111.7	110.3	59.5, 54.1	53.3, 53.0	28.3, 21.0, 20.5, 20.4	198.6	138.8	130.9	121.5	153.8	168.7		20.9
6	193.8	166.5	159.7	159.2	156.7	111.8	110.6	59.6, 54.1	53.4, 53.1	28.4, 21.0, 20.5, 20.5	199.1	141.6	129.8	129.2	141.4		45.4	
10	192.2	165.1	157.1	156.6	156.8	110.8	109.8	59.0, 53.8	52.8, 52.5	28.4, 20.0. 19.8, 19.6	197.0	128.1	131.5	112.6	153.3			
11	193.8	166.5	159.2	158.8	156.6	111.8	110.5	59.6, 54.2	53.3, 53.0	28.3, 20.9, 20.5, 20.5	199.0	136.5	130.8	119.1	142.5	169.0		24.5

[a] In $CDCl_3$ solution, unless otherwise stated. [b] In [$^2H_6$]dimethyl sulfoxide solution. [c] In CD_3OD solution, containing 1 equivalent of sodium.

Table 2 Yield and microanalytical data (%) for the new complexes

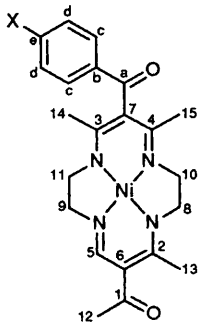
		Found				Calculated		
Complex	Yield	C	H	N	Formula	C	H	N
2[a]	82	55.7	5.4	11.7	$C_{22}H_{25}ClN_4NiO_2$	56.05	5.3	11.9
3[b]	45	48.1	4.8	9.4	$C_{22}H_{25}IN_4NiO_2{\cdot}0.5C_4H_8O$	47.95	4.85	10.05
4	90	52.5	4.8	13.4	$C_{22}H_{25}N_5NiO_4{\cdot}0.5CH_3OH{\cdot}H_2O$	52.4	5.6	13.6
5	53	58.3	5.7	11.7	$C_{24}H_{28}N_4NiO_4$	58.2	5.7	11.3
7	40	60.7	6.2	12.8	$C_{23}H_{28}N_4NiO_2$	61.3	6.2	12.4
8	50	60.2	5.9	11.75	$C_{24}H_{28}N_4NiO_2{\cdot}H_2O$	59.9	6.2	11.6
10	53	57.9	6.1	14.3	$C_{22}H_{27}N_5NiO_2{\cdot}C_2H_6O$	57.9	6.6	14.1
11	60	56.6	6.1	13.6	$C_{24}H_{29}N_5NiO_3{\cdot}H_2O$	56.3	6.1	13.7
12	55	58.3	5.8	12.5	$C_{22}H_{26}N_4NiO_3$	58.3	5.7	12.4

[a] Cl 7.5 (7.5)%. [b] I 21.2 (21.0)%.



Z

1 H
2 4-ClC_6H_4CO
3 4-IC_6H_4CO
4 4-$NO_2C_6H_4CO$
5 4-$CH_3CO_2C_6H_4CO$
6 4-$BrCH_2C_6H_4CO$
7 4-$CH_3C_6H_4CO$
8 4-$CH_2CHC_6H_4CO$
9 4-$Br_2CHC_6H_4CO$
10 4-$NH_2C_6H_4CO$
11 4-$CH_3CONHC_6H_4CO$
12 4-HOC_6H_4CO



between a symmetric difunctional macrocycle and a wide range of acid chlorides, producing a whole family of new species.

In the present work a solution of complex **1** in dichloromethane, in the presence of a stoichiometric amount of triethylamine, reacted with a range of *para*-substituted aromatic acid chlorides, 4-XC_6H_4COCl (X = Cl, I, NO_2, CH_3CO_2, $BrCH_2$, CH_3, or $CHCH_2$) to produce the desired products **2**–**8**. The reactions proceeded smoothly at room temperature and, with the exception of the bromomethyl derivative **6** (see below), the products were isolated, following column chromatography on neutral alumina, in good to high yield. These materials could then either further react to produce species capable of reacting with a functionalised polymer or, in the case of the 4-vinylbenzoyl derivative, copolymerise with selected co-monomers.

Complexes **2**–**8** were readily characterised by spectroscopy, particularly from their ^{13}C and ^1H NMR spectra (Table 1) and, again with the exception of complex **6**, from microanalytical data (Table 2). It should be noted that both the ^{13}C and ^1H NMR spectra were strongly indicative of the asymmetric nature of the compounds, with separate resonances appearing for each carbon atom and also for the protons on each carbon atom, although at 200 MHz the methylene protons of the macrocyclic ring gave rise to a complex multiplet which could not be assigned readily.

From comparison of the ^1H NMR spectra of complex **1** and the various products the most significant feature was the characteristic loss of the signal due to proton H^7 of **1** upon substitution. This was accompanied by a corresponding shift in the ^{13}C NMR signal of C^7 from δ 97.5 to 110. The assignments were confirmed with the aid of the results of a DEPT (distortionless enhancement by polarisation transfer) experiment which clearly showed that C^7 of **1** bore a single hydrogen atom while, in all of the products, C^7 was a quaternary carbon atom. Apart from this shift, the chemical shifts of the atoms of the macrocycle were largely unperturbed as a result of the substitution reaction, even with X groups of widely varying electronic properties, for example NO_2 and NH_2 (formed by reduction of the nitro group, see below). This is understandable in that the 4-XC_6H_4CO group is constrained to be orthogonal to the macrocyclic ring, by steric interaction with the methyl groups which are positioned α to C^7. These two methyl groups have the effect of raising the barrier to rotation about the C^7–C_a bond, causing the substituted macrocycles to be rigid on the NMR time-scale. This is in contrast to the situation encountered with some other macrocycles where only one of the α positions has a methyl substituent. These molecules display fluxional behaviour on the NMR time-scale, associated with rotation of the benzoyl group with respect to the main macrocyclic ring.[19] A similar steric effect has been reported in an extensive study of two acyclic complexes of nickel(II) with acetyl groups in the positions equivalent to C^7.[22] The X-ray crystal structure of the compound with only one α-methyl indicates that the acetyl group is in almost the same plane as the rest of the complex, allowing a pathway for electron delocalisation. For the complex with two α-methyls the acetyl group is rotated some 58.2° out of the plane of the complex, thereby restricting the delocalisation of electron density.

The IR spectra of the products supported the presence of the expected functional groups and the relevant data are listed in Table 3. Comparing the spectra of **1** and the products provided a useful marker for the success of the substitution process. The parent complex **1** has a strong peak at 1105 cm^{-1}, assigned to a deformation involving the C^7H group, and this signal disappeared once substitution had been achieved.

The electronic spectra of the complexes were unremarkable. The complexes were all red-orange in colour and displayed a single transition in the visible region of the spectrum at *ca.* 420 nm. Generally this peak was ill defined, appearing merely as a shoulder on a series of intense bands which are assigned

Table 3 Infrared spectroscopic data (cm^{-1})

Complex	ν(C=O)	ν(C=N, C=C)	Others
1	1625	1582	1105 (C–H def.)
2	1640, 1624	1579, 1541	
3	1648, 1628	1587, 1575, 1546	
4	1625	1580, 1542	1518, 1344 (NO_2)
5	1775, 1643, 1625	1577, 1545	
6	1640	1585, 1550	
7	1641	1582, 1545	
8	1630	1579, 1548	
10	1656, 1610	1574, 1545	3338, 3209 (NH_2)
11	1691, 1625	1581, 1543	3300, 3255, 3185, 3090 (NH)
12	1628	1580, 1540	3130 (OH)

as allowed electronic transitions of the ligand and occur just into the ultraviolet region of the spectrum. The colour and electronic spectra of the complexes, coupled with the observed diamagnetism, as evidenced by their sharp, unshifted NMR spectra, indicated that the nickel(II) ion was in the four-co-ordinate, square-planar environment predicted for such macrocyclic complexes.

As mentioned above, complex **6** behaved rather differently to the other derivatives. The 4-bromomethylbenzoyl chloride used in preparation of **6** was itself prepared by a literature method, involving bromination of *p*-toluic acid with *N*-bromosuccinimide followed by reaction of the bromo acid with thionyl chloride.[23] The ^1H NMR spectrum of an unpurified sample of **6** indicated that it contained small quantities of the *p*-toluoyl derivative **7** and the corresponding 4-dibromomethylbenzoyl derivative **9**. Attempts to purify the crude sample of **6** by column chromatography were unsuccessful due to reaction of the complex on the column, producing an intractable mixture. This reaction must involve the bromomethyl group, since a genuine sample of the corresponding methyl derivative **7** behaved normally under the same conditions.

In sharp contrast to the facile reaction of complex **1** with aromatic acid chlorides, a reaction involving 4-chlorobutyryl chloride produced a complex mixture of products from which only the parent macrocycle could be isolated cleanly. This difference is presumably due to the *in situ* formation of the ketene of 4-chlorobutyryl chloride by triethylamine-promoted loss of HCl from the acid chloride. This ketene reacted to produce the range of materials. Similar behaviour has been reported by Busch and co-workers[24] and it is a general problem in the reaction of acid chlorides which have hydrogen atoms α to the carbonyl group.[25] It is interesting that Busch and co-workers[26] have also reported the successful use of some aliphatic diacid chlorides in the bridging of a difunctional macrocycle. Presumably in that case the macrocycle provides a more reactive nucleophile which reacts to form the desired product before ketene formation and subsequent dimerisation become a major problem. Substitution at C^7 with aliphatic acid chlorides can be achieved by using pyridine as the base which is required for the trapping of the HCl by-product. The chemistry of these aliphatic derivatives will form the subject of a separate report.

Reactions of Functionalised Macrocycles.—A number of other new complexes were prepared by further reaction of some of the complexes described above. In each case reactions were carried out to produce monofunctionalised macrocycles capable of direct reaction with suitably functionalised polymers.

The nitro derivative **4** was reduced to the corresponding primary amine derivative **10** *via* two different routes. The conventional technique of heterogeneous catalytic hydrogenation at room temperature, using gaseous hydrogen, a Pd/C catalyst, and ethyl acetate as solvent, produced the desired product but the rate of the reaction was very slow, presumably due to the very low solubility of the nitro complex in the reaction medium. An alternative reduction technique, transfer hydrogenation,[27] involving hydrogen transfer from cyclohexene in the presence of a Pd/C catalyst, proved much more successful. The overall yields of the reduction were very similar but much larger amounts of material could be used in the transfer hydrogenation reaction. This is because the reaction was carried out using ethanol at reflux as solvent and under these conditions the nitro compound is considerably more soluble.

Complex **10** was characterised by spectroscopy (Table 1) and by microanalysis (Table 2). Apart from the appearance of a signal at δ 4.12, assigned to the NH_2 group, the most significant change in the ^1H NMR spectrum, relative to that of parent complex **4** was the shift of the aromatic resonances to much higher field, particularly for protons H_d (δ 8.23 to 6.52). The ^{13}C NMR spectra of **10** and **4** showed significant shifts for resonances associated with the aromatic grouping, with signals assigned to both C_b and C_d displaying significant shifts to higher field (by 19.0 and 11.1 ppm respectively). These changes are entirely consistent with the transformation of an electron-withdrawing NO_2 into an electron-donating NH_2 group. As stated above, there is remarkably little change in the remainder of both the ^1H and ^{13}C NMR spectra, due to the orthogonality of the aromatic ring with respect to the rest of the macrocycle.

The ^1H NMR spectrum of complex **10** was also run in $(CD_3)_2SO$ solution and some interesting solvent shifts were observed (Table 1), particularly for the NH_2 protons, which are shifted 1.9 ppm to lower field, while protons H_c are shifted 0.3 ppm to higher field.

The IR spectrum of complex **10** was also consistent with the proposed structure with the appearance of two bands assigned to the symmetric and asymmetric stretch of the NH_2 group, at 3338 and 3209 cm^{-1}, coupled to the non-appearance of bands in the NO_2 stretching region. Two bands above 1600 cm^{-1} were ascribed to vibrations of the carbonyl groups.

As a preliminary test of the reactivity of the aromatic amine-containing macrocycle **10**, it was treated with acetyl chloride in the presence of triethylamine to generate smoothly the acetamide derivative **11**. This complex was characterised by spectroscopy and by microanalysis. The ^1H NMR spectrum showed signals at δ 2.41 (3 H) and 8.12 (1 H) assigned to the $COCH_3$ and NH protons respectively, and a dramatic downfield shift for the resonance ascribed to H_d of the aromatic group was observed, from δ 6.52 for **10** to δ 7.88 for **11**, consistent with acetylation having occurred at the NH_2 group. The ^{13}C NMR spectrum had resonances at δ 169.0 and 24.5 assigned to the acetyl group and substantial downfield shifts in the position of signals assigned to C_b, C_d and C_e of the aromatic ring were noted, relative to the spectrum of **10**.

The IR spectrum had a band at 1691 cm^{-1} assigned to ν(C=O) of the amide group, and a series of four bands above 3000 cm^{-1}, in the region predicted for ν(N–H). The origin of the four

bands is not clear but they may arise from differential packing effects in the solid state, leading to different degrees of hydrogen bonding involving the amide hydrogen atom. It should be noted that none of the four bands corresponds to the ν(N–H) bands of **10**, suggesting that they arise from the amide product and not from a mixture containing the starting amine.

Although the acetyl derivative formed readily, reaction of complex **10** with *N*-acryloxysuccinimide, 4-nitrophenyl acetate or 3-acetoxyl-1,2,3-benzotriazin-4(3*H*)-one were all unsuccessful with only starting materials being recovered from the reaction mixtures. This indicates that, as expected, the aromatic amine-substituted complex is a weak nucleophile, reacting only with strongly electrophilic reagents.

Base-catalysed hydrolysis of the 4-acetoxy derivative **5** resulted in formation of the corresponding 4-hydroxy derivative **12**. This species proved to be very insoluble, preventing direct determination of its ^{1}H NMR spectrum. The fast atom bombardment (FAB) mass spectrum had peaks at *m*/*z* 452 and 454, in agreement with the values predicted for M^+ (^{58}Ni and ^{60}Ni respectively). The IR spectrum had a peak at 3130 cm^{-1} assignable to ν(O–H), and no peak for an ester carbonyl stretch. The microanalytical results were in good agreement with the proposed structure. Treatment of complex **12** with 1 equivalent of sodium methoxide in methanol generated the soluble sodium aryl oxide salt, the ^{1}H NMR spectrum of which was consistent with the proposed structure of the anion (Table 1).

Preparation of Polymer-bound macrocycles.—(*i*) *via Copolymerisation.* The 4-vinyl derivative **8** was copolymerised with styrene, using free-radical initiation. Polymerisation was carried out both in the bulk and in solution in benzene. In bulk the monomer ratio was *ca.* 170:1 and in solution *ca.* 85:1. In each case the reaction was allowed to proceed to *ca.* 30% conversion. The resulting polymers were characterised by NMR spectroscopy and by microanalysis. Since the signal due to the protons adjacent to the ring nitrogen atoms can be clearly identified on the NMR spectra, integration of the spectra provides a good method for characterisation of the composition of the copolymers.

The solution polymerisation produced a copolymer with a styrene:complex ratio of *ca.* 80:1, as determined from the integrals of the ^{1}H NMR spectrum. This is very close to the monomer feed ratio and implies that the reactivity of the vinyl group of the macrocycle is similar to that of styrene itself, indicating that the vinyl group is largely unaffected by the presence of the macrocyclic complex. The number average molecular weight (M_n) of the copolymer was determined by gel permeation chromatography as *ca.* 27 300, with a polydispersity (M_w/M_n) of 3.08. The glass transition temperature (T_g) of the copolymer was 376 K, which is very close to the value of polystyrene itself (373 K).

The product from the bulk copolymerisation displayed some slight differences in its properties. The NMR spectrum indicated that the styrene:complex ratio was *ca.* 230:1. This is slightly higher than the feed ratio of the monomers and suggests that the growing chain reacts more readily with another styrene than with a macrocyclic vinyl group. This probably is a reflection of the rather low solubility of the macrocycle in the bulk medium. The figure of 0.25 g of macrocycle in 10 cm^3 of styrene represents the limit of solubility and it may be that some association of the macrocycles in solution occurs, making the vinyl group of the macrocycle less accessible for reaction with the growing polymer chain. The value of M_n for the copolymer was 28 000, the polydispersity was 2.03, and T_g was 380 K.

(*ii*) *via Reaction with a functionalised copolymer.* Deprotonation of the 4-hydroxy derivative **12** with a methanol solution of sodium methoxide gave a solution containing the aryl oxide anion. Reaction of this anion with a solution of a copolymer of butyl methacrylate and *N*-acryloxysuccinimide over a period of several days resulted in formation of the desired copolymer-supported macrocycle. The red product polymer was much more soluble in methanol than the parent, making purification more difficult. The ^{1}H NMR spectrum of the product showed the appearance of signals characteristic of the macrocycle, allied to loss of the signal ascribed to the succinimido protons, and the IR spectrum clearly indicated the loss of the carbonyl stretch of the succinimido group. Studies with these fascinating polymer–complex systems are continuing.

Conclusion

The parent macrocyclic complex **1** has a single site of strong nucleophilic character, C^7, available for reaction with electrophilic reagents and the reactivity of this site has been established in this work. This has resulted in the formation of a variety of new substituted macrocyclic complexes, the key feature of which is the asymmetric pattern of substitution around the macrocyclic ring. Each of the new macrocycles has a unique functional group available for further reaction. The chemistry of these new macrocycles has been investigated and, in particular, three complexes have been identified (the 4-vinyl **8**, 4-amine **10** and the 4-hydroxy **12**) which can be exploited in preparing polymer–complex mixtures. Two such polymer–complex systems have been prepared utilising two different synthetic routes: copolymerisation of the 4-vinyl complex with styrene as comonomer and nucleophilic substitution of the deprotonated 4-hydroxy complex with pre-formed butyl methacrylate-*N*-acryloxysuccinimide copolymer.

Experimental

All materials were reagent grade and were used without further purification, except for solvents which were dried by standard methods. The NMR spectra were recorded on a Bruker WP200 spectrometer, operating at 200.133 (^{1}H) or 50.323 MHz (^{13}C) respectively. Chemical shifts are reported with respect to an external tetramethylsilane reference (positive to low field). Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer, IR spectra as Nujol mulls, or thin films for polymer samples, on a Perkin-Elmer 580 spectrophotometer.

Preparation of Complexes.—Complex **1** was prepared using the literature procedure.[3]

Complexes **2–8** were prepared by the same general method and details are given for only **4**. To a solution of complex **1** (3.02 g, 9.0 mmol) in dichloromethane (50 cm^3) containing triethylamine (1.4 cm^3, 9.0 mmol) was added, dropwise with stirring, a solution of 4-nitrobenzoyl chloride (1.7 g, 9.0 mmol) in dichloromethane (20 cm^3). The colour of the solution darkened during the addition. The reaction mixture was stirred for *ca.* 30 min, at the end of which TLC analysis [silica plates, dichloromethane–acetone (10:1) eluent] indicated that no starting material remained. The reaction mixture was washed twice with water (100 cm^3) and the organic layer was dried over $MgSO_4$. The solvent was removed *in vacuo* and the solid residue was chromatographed on a neutral alumina column using dichloromethane as eluent. The fast moving red band was collected and the solvent removed to yield the desired product (3.93 g, 90%).

[6-*Acetyl*-13-(p-*aminobenzoyl*)-7,12,14-*trimethyl*-1,4,8,11-*tetraazacyclotetradeca*-4,6,11,13-*tetraenato*(2−)]*nickel*(II) **10**. This complex was prepared by reduction of **4** using two different methods.

(*a*) *Catalytic reduction with hydrogen gas.* Complex **4** (0.205 g, 4.26 × 10^{-4} mol) was dissolved in ethyl acetate (150 cm^3) and 5% Pd/C catalyst (0.2 g) was added. The reaction mixture was placed in an atmosphere of hydrogen gas and then stirred at room temperature for 4 h, whereupon more catalyst (0.3 g) was added. After 12 h the reaction mixture was filtered and the orange filtrate taken to dryness. Extraction of the residue with chloroform gave a second crop of product. Yield: 0.126 g (66%).

(*b*) *Transfer hydrogenation.* Complex **4** (2.0 g, 4 × 10^{-3} mol)

was suspended in ethanol (100 cm^3) and cyclohexene (1 cm^3, 9.9 × 10^{-3} mol) and 5% Pd/C (0.5 g) added. The reaction mixture was heated at reflux for several hours and further portions of cyclohexene were added until the reaction was adjudged complete by TLC. The reaction mixture was filtered and the orange filtrate was reduced to dryness *in vacuo* to yield an orange solid. Yield: 1.04 g (58%).

[13-(p-*Acetamidobenzoyl*)-6-*acetyl*-7,12,14-*trimethyl*-1,4,8,11-*tetraazacyclotetradeca*-4,6,11,13-*tetraenato*(2−)]*nickel*(II) **11**. To a solution of complex **10** (0.14 g, 3.12 × 10^{-4} mol) in dichloromethane (50 cm^3) containing triethylamine (0.05 cm^3, 4 × 10^{-4} mol) was added acetyl chloride (0.03 cm^3, 3.12 × 10^{-4} mol). The reaction mixture was stirred at room temperature for 20 min, then washed twice with water (100 cm^3). The organic layer was dried over Na_2SO_4 and taken to dryness *in vacuo*, to yield the product as a dark red solid. Yield: 0.096 g (60%).

[6-*Acetyl*-13-(p-*hydroxybenzoyl*)-7,12,14-*trimethyl*-1,4,8,11-*tetraazacyclotetradeca*-4,6,11,13-*tetraenato*(2−)]*nickel*(II) **12**. To a slurry of complex **5** (0.5 g, 1.12 mmol) in methanol (20 cm^3) was added potassium *tert*-butoxide (0.125 g, 1.12 mmol) whereupon all of the solid dissolved. The reaction mixture was stirred overnight and then some Amberlite I.R. 120 ion-exchange resin (3 cm^3) was added. Stirring was continued for 2 h during which time a red precipitate appeared. This solid was collected by careful decanting. Yield: 0.25 g (55%).

Preparation of 4-*Bromomethylbenzoic Acid*.—This compound was prepared according to the method reported by Rich.[23] To a suspension of *p*-toluic acid (2.0 g, 0.015 mol) in dry benzene (50 cm^3) were added *N*-bromosuccinimide (2.6 g, 0.015 mol) and azobis(isobutyronitrile) (aibn) (0.02 g). The reaction mixture was heated at 60 °C for 6 h, under an atmosphere of N_2. The solvent was removed *in vacuo* and the resulting solid was washed with hot water, dried and crystallised from methanol.

Preparation of 4-*Acetoxybenzoic Acid*.[28]—To a sample of 4-hydroxybenzoic acid (20 g, 0.145 mol) was added acetic anhydride (54.1 g, 0.53 mol) and the mixture was heated at reflux for *ca.* 3 h. Upon cooling white crystals appeared and these were recrystallised from chloroform. Yield: 5.5 g (21%).

Preparation of 4-*Bromomethylbenzoyl Chloride and* 4-*Acetoxybenzoyl Chloride*.[28]—To the appropriate aryl acid (*ca.* 0.2 g) was added thionyl chloride (15 cm^3) and the reaction mixture was heated at reflux for *ca.* 30 min, under an atmosphere of N_2. The excess of thionyl chloride was removed *in vacuo* to yield the desired product. Yield: *ca.* 90%.

Polymerisation Reactions.—*Copolymerisation of butyl methacrylate and* N-*acryloxysuccinimide*. A solution of freshly distilled butyl methacrylate (20 cm^3, 0.125 mol), *N*-acryloxysuccinimide (1.17 g, 6.92 × 10^{-3} mol) and aibn (0.1 g, 6.09 × 10^{-4} mol) in chloroform (70 cm^3) was deoxygenated by bubbling wih N_2 for 40 min. The solution was then brought rapidly to reflux for 30 min. The chloroform was removed *in vacuo* and the remaining liquid was precipitated into methanol. The polymer was purified by three further dissolution–reprecipitation cycles and then dried under vacuum. Yield: 1.77 g, *ca.* 10% conversion. The monomer feed ratio was: 18:1 and the polymer composition (determined by integration of the ^1H NMR spectrum) was methacrylate:succinimide 3.83:1.

Copolymerisation of complex **8** *with styrene*. (*a*) *Bulk polymerisation*. The complex (0.25 g, 5.4 × 10^{-4} mol), styrene (10 cm^3, 0.087 mol), and aibn (0.04 g, 2.4 × 10^{-4} mol) were placed in a polymerisation tube and thoroughly degassed by five freeze–pump–thaw cycles, before the tube was sealed under vacuum. The reaction mixture was heated at 333 K for 4 h before being rapidly cooled to 77 K. The tube was opened and the contents allowed to warm. The resulting viscous liquid was precipitated into methanol and the solid polymer was purified by thrice dissolving it in dichloromethane and reprecipitating into methanol. The solid product was dried under vacuum. Yield: 3.15 g, 34% conversion.

(*b*) *Solution polymerisation*. The complex (0.05 , 1.08 × 10^{-3} mol), styrene (10 cm^3, 0.087 mol), benzene (5 cm^3) and aibn (0.01 g, 6.0 × 10^{-5} mol) were placed in a polymerisation tube and thoroughly degassed by five freeze–pump–thaw cycles before the tube was sealed under vacuum. The tube was heated at 333 K for 15 h before being rapidly cooled to 77 K. It was opened and the contents allowed to warm. The polymer was precipitated into methanol then purified thrice by dissolution in dichloromethane and reprecipitation from methanol before being dried under vacuum. Yield: 2.59 g, 27% conversion.

Reaction of complex **12** *with butyl methacrylate*–N-*acryloxysuccinimide copolymer*. To a suspension of complex **12** (0.144 g, 3.18 × 10^{-4} mol) in dry methanol was added sodium metal (0.0073 g, 3.17 × 10^{-4} mol) whereupon the macrocycle dissolved to give a deep red solution. This was added to a solution of the copolymer (0.24 g) in dichloromethane (50 cm^3), containing 3.18 × 10^{-4} mol of succinimido groups. The reaction mixture was stirred, under a blanket of N_2, at room temperature for 5 d. The organic layer was washed with water (3 × 50 cm^3) and filtered through glass wool to remove a small amount of red precipitate, then the solvent was removed *in vacuo* to yield the polymer–complex product.

Acknowledgements

We thank the SERC and BOC plc for provision of a CASE award (to H. B. H.), Dr. B. Hunt (University of Lancaster) for the GPC and DSC data, and the SERC Mass Spectrometry facility at Swansea for the FAB mass spectrum. We also thank Dr. J. J. Liggat for useful discussion and the referees for helpful comments.

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Received 22*nd July* 1991; *Paper* 1/03726I