Peripheral Functionalisation of the Nickel(II) Complex of a Tetradentate (N_3O) Ligand *via* a Pendant Amine Substituent

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The reactivity of the nickel(II) complex (**1**) of a tetradentate (N_3O) ligand containing a pendant amine group has been demonstrated by reaction with a variety of electrophilic reagents, including iodomethane, acetyl chloride, benzoyl chloride, 4-vinylbenzoyl chloride, acryloyl chloride, toluene-*p*-sulphonyl chloride, *N*-acryloylsuccinimide, and the copolymer of *N*-acryloylsuccinimide and n-butyl acrylate, yielding a series of new complexes. The complex containing a *p*-vinylbenzoyl substituent group behaved as a comonomer in free-radical-initiated copolymerisation with methyl methacrylate to produce a polymer containing a covalently bound complex. A new fifteen-membered asymmetric macrocyclic complex has been prepared by the self-condensation reaction of complex (**1**).

Peripheral functionalisation of the ligand in linear multidentate and macrocyclic transition-metal complexes is a topic of growing importance.[1] Such peripheral groups have been termed the 'ligand superstructure' to indicate that, while not directly in contact with the metal centre, they are important in controlling the physical properties of the resulting complex.[2]

A very large number of papers have appeared recently describing both multidentate and macrocyclic ligands having pendant functional groups. With non-cyclic ligands, for example, Kanda *et al.*[3] have prepared cobalt(II) complexes of analogues of *NN'*-ethylenebis(salicylideneiminate) with pendant amine, ether, and thioether groups that, at room temperature, remain unco-ordinated to the metal ion; Gomez-Romero *et al.*[4] have reported the preparation of a complex containing a pendant 2-hydroxyethyl group, suitable for further reaction, and Saito *et al.*[5] have reported on synthetic models for bleomycin involving the addition of DNA binding groups to a pendant carboxylic acid function of a linear multidentate ligand.

The area of macrocyclic complexes bearing pendant functional groups has been explored extensively. Some recent examples include work by Busch and co-workers[6] concerning some reactions of a hydroxy-substituted tetra-aza macrocyclic ligand; Hay *et al.*[7] have demonstrated that a tetra-aza macrocyclic complex can be functionalised with an alkyl nitro group which, after reduction to the primary amine derivative, is capable of intramolecular co-ordination to the metal ion; Kimura *et al.*[8] have reported a triaza macrocycle containing a pendant phenol group and Achilleos *et al.*[9] have described an encapsulated complex of a hexa-amine macrocyclic ligand which has a pendant arm containing an amino function.

Crown ethers with pendant arms to aid metal-ion co-ordination have also been studied. For example, Gokel *et al.*[10] have reported work using both mono- and bis-substituted 'lariat ethers' and examined the ability of these ligands to bind alkali-metal ions.

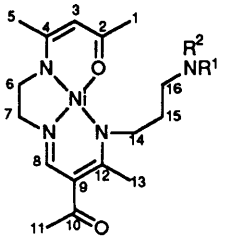
The subject of the incorporation of metal chelates into polymer supports has been reviewed.[11] Of particular interest to this work is the immobilisation of transition-metal complexes on or within host supports. Three preparative routes to such species may be identified. (1) *In situ* synthesis of the ligand using functional groups bound to the supporting medium. For example, Drago and co-workers[12] have produced complexes of Schiff-base ligands formed by the *in situ* condensation of a polystyrene-bound triamine with salicylaldehyde. (2) Reaction of the complex with a suitably functionalised support. For example, Lindoy and co-workers[13] have bound a N_3O_2 macrocyclic ligand to a silica gel substrate *via* one of the ligand amine groups and, very recently, a polyorganosiloxane polymer containing a cobalt(II) phthalocyanine complex has been reported.[14] (3) Copolymerisation of a complex bearing a polymerisable group with a selected comonomer. Pomogailo and co-workers,[15] for example, have prepared a number of complexes containing polymerisable functions and studied the copolymerisation reactions of these novel monomers. Undoubtedly this burgeoning subject will continue to grow.

Recently we have been interested in the preparation of linear multidentate and macrocyclic ligands bearing a single pendant group for use in subsequent inclusion of the complex into the structure of a polymer since materials of this type are of interest in the production of novel membrane systems. For membrane-forming purposes, soluble polymers are desired and difunctional complexes have proven unsuitable as reagents because the polymers that they produce are extensively cross-linked and insoluble, behaving as solvent-swellable gels.[16]

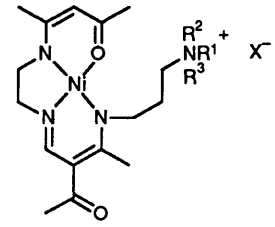
A suitable precursor complex, (**1**), first reported in 1985, was selected as the basis for this study.[17] This species has a pendant primary amine function which remains unco-ordinated in the nickel(II) complex and is thus available for modification. In this paper we report on the range of reactivity of this pendant amino group, in particular the use of this complex and its derivatives in the formation of novel macromolecular species containing transition-metal complexes covalently bound to the polymer backbone. The preparation of a new, asymmetric fifteen-membered macrocyclic ligand is also reported.

Results and Discussion

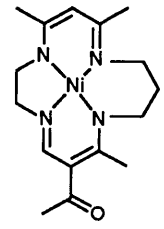
Derivatives of Complex (**1**).—The linear multidentate nickel(II) complex (**1**) was prepared *via* a modification of the literature method.[17] Analytical and i.r. spectroscopic data indicate that the compound is isolated as the monohydrate (Table 1). The ^1H n.m.r. spectrum is in good agreement with the literature data (Table 2).[17] The ^{13}C n.m.r. data are consistent with the proposed structure (Table 3), assignment of the ^{13}C n.m.r. spectrum being aided by the results from a distortionless enhancement by polarisation transfer (DEPT) experiment. The asymmetry of the complex is clearly demonstrated in that each carbon atom has a separate signal. Broadening of the signals



	R^1	R^2
(1)	H	H
(2)	COMe	H
(3)	COPh	H
(4)	$COC_6H_4CHCH_2$-4	H
(5)	$SO_2C_6H_4Me$-4	H
(7)	$COCHCH_2$	H
(10)	Me	Me



	R^1	R^2	R^3	X
(6)	H	H	H	$ONCO(CH_2)_2CO$
(8)	H	H	H	I
(9)	Me	Me	Me	I



(11)

due to carbon atoms 15 and 16 indicates that this part of the molecule is fluxional on the n.m.r. time-scale.

Reaction with Acid Chlorides.—Complex (**1**) in solution in dichloromethane, reacts readily with a variety of acid chlorides to produce, in high yield, the corresponding amide derivatives as orange-red solids. The acetyl, benzoyl, 4-vinylbenzoyl, and toluene-*p*-sulphonyl derivatives were prepared as examples and these products are readily characterised spectroscopically as having structures (**2**)—(**5**) respectively. Microanalytical data for the complexes are included in Table 1. In many cases the complexes are isolated as hydrates and this is confirmed by evidence from their i.r. spectra.

The ^1H and, where appropriate, the ^{13}C n.m.r. spectroscopic data are listed in Tables 2 and 3. Assignment of the ^{13}C n.m.r. spectrum was aided by the results of a DEPT experiment and signals were identified for each of the carbon atoms of the molecules. Apart from the appearance of new signals for the various substituent groups, the spectra are little different from that of complex (**1**). Notably the fluxionality associated with the $(CH_2)_3N$ group is absent for these amido derivatives, implying a more rigid structure for the molecules. The ^1H n.m.r. spectra display rather greater differences relative to the spectrum of (**1**), with the electron-withdrawing power of the substituent group having a marked affect on the position of resonances of protons adjacent to the amido function (see Table 2). The protons attached to C^{16}, α to the amide nitrogen, have a signal that is shifted by 0.37—0.92 relative to the same signal of (**1**). The signal appears as a quartet as a result of coupling both to the two protons of C^{15} and the amido H atom with, coincidentally, the same coupling constant. Similarly, the signal of the amide proton itself appears as a broadened triplet in the range δ 5.37—6.97. The observed trends are readily explained by consideration of the abilities of the substituents in withdrawing electron density from the amide nitrogen atom: toluene-*p*-sulphonyl < acetyl < benzoyl.

Table 1. Analytical data[a]

		Analysis/%		
Complex	Yield/%	C	H	N
(**1**)[b]	40	50.6 (50.2)[c]	7.1 (7.3)	14.8 (14.6)
(**2**)	61	51.7 (51.9)[d]	6.7 (7.0)	13.0 (13.5)
(**3**)	70	57.9 (57.8)[d]	6.5 (6.7)	11.8 (11.7)
(**4**)	82	54.55 (54.7)[e]	6.25 (6.9)	10.6 (10.2)
(**5**)[f]	52	52.7 (53.2)	6.3 (6.2)	8.4 (10.8)
(**6**)	77	46.2 (46.6)[g]	6.1 (6.8)	13.6 (13.6)
(**8**)	90	38.9 (39.0)	5.6 (5.5)	11.4 (11.4)
(**9**)	78	37.45 (37.6)[h]	5.85 (6.8)	9.3 (9.2)
(**11**)	2.7	52.1 (52.7)[c]	6.8 (7.1)	15.4 (15.35)

[a] Calculated values in parentheses. [b] Ni 14.4 (15.3%). [c] Monohydrate. [d] Calculated for hemihydrate. [e] Trihydrate. [f] S 6.2 (6.2%). [g] Dihydrate. [h] Tetrahydrate.

In all cases the spectra clearly indicate that reaction occurs exclusively at the amine nitrogen atom. This is important because potentially carbon atom 3 has nucleophilic properties and could, in principle, react with the acid chlorides. This is further discussed below.

The 4-vinylbenzoyl derivative (**4**) is unusual in that its solubility is extremely low in most common solvents and it also displays a rather broad ^1H n.m.r. spectrum. This behaviour is probably due to enhanced aggregation of molecules of (**4**), favoured by the high degree of planarity of the 4-vinylbenzoylamide group. This serves both to inhibit solvation of the complex and to reduce the rate of molecular tumbling in solution, decreasing the rate of relaxation of the protons during the n.m.r. experiment.

The visible spectra of the amides are similar and clearly indicate that the nickel(II) ion retains the N_3O co-ordination environment of the parent complex (**1**). The data are listed in Table 4. All have $\lambda_{max.}$ *ca.* 540 nm (ε *ca.* 200 $dm^3\ mol^{-1}\ cm^{-1}$), consistent with square-planar Ni^{II}.[18]

The i.r. spectra of the complexes have bands in the ranges 3 290—3 318 cm^{-1} and, with the exception of the sulphonamide, 1 620—1 642 cm^{-1}, assigned to the N–H stretch and C=O stretch of an amide, respectively. The sulphonamide has bands at 1 160 and 1 328 cm^{-1} assigned to vibrations of the SO_2 function. Further evidence for this complex comes from its mass spectrum, which has parent ion peaks at *m/z* 518 (^{58}Ni) and 520 (^{60}Ni).

Reaction with Succinimido Species.—A copolymer of n-butyl acrylate and *N*-acryloylsuccinimide was prepared using standard free-radical polymerisation techniques and its composition was determined by ^1H n.m.r. spectroscopy. A dichloromethane solution of this copolymer, containing the oxysuccinimide leaving group, was treated with complex (**1**)

Table 2. Proton n.m.r. data for the complexes[a]

Complex	H^8	H^3	H^{16}	H^{14}	$H^{6,7}$	H^{15}	$H^{11,13}$ $H^{1,5}$	NH	Substituent(s)
(1)	7.25 (s, 1 H)	4.90 (s, 1 H)	3.08 (t, 2 H)	3.30 (t, 2 H)	3.08, 2.93 (2 × t, 4 H)	1.96 (qnt, 2 H)	2.32, 2.18, 1.86, 1.74 (4 × s, 12 H)	1.68 (br s, 2 H)	
(2)	7.25 (s, 1 H)	4.93 (s, 1 H)	3.63 (q, 2 H)	3.32 (t, 2 H)	3.10, 2.95 (2 × t, 4 H)	1.93 (qnt, 2 H)	2.33, 2.19, 1.88, 1.76 (4 × s, 12 H)	6.07 (br s, 1 H)	1.93 (s, 3 H)
(3)	7.22 (s, 1 H)	4.90 (s, 1 H)	3.90 (q, 2 H)	3.40 (t, 2 H)	3.07, 2.92 (2 × t, 4 H)	2.03 (qnt, 2 H)	2.32, 2.17, 1.82, 1.66 (4 × s, 12 H)	6.97 (br t, 1 H)	7.3—7.8 (m, 5 H)
(4)	7.27 (s, 1 H)	4.95 (s, 1 H)	4.00 (q, 2 H)	3.46 (t, 2 H)	3.13, 3.00 (2 × t, 4 H)	2.08 (qnt, 2 H)	2.38, 2.23, 1.90, 1.70 (4 × s, 12 H)	6.75 (br, 1 H)	5.35 (dd, 1 H) 5.83 (d, 1 H) 6.75 (d, 1 H) 7.45 (d, 2 H) 7.72 (d, 2 H)
(5)	7.25 (s, 1 H)	4.95 (s, 1 H)	3.45 (q, 2 H)	3.25 (t, 2 H)	3.03, 2.90 (2 × t, 4 H)	1.88 (qnt, 2 H)	2.40, 2.20, 1.88, 1.75 (4 × s, 12 H)	5.37 (t, 1 H)	2.23 (s, 3 H) 7.50 (AB q, 4 H)
(6)[b]	7.55 (s, 1 H)		3.38 (m, 2 H)	3.30 (m, 2 H)	3.20, 3.05 (2 × t, 4 H)	2.25 (br, 2 H)	2.22, 2.20, 1.95, 1.75 (4 × s, 12 H)		2.60 (br s, 4 H)
(7)[c]	7.26 (s, 1 H)	4.97 (s, 1 H)	3.70 (q, 2 H)	3.32 (t, 2 H)	3.10, 2.97 (2 × s, 4 H)	1.97 (qnt, 2 H)	2.30, 2.19, 1.90, 1.78 (4 × s, 12 H)		6.06, 6.18, 5.59 (ABX m, 3 H)
(8)[b]	7.55 (s, 1 H)	5.13 (s, 1 H)	3.39 (t, 2 H)	3.30 (t, 2 H)	3.15, 3.00 (2 × t, 4 H)	2.28 (qnt, 2 H)	2.20, 2.18, 1.93, 1.75 (4 × s, 12 H)		
(9)[d]	7.45 (s, 1 H)	5.00 (s, 1 H)	3.35 (br)		3.15, 2.95 (2 × t, 4 H)	2.05 (br, 2 H)	2.28, 2.11, 1.88, 1.74 (4 × s, 12 H)		3.08 (s, 9 H)
(10)	7.30 (s, 1 H)	4.95 (s, 1 H)	3.72 (m, 2 H)	3.40 (m, 2 H)	3.16, 3.00 (2 × t, 4 H)	*e*	2.38, 2.22, 1.90, 1.79 (4 × s, 12 H)		3.48 (s, 6 H)
(11)	7.43 (s, 1 H)	4.56 (s, 1 H)	3.62 (t, 2 H)	3.15 (t, 2 H)	3.10, 2.94 (2 × t, 4 H)	1.80 (qnt, 2 H)	2.37, 2.23, 1.92, 1.88 (4 × s, 12 H)		

[a] In $CDCl_3$ solution, unless otherwise stated. [b] In D_2O solution. [c] In CD_2Cl_2 solution. [d] In $(CD_3)_2SO$ solution. [e] Signal obscured.

Table 3. ^{13}C N.m.r. data for the complexes

Complex	C^{10}	C^2	C^{12}	C^4	C^8	C^9	C^3	C^7	C^6	C^{14}	C^{16}	C^{15}	C^{11}	C^1	C^5	C^{13}	Substituent
(1)	192.2	174.9	167.6	165.0	156.4	113.1	99.2	59.6	51.6	45.7	39.8	35.8	27.3	24.0	21.2	18.0	
(2)	192.8	175.3	168.4	165.5	156.8	113.8	99.7	59.9	52.0	45.5	37.6	31.4	27.7	24.4	21.5	19.8	170.0, 23.2
(3)	192.7	175.4	168.4	165.5	156.8	113.7	99.7	59.8	51.8	44.5	38.0	31.2	27.7	24.3	21.5	19.7	167.5, 134.8, 131.8, 128.3, 126.9
(5)	192.9	175.2	168.6	165.6	156.7	113.7	99.9	59.9	51.9	44.9	41.4	31.0	27.8	24.3	21.4	19.9	143.0, 137.2, 129.5, 127.1, 21.6
(7)	192.6	175.0	168.1	165.3	156.7	113.3	99.5	59.7	51.7	45.6	37.4	31.1	27.4	24.1	21.3	19.6	171.7, 130.9, 125.6
(11)	192.6	157.8	167.8	159.6	156.2	113.2	99.5	59.4	51.6	45.5	46.2	27.9	27.4	21.0	21.0	18.5	

Table 4. Selected spectroscopic data for the complexes

Complex	$\lambda_{max.}$[a]/nm (ε/dm^3 mol^{-1} cm^{-1})	I.r. (cm^{-1}) ν(N–H)	I.r. (cm^{-1}) ν(C=O)	*m/z*
(1)	541 (170)	3 342, 3 290	1 578	364, 366
(2)	541 (210)	3 318	1 642	
(3)	535 (210)	3 320	1 630	
(4)	531 (195)	3 310	1 620	
(5)	537 (190)	3 290	—	518, 520
(6)	518 (165)[b]		1 670, 1 648	
(7)	535 (190)	3 300	1 652, 1 622	
(8)	520 (195)[b]	2 500, 2 030 (NH_3^+ bands)	1 626, 1 565	
(9)	532 (165)[c]		1 624, 1 572	
(11)	543 (180)		1 582	346, 348

[a] In $CHCl_3$ solution, unless otherwise indicated. [b] In water. [c] In $(CH_3)_2SO$ solution.

[mole ratio (**1**):oxysuccinimide 1:1]. Immediately a red-orange precipitate formed which was identified as the ammonium salt of (**1**), with oxysuccinimide as the anion. This salt is formed as a result of two reactions; first complex (**1**) behaves as a nucleophile, reacting with the copolymer to produce the polymer-bound complex and *N*-hydroxysuccinimide; secondly complex (**1**) behaves as a base, abstracting a proton from *N*-hydroxysuccinimide and producing the salt (**6**). The nature of this second reaction was confirmed by direct reaction of (**1**) with *N*-hydroxysuccinimide, resulting in further production of (**6**). The ^1H n.m.r. spectrum of (**6**) (Table 2), in D_2O solution, shows that several signals are shifted to lower field by 0.2—0.3 p.p.m. relative to the equivalent resonances in the spectrum of complex (**1**). The signal due to the NH_3^+ protons is not observed due to exchange with deuterium from the solvent. The protons of the oxysuccinimido anion appear as a broad peak at δ 2.6. It is perhaps surprising that the peak due to the proton of C^3, expected at *ca.* δ 5.1 is absent, particularly since it is observed in the spectrum of another salt of the same cation but with iodide as the counter ion (see below). It appears that in the presence of the oxysuccinimide anion this proton is acidic enough to undergo exchange with deuterium from the solvent.

The overall stoicheiometry of the reaction is as in equation (1)

$$2\ \text{R–NH}_2 + \underset{\textbf{(1)}}{\text{pol–COOsucc}} \longrightarrow \underset{\textbf{(6)}}{\text{pol–CONHR}} + \text{RNH}_3^+\ \text{Osucc}^- \quad (1)$$

where $Osucc^-$ = oxysuccinimido anion and pol = polymer. The polymer–complex mixture was isolated as a red solid by first concentrating the dichloromethane solution, then precipitating the product with cold methanol. Surprisingly, this product was insoluble in all solvents, apparently as a result of

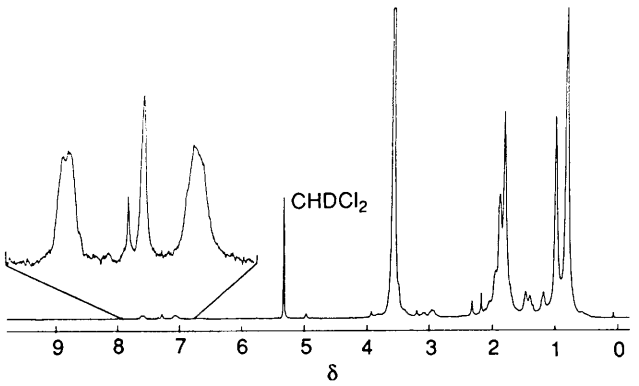


Figure. Proton n.m.r. spectrum of the copolymer of complex (**4**) with methyl methacrylate (mole ratio 0.012:1)

the polymer cross-linking during the work-up process. The nature of this cross-linking reaction is unknown but it is believed to involve nucleophilic attack on unreacted succinimido sites on the polymer backbone by carbon atom C^3. As mentioned above, the equivalent position in other complexes is known to have mild nucleophilic properties.[19] Support for this hypothesis comes from results from the reaction of the same copolymer with a large excess of complex (**1**), in an attempt to ensure that all of the succinimido groups are replaced by the complex. This reduces markedly the tendency toward cross-linking, although it does not remove it entirely.

The complex is further implicated as the origin of cross-linking from the results of a test reaction between the copolymer and propylamine. This produces the substituted copolymer and a white precipitate, identified spectroscopically as propylammonium *N*-oxidosuccinimide. The copolymer shows no evidence for cross-linking, implying that it is indeed the complex which is responsible for the cross-linking behaviour.

Direct reaction of complex (**1**) with *N*-acryloylsuccinimide produced the ammonium salt, (**6**), and the acryloyl-substituted complex (**7**). The ^1H n.m.r. spectrum of (**7**) is rather broad but clearly the proton attached to C^3 is present, implying that C^3 is not able to compete with the primary amine function in reaction with *N*-acryloylsuccinimide. The data from the ^{13}C n.m.r. spectrum are included in Table 3 and support the assigned structure. Complex (**7**) was prepared by an alternative route, by reaction of (**1**) with acryloyl chloride in the presence of triethylamine. Material prepared by this route is of higher purity and gives a sharp ^1H n.m.r. spectrum, for example clearly displaying the ABX splitting pattern of the acryloyl group.

Reaction with Iodomethane.—Reaction of a dichloromethane solution of complex (**1**) with an excess of iodomethane results in the formation of an orange-red precipitate, suspended in a dark red solution. The orange-red solid is water soluble and gives a positive test for iodide ion with $AgNO_3$ solution. The i.r. spectrum of the solid implies that it is an alkylammonium salt, with bands at 2 500 and 2 100 cm^{-1}. The species is assigned structure (**8**). The ^1H n.m.r. spectrum is virtually identical to that of the oxysuccinimide salt of the same cation, (**6**), except that a resonance due to the proton of C^3, at δ 5.13, is visible in this case. Treatment of (**8**) with triethylamine regenerates the starting material (**1**).

Work up of the deep red solution phase results in the isolation of a cherry red solid that has been characterised as the product of trimethylation of complex (**1**), the quaternary iodide salt (**9**). The most important spectroscopic feature of this complex is the singlet that is evident on the ^1H n.m.r. spectrum at δ 3.08, assigned to the protons of the $RNMe_3^+$ group (Table 2). Complex (**9**) is the expected product for the reaction of a primary amine with an excess of a methylating agent.

If a lower concentration of MeI is used in the reaction then the major product isolated from the reaction filtrate is the dimethylated material, (**10**). The ^1H n.m.r. spectrum of this complex has a singlet at δ 3.48, assigned to the protons of the $RNMe_2$ group (Table 2).

Polymerisation Reactions.—Complex (**4**) was copolymerised with methyl methacrylate. This acrylate ester was selected as previous work had demonstrated that it reacts readily with 4-vinylbenzoyl-substituted transition-metal complexes.[16] The free-radical-initiated polymerisation reaction was carried out in $CHCl_3$ solution, to ensure a homogeneous mixture of the comonomers. Chloroform is not generally regarded as a suitable solvent for free-radical polymerisation since it is well known to participate in chain-transfer reactions, leading to the production of short-chain polymers, but the low solubility of complex (**4**) in other solvents meant that no suitable alternative solvent for the polymerisation reaction was available.

Since the reactivities of styrene and methyl methacrylate with respect to free-radical polymerisation are similar, a random copolymer is expected, with approximately the same composition as that of the initial monomer mixture. This is borne out by experiment; in one polymerisation reaction, the initial mole ratio of complex to methyl methacrylate was 0.022:1 and analysis of the integral of the ^1H n.m.r. spectrum of the resulting copolymer indicated that the mole ratio was 0.029:1. This ratio is subject to variation. In a second polymerisation reaction, with the same mole ratio of reagent but with a shorter reaction time, the copolymer had a mole ratio of 0.012:1 (Figure).

The molecular weight of this second polymer was determined by gel permeation chromatography, using tetrahydrofuran (thf) as the eluant. The number average molecular weight, M_n, of the polymer was 7 900 g mol^{-1}, giving an average chain length of *ca.* 80 units. Thus, on average, there is one nickel(II) complex covalently bound to each polymer chain. Although the polymer is of relatively low molecular weight, as a result of the chain-transfer reactions promoted by the $CHCl_3$ solvent, the results clearly indicate that the complex has been incorporated successfully into the structure of the polymer *via* this copolymerisation route. The use of complexes with more advantageous solubility properties than complex (**4**) will allow production of polymers of higher molecular weight.

Synthesis of Macrocyclic Complex.—Formation of a 14-membered macrocyclic complex has been reported in the condensation reaction of 1,2-diaminoethane with the nickel(II) complex of 3-acetyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione (**12**).[17,20] The corresponding reaction using 1,3-diaminopropane produces, as the major product, complex (**1**), containing the pendant primary amine group.[17] Failure to achieve macrocyclic formation in the latter reaction has been rationalised in the literature in terms of the greater strain inherent in the trimethylene chain when forming the six-membered chelate ring of the 15-membered macrocycle. The condensation reaction occurs readily at the carbonyl carbon atom adjacent to the acetyl group but, unless the second carbonyl carbon atom is close to an electron-withdrawing group, which reduces the activation energy for formation of the strained transition state, subsequent ring closure does not occur. However, formation of the 15-membered macrocyclic complex (**11**) does in fact occur. By working up the filtrate from the isolation of complex (**1**), a small amount of dark red solid was isolated and this was characterised as complex (**11**).

The i.r. spectrum of complex (**11**) shows the absence of peaks due to N–H vibrations, implying formation of the imine. The ^1H and ^{13}C n.m.r. spectroscopic data are included in Tables 2 and 3

and fully support the proposed structure. Comparison with the spectra of complex (**1**) reveals some interesting features. In the ^{1}H n.m.r. spectrum of (**11**) the signal due to the protons of C^{16} appears some 0.54 p.p.m. downfield relative to the position of the equivalent protons in complex (**1**), consistent with the change in chemical environment of these protons upon cyclisation. Comparing the ^{13}C n.m.r. spectrum of (**11**) with that of (**1**), the resonance of C^2 is shifted to considerably higher field, by some 17.1 p.p.m., the signal for C^4 is shifted upfield by 5.4 p.p.m., the signal assigned to C^1 moves slightly upfield and overlaps with the signal ascribed to C^5, and the resonance position of C^{16} is moved 6.4 p.p.m. down field. All of these shifts are consistent with the replacement of a keto carbonyl and a primary amine by an imine as a result of the cyclocondensation reaction. The macrocyclic structure is further supported by the mass spectrum which has peaks at *m/z* 346 and 348, assigned to M^+ (^{58}Ni) and M^+ (^{60}Ni) of the molecular ion.

This 15-membered macrocycle has an interesting structural asymmetry and, in contrast to the 14-membered analogue, is likely to deviate from planarity as a result of the presence of the six-membered chelate ring containing the trimethylene chain. However, further studies of this complex are hampered by the low yield of the macrocyclic complex. Attempts to improve the yield by modifying the reaction conditions have so far proved unsuccessful.

Conclusion

The pendant amine substituent of a known complex, (**1**), has been shown to be a potent nucleophilic site and a number of derivatives have been prepared and characterised. The basic nature of the amine substituent has also been demonstrated and some alkylammonium salts isolated and identified. Complexes bearing polymerisable side chains have been prepared and one of these, the 4-vinylbenzoyl-substituted complex, undergoes copolymerisation with methyl methacrylate, under free-radical-initiated conditions, to produce a novel copolymer containing a covalently attached metal complex. An alternative route to complex/polymer species has been established, involving reaction of complex (**1**) with a suitably functionalised copolymer, although this species undergoes cross-linking of the polymer upon subsequent handling. Contrary to a literature report, a 15-membered macrocycle can be prepared by condensation of 1,3-diaminopropane with the nickel complex of 3-acetyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione, albeit in low yield.

Experimental

All materials were reagent grade. Solvents were purified by standard methods. *N*-Acryloylsuccinimide was prepared by the literature procedure.[21] N.m.r. spectra were recorded on a Bruker WP200 spectrometer, operating at 200.133 (^{1}H) or 50.323 MHz (^{13}C). Chemical shifts are reported with respect to an external tetramethylsilane reference (positive shifts to low field). Electronic spectra were recorded on a Shimadzu UV-240 spectrophotometer, i.r. spectra as Nujol mulls using a Perkin-Elmer 580 spectrophotometer, and mass spectra using a VG updated MS 9 spectrometer.

Preparation of Complexes.—(10-*Acetyl*-15-*amino*-4,11-*dimethyl*-5,8,12-*triazapentadeca*-3,8,10-*trien*-2-*onato*-N^5,N^8,N^{12},O)*nickel*(II), (**1**). This complex was prepared by a modification of the literature procedure.[17] A mixture of the precursor complex (**12**) (3 g, 9.7×10^{-3} mol) and 1,3-diaminopropane (30 cm^3) was heated at reflux for 30 min and allowed to cool. An equal volume of water was added and the mixture stored in a freezer overnight. The resulting red precipitate was collected by filtration and washed well with water and diethyl ether (1.4 g, 40%).

Complexes (**2**)—(**5**), and (**7**) were prepared by the same procedure and details are given for only one example. To a solution of complex (**1**) (0.200 g, 5.5×10^{-4} mol) in dichloromethane (20 cm^3) was added triethylamine (0.1 cm^3, 7.1×10^{-4} mol) and, dropwise with stirring, a solution of acetyl chloride (0.043 g, 5.5×10^{-4} mol) in dichloromethane (5 cm^3). After addition was complete, the reaction mixture was stirred for 15 min, then extracted with water. The organic layer was dried and the solvent was removed *in vacuo* to yield the product as a red solid.

(10-*Acetyl*-15-*ammonio*-5,11-*dimethyl*-5,8,12-*triazapentadeca*-3,8,10-*triene*-12-*onato*-N^5,N^8,N^{12},O)*nickel*(II) N-*oxidosuccinimide*, (**6**). To a solution of complex (**1**) (0.050 g, 1.3×10^{-4} mol) in dichloromethane (10 cm^3) was added *N*-hydroxysuccinimide (0.015 g, 1.3×10^{-4} mol). After 1 min a pinkish red solid precipitated which was collected by filtration, washed with dichloromethane and diethyl ether, and then dried (0.048 g, 77%).

(10-*Acetyl*-15-*acrylamido*-4,11-*dimethyl*-5,8,12-*triazapentadeca*-3,8,10-*triene*-12-*onato*-N^5,N^8,N^{12},O)*nickel*(II), (**7**). To a stirred solution of *N*-acryloylsuccinimide (0.5 g, 2.95×10^{-3} mol) in dichloromethane (30 cm^3) was added a solution of complex (**1**) (2.14 g, 5.9×10^{-3} mol) in dichloromethane (30 cm^3). After addition was complete, the reaction mixture was stirred for 1 h and the orange-red precipitate collected by filtration and identified from its i.r. spectrum as the oxysuccinimide salt, (**6**). The filtrate was evaporated to dryness then resolvated in dichloromethane. Addition of diethyl ether produced a pink solid (1.1 g, 90%).

Reaction of Complex (**1**) *with the Copolymer of* N-*Acryloylsuccinimide and n-Butyl Acrylate.*—Analysis of the ^{1}H n.m.r. spectrum of the copolymer indicated that the ratio of *N*-acryloylsuccinimide:n-butyl acrylate was 1:9.9. A sample of this copolymer (0.14 g) was dissolved in dichloromethane (6 cm^3) and complex (**1**) (0.050 g, 1.3×10^{-4} mol) was added to the stirred solution. After 5 min a solid had appeared and this was collected by filtration and identified from its i.r. spectrum as the salt (**6**). The filtrate was taken to dryness, leaving a sticky red solid. The i.r. spectrum of this material showed bands due to the complex, at 1 580 and 1 520 cm^{-1}, as well as bands due to the copolymer support. The sticky solid was redissolved in fresh dichloromethane and precipitated into methanol. The red solid obtained by this method would not redissolve, implying that cross-linking of the polymer chains had occurred during the purification procedure.

Reaction of Complex (**1**) *with Iodomethane: Production of Complexes* (**8**)—(**10**).—A series of reactions were performed at differing stoicheiometries. Typically, complex (**1**) (0.20 g, 5.5×10^{-4} mol) was dissolved in dichloromethane (30 cm^3) and iodomethane (0.2 cm^3, 3.21×10^{-3} mol) was added to the stirred solution. After a few minutes an orange precipitate was evident. The reaction mixture was stirred for 1 h, the precipitate was collected by filtration, and the filtrate reduced to dryness *in vacuo*. The orange precipitate was identified spectroscopically and chemically as the iodide salt (**8**) (0.156 g, 90%). The filtrate was taken to dryness by rotary evaporation and CH_2Cl_2 was added, resulting in the precipitation of a cherry red solid, complex (**9**) (0.08 g, 78%). If less MeI was used, the filtrate was soluble in CH_2Cl_2 and the major product isolated, after column chromatography on neutral alumina with CH_2Cl_2 as eluant, was the dimethylated derivative (**10**).

Copolymerisation of Complex (**4**) *with Methyl Methacrylate.*—A mixture of complex (**4**) (0.200 g, 4.05×10^{-4} mol), methyl

methacrylate (2.00 g, 2.0×10^{-2} mol), azobis(isobutyronitrile) (0.01 g, 6.1×10^{-5} mol), and chloroform (6 cm^3) was placed in a Pyrex tube and thoroughly degassed by the freeze–pump–thaw technique. The tube was sealed under vacuum and heated at 60 °C for 6 h. The polymeric product was isolated by precipitation with methanol and purified by three reprecipitations. The resulting red solid was dried in a vacuum oven.

[6-*Acetyl*-7,13,15-*trimethyl*-1,4,8,12-*tetra-azacyclopentadeca*-4,6,12,14-*tetraenato*(2−)]*nickel*(II) (**11**).—Reaction of complex (**12**) (1.56 g, 5.06×10^{-3} mol) with 1,3-diaminopropane (25 cm^3) produced complex (**1**), as described above. The excess of 1,3-diaminopropane was removed from the filtrate by successive addition of water and rotary evaporation of the resulting solution. When most of the diamine had been removed a dark red solid precipitated from solution and this was collected by filtration (0.048 g, 2.7%).

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