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SYNTHESIS AND REACTIONS OF NICKEL(III) COMPLEXES

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CONTENTS

A. INTRODUCTION

Although complexes of nickel(III) have been considered to be quite a recent discovery, a large number of complexes with this metal in a formally tervalent state have been reported [1], the earliest note dating back to 1936

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[2]. The first examples [2,3] were trihalophosphines, $Ni(PPh_3)X_3$ (X = Cl, Br, I) which were considered to be trigonal bipyramidal.

A major set-back in investigations into tervalent nickel complexes was the lack of a suitable method of authentication of the 3+ metal centre. Characterisation relied on magnetic susceptibility measurements, which showed only the presence of a single unpaired electron, not its location. Whether the electron was truly centred on the metal in a d^7 configuration for nickel(III), or was delocalised over the coordinated ligand(s) in a nickel(II)-stabilised radical could not be discerned by such means. Application of electron spin resonance spectroscopy has clarified the situation, the latter species exhibiting an isotropic signal with a g value close to that of the free electron (2.0032 g). This characteristic, like that of organic free radicals, indicates the unpaired electron to be unassociated with any particular (metal) centre. Authentic Ni(III) complexes are predicted to display anisotropic resonances, consistent with low spin d^7 systems, the odd electron associated mainly with the d_z^2 orbital [4].

Examples displaying this ambiguity include the large number of dithiolate complexes of nickel [5]. These were first thought to contain nickel(III), but were later shown by ESR to be nickel(II)-stabilised ligand radicals [6]. An earlier report had already shown that for such a complex containing the ^{61}Ni isotope little unpaired spin resided on the metal [7], since very little hyperfine splitting was observable. Many similar complexes are also best described by such electronic structures, for example $[Ni(diars^*)_2Cl_2]Cl$ [8], $[Ni(diars)_2X_2]Y$ (X = Br, I, SCN; Y = Br, I, SCN, ClO_4, 1/2 $PtCl_6$) [9] (μ_{eff} ranging from 1.88 to 1.96), and a triarsine nickel complex [10] $NiTBr_3$ **. Kreisman et al. [11] showed conclusively that the $[Ni(diars)_2Cl_2]^+$ cation was indeed a radical species by comparison with the uncomplexed $(diars)^+$ radical, which exhibited a very similar ESR spectrum. Further, the X-ray structure of the nickel complex showed the Ni–As bond lengths to be greater than in the corresponding $Ni(diars)_2I_2$ species [12]. Similarly, sulphur [13] and nitrogen/sulphur [14] donor-containing ligands have been shown by ESR and by polarography to form nickel(II)-radicals.

Theoretical ESR spectra of low spin d^7 nickel(III) complexes may be calculated [4] to have two resonance features, with $g_{\parallel} = 2.002$ and $g_{\perp} = 2.002 - 6\lambda/\Delta E_{z^2-xz,yz}$ ***. The first successful application of this approach was provided by Gore and Busch [15]. They verified the nickel(III) centre in a series of complex cations $[NiLX_2]^+$ where L is the tetraaza macrocycle,

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* diars = o-phenylenebis(dimethylarsine).

** $T = CH_3As(CH_2)_3As(CH_3)2$.

*** λ = spin-orbit coupling constant; $E_{z^2-xz,yz}$ = crystal-field splitting for a tetragonal d^7 complex.

$Me_2[14]aneN_4$, and X is Cl, Br, NCO, NO_3 and 1/2 SO_4 (vide infra). Prior to this report, several workers had published work on oxidized products of nickel(II) tetraaza macrocycles which were purported to contain true nickel(III) centres [16–18]. Further work [19,20] has shown that complexes containing such ligands do, in fact, stabilise the tervalent nickel state.

Why some ligands stabilise this 'unusual' oxidation state and others do not has been discussed by Drago and Baucom [21]. They have reported the preparation and characterisation of a borderline (between Ni(III) and Ni(II)-radical) complex of pyridine oxime ligands, $Ni(BPO)_3$ *. The electronic effects of the ligands are explained in terms of *E* and *C* parameters [22], relating to concentration of charge on donor atoms and σ-donor properties of these atoms respectively. Generally, it appears that saturated nitrogen-donor macrocycles (which are highly resistant to dissociation from a central metal ion [23]) have high *E* and *C* values, and stabilize the high oxidation state very well. Conversely, ligands with (i) donor atoms of low *E* and *C* value (for example As in diars), or (ii) large conjugated π systems (for example *o*-phenylenediamine [14]) tend to delocalise the unpaired electron throughout the ligand.

In addition to the examples referred to above, there are a large number of complexes containing such ligands, existing as nickel(II)-stabilised radicals [1,24]. However, it is the primary purpose of this article to review the chemistry and reactivity of complexes of nickel(III). With the discovery of facile routes to the syntheses of many macrocyclic and related nitrogen-donor ligands [25] has come a number of investigations into the chemistry of their coordination complexes. In this report we will describe the types of ligand stabilising the tervalent nickel centre, and the synthesis, characterisation, solution chemistry and kinetic behaviour of these metal complexes.

After this review had been submitted, the existence of another article on the unusual oxidation states of nickel was made known to the authors. In this **, an account of mono-, tri- and tetravalent nickel complexes is presented. Attention is paid to oxides, cyano and fluoro complexes and organometallic systems as well as to nitrogen donor and macrocyclic ligands. Various metal–ligand radical systems are also discussed. Some overlap of material especially in ESR and electrochemical data occurs when compared with this review. The emphasis here on the trivalent state and the approach

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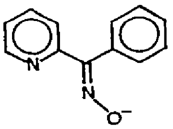
* BPO = benzoylpyridine oximato



** K. Nag and A. Chakravorty, Coord. Chem. Rev., 33 (1980) 87.

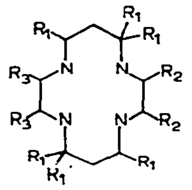
in presentation are quite different. We have also included some recent data on kinetics and mechanisms which may be seen as complementary to some of the aspects presented previously.

B. STABILITY AND LIGAND TYPE

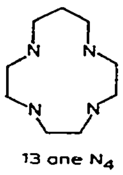
There are several main categories of ligands which stabilise tervalent nickel in both the solid state and in solution.

(i) Tetraaza macrocycles

Such ligands, having varying degrees of saturation, ring size and numbers of substituents (Structures I(a) and I(b)) are fairly readily synthesized [26]. Their chemical properties, and those of their nickel(II) complexes have been thoroughly studied and reviewed previously [27].



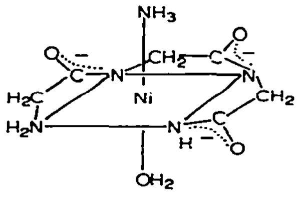
I (a)



I (b)

(ii) Deprotonated peptides

Studies into nickel [28] (and copper [29]) complexes containing oligopeptide ligands have shown these biologically significant species to stabilise the tervalent state. As in the previous ligand-type, these peptides form square-planar geometries about the metal ion, coordinating via four nitrogens [30] (see II).



II

(iii) Porphyrins

Transition metal complexes of these ligands are well known [31] for their multi-faceted electrochemical behaviour. In spite of their predictable ready formation of ligand-radicals on electron transfer, Ni(III) complexes have been observed and characterised (vide infra).

(iv) α-Diimines

Although these ligands are highly unsaturated, for example, *o*-phenanthroline, they have recently been shown to stabilise Ni(III) in non-aqueous [32] and in strongly acidic [33] aqueous media.

(v) Amines and aminocarboxylates

Ni(III) complexes of ammonia [34], ethylenediamine and glycine [35] may be formed. The transient nature of these species is doubtless due to their substitution-lability, and the medium in which they were prepared. These complexes will be considered later. EDTA has also been shown to stabilise Ni(III) for several days [36].

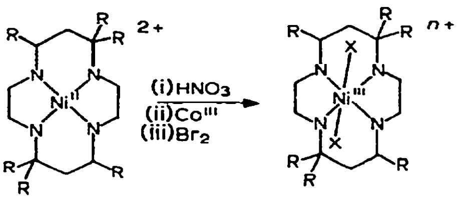
C. SYNTHESIS

A list containing the names and abbreviations of ligands referred to in this article is given in Table 1.

A variety of methods has been utilised to generate Ni(III) complexes, via oxidation of the Ni(II) analogue. These include chemical and electrolytic reactions in both aqueous and non-aqueous media, in addition to pulse radiolytic and flash photolytic techniques.

(i) Chemical oxidation

The first reported preparation of an authentic nickel(III) complex was by Cook and Curtis [16], using concentrated nitric acid. They found that addition of the acid to aqueous solutions of $[Ni(II)L](ClO_4)_2$ (L = tet-*a* or tet-*b*) produced dark green solutions. Compounds of formula $[Ni(III)L(NO_3)_2]ClO_4$ were isolated on dilution. The magnetic moments of the products indicated a single unpaired electron. In the presence of sulphate



(i) R = H, Me. conc. HNO_3, $X = NO_3^-$ $n = 1$

(ii) R = H, Me. 1.0M $HClO_4$, $X = OH_2$ $n = 3$

(iii) R = H. $X = Br^-$ $n = 1$

TABLE 1
Nomenclature and abbreviations of ligands [a] referred to in text

Name	Abbreviation	Structure [b]
(1) Tetraazamacrocycles		
1,4,8,11-tetraazacyclotetradecane	[14]aneN_4 or cyclam	$R_1 = R_2 = R_3 = H$ (I(a))
2,3-dimethyl	Me_2[14]aneN_4 or Me_2cyclam	$R_1 = R_3 = H$; $R_2 = Me$
2,3,9,10-tetramethyl	Me_4[14]aneN_4 or Me_4cyclam	$R_1 = H$; $R_2 = R_3 = Me$
5,7,7,12,14,14-hexamethyl	*ms*-(5,12)-Me_6[14]aneN_4, Me_6cyclam or tet-*a*	$R_1 = Me$; $R_2 = R_3 = H$
5,5,7,12,14,14-	*rac*-(5,14)-Me_6[14]aneN_4 or tet-*c*	
1,4,7,10-tetraazacyclotetranonane	[13]aneN_4	Structure I(b)
(2) Unsaturated versions of structure I [c]		
3,4:7,8:11,12:15,16-Bzo_4-[16]-1,3,5,7,9,11,13,15-octaene-1,5,9,13-N_4 (Bzo_4[16]octaeneN_4)	TAAB	See text (VII)
Tetraphenylporphine	TPP	
2,13-dimethyl-3,6,9,12,18-pentaazabicyclo-[12.3.1]-octadeca-1-(18)14,16-triene-(Me_2pyo[15]eneN_5)	Pyane N_5	See text (X)
Ditrityldihydrooctaaza[14]annulene anion	$DTOA^{2-}$	See text (XI)
1,10-phenanthroline	Phen	
2,2′-dipyridyl	Bipy	

[a] Peptide abbreviations given in Tables 2 and 4.
[b] See structure I(a) in text.
[c] Named using the same numbering system.

ions, the same reaction produced material of formula [Ni(III)LSO$_4$]ClO$_4$. It is interesting to note that oxidation of nickel(II) complexes containing unsaturated-ligands results in oxidative dehydrogenation of the ligand [37]. Other oxidants have been used successfully in aqueous media to generate relatively stable nickel(III) complexes. Ce(IV) and Co(III) aquo ions [38] have been employed in the oxidation of the [Ni(II)cyclam]$^{2+}$ cation in aqueous perchloric acid **. Peroxodisulphate ion has been used preparatively in several instances. Gore and Busch [15] used the ammonium salt to oxidise the [Ni(II)(Me$_2$[14]aneN$_4$)$^{2+}$ cation producing [Ni(III)LSO$_4$]$^+$. This sulphate complex is remarkably stable, as are its analogues for L = tet-*a* [39] and cyclam [20,39]. There is some ambiguity as to the exact nature of these Ni(III) sulphate complexes. Cook and Curtis [16] assigned the anomalous magnetic behaviour of their sample to an antiferromagnetic mechanism via superexchange through bridging SO_4^{2-} ligands in the solid state. Gore and Busch [15] found the complex to be a 1 : 1 electrolyte from conductance measurements, and assigned a *cis* configuration to the macrocycle. Busch and co-workers [40] have also used $(NH_4)_2S_2O_8$ to oxidise a pentadentate macrocyclic nickel(II) complex, [Ni(II)(pyaneN$_5$)(OH$_2$)]$^{2+}$. They characterised the Ni(III) product as the monoaquo(ligand)nickel(III) cation, but made no mention of a sulphate adduct. The hexachloroiridate ion, $IrCl_6^{2-}$, has been used by Bossu and Margerum [28] to quantitatively oxidise nickel(II) peptides to the corresponding nickel(III) complexes. The same technique has been adopted by Sugiura and Mino [41] in their production of nickel(III) complexes of histidine-containing tripeptides and bleomycin. Bossu et al. [42] have shown that molecular oxygen produces a tervalent nickel peptide complex which is the reactive intermediate in the autoxidation of nickel(II) tetraglycine.

Non-aqueous chemical methods of generation of nickel(III) complexes have been investigated by Barefield and Busch [43]. Both *rac*-(5,14)-(*cis*-) and *ms*-(5,12)-(*trans*)Me$_6$[14]aneN$_4$ complexes * of Ni(II), as well as [Ni(II)cyclam]$^{2+}$ were cleanly oxidized by NO$^+$ in acetonitrile producing high yields of the corresponding dark green [Ni(III)L(MeCN)$_2$]$^{3+}$ species, and nitric oxide.

$$NO^+ + Ni^{II}L \xrightarrow{CH_3CN} Ni^{III}L(CH_3CN)_2 + NO$$

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* Here the isomerism refers to the positions of the *gem* dimethyl groups in the ligands. Unless otherwise indicated, the *ms*-(5,12)- isomer is referred to in the text.

** CAUTION: Many of these complexes have been isolated as perchlorate salts. Although most may be handled under normal laboratory conditions, these species should be regarded as potential hazards. Care should be taken when dealing with solutions in organic solvents and when evaporating solutions containing perchlorates.

The two solvent molecules are not removed in vacuo. Magnetic moments ($\mu_{\text{eff}} = 2.0$ BM for L = cyclam and 2.15 BM for *cis*-$Me_6[14]aneN_4$) indicate a single unpaired electron. Infrared spectra indicate no oxidation of the ligands (N–H bands present, C = N bands absent), and confirm the presence of acetonitrile ($C \equiv N$ bands). Although five-coordinate complexes of the type $Ni(DPG)_2X$, formed by the oxidation of $Ni(DPG)_2$ (DPG = diphenyl glyoximato) by X_2 in the solid state, are inclusion-like complexes of nickel(II) [44], an authentic nickel(III) complex is formed when the reaction is carried out in a nitrogen-donor solvent [45]. In pyridine solvent, the $[Ni(III)(DPG)_2(py)_2]^+$ cation ($\mu_{\text{eff}} = 2.07$ BM) is produced. This species is unstable in aqueous solution. Spacu et al. [46] reported the oxidation of nickel(II) complexes of paludrine by ClO_2^- in DMSO. The products, $[NiL_3]Cl_3$, $[NiL]Cl_3$ and $[NiL_2(OH_2)_2](OH)_3$ were assumed to be Ni(III) complexes on the basis of their microanalysis, magnetic moments (1.78, 1.63 and 1.69 BM respectively) and the formation of the respective Ni(II) complexes on reaction in alcohol with reducing agents such as $H_2PO_2^-$, $SnCl_2$, BH_4^-, and $N_2H_4 \cdot HCl$. Reversible one-electron polarograms in DMF were also observed for the nickel(III) species.

(ii) Electrolytic oxidation

This is by far the most widely used of the methods for generating nickel(III) complexes. The technique was first employed by Olsen and Vasilevskis [47]. Generally, a suitable quantity (ca. 0.1 g per 100 ml solvent) of nickel(II) complex is oxidised in acetonitrile solvent under an inert atmosphere, at platinum electrodes. A tetraalkylammonium salt (usually the perchlorate) is present as supporting electrolyte (ca. 0.1 M), and the constant potential which is applied is slightly in excess of the measured electrode potential of the complex under investigation. The procedure is carried out in the dark at ca. 5°C. The latter precautions are advisable to counter the often labile nature of the products, and to avert possible photoreduction reactions [48].

In this manner, Olsen and Vasilevskis [47] isolated the dark green complexes $[Ni(III)L(MeCN)_2]^{3+}$, for L = cyclam, *rac*-(5,14)- and *ms*-(5,12)-$Me_6[14]aneN_4$ and the corresponding 4,11- and 4,13-dienes. Following this pioneering work, Busch and co-workers [19] provided an in-depth electrochemical study of nickel(II) complexes, comprising some twenty-seven tetraaza macrocyclic ligands. The implications of this work are discussed below. Electrolytic reduction of $[Ni(TAAB)](ClO_4)_2$ in acetonitrile produced the dark green species $[Ni(TAAB)]ClO_4$, which has been shown to contain a Ni(III) centre with a dianionic ligand [49]. Solid nickel(III) complexes of the type $[Ni(III)(LL)_3]^{3+}$ have been isolated [32] as the perchlorate salts by the above method. The bidentate ligands, LL, include 1,10-phenanthroline and its substituted derivatives, X-phen (X = 5-Me, 5-Cl, 5-NO_2 and 4,7-$Me_2$2,2′-bipyridyl and 4,4′-$Me_2$2,2′-bipyridyl.

Electrolysis in aqueous solution is less popular owing to the instability of many nickel(III) complexes in water at high pH [50]. However, the stability increases dramatically with increased [H^+] and $[Ni(III)(bipy)_3]^{3+}$ has been prepared in situ [33] by electrolysis of the Ni(II) analogue in 2.0 M perchloric acid. Very low yields were obtained, however, owing to the extremely low solubility of the diperchlorate salt, and the unstable nature of the product in the medium.

The most successful application of aqueous electrolysis has been the work of Margerum and co-workers with oligopeptide complexes of nickel(II) [28,51,52]. A flow electrolysis system was used, which contained a graphite powder working electrode packed in a porous glass column, wrapped externally with a platinum wire electrode [51]. It is notable that these complexes are relatively stable in aqueous solution, their electrode potentials being measured at pH 9.3 [28]. Axial coordination by ammonia enhances the stability of the Ni(III) complexes [53]. Since the discovery [15] that axial coordination of simple ligands stabilises nickel(III) complexes dramatically, some electrolytic oxidations have been performed in the presence of such ligands. Meyerstein and co-workers [20] thus prepared sulphate adducts of nickel(III) macrocycles. Phosphate ion similarly enhances stability [54], although to a lesser extent. It has been observed [54] that non-aqueous electrolysis of $[Ni(II)cyclam]^{2+}$ using Et_4NX (X = Cl, Br) as supporting electrolyte yields $[Ni(III)(cyclam)X_2]^+$ as the product.

(iii) Pulse-radiolysis/flash photolysis

These techniques involve oxidation of nickel(II) complexes in aqueous solution by X_2^- radicals [56]. Such radicals are generated by (i) reaction of $\dot{O}H$ radicals (from pulse-radiolysis of water) with X^- ions, or (ii) by a similar route, using $\dot{O}H$ radicals from flash photolysis of hydrogen peroxide [57]. These highly specialised techniques are not normally used preparatively. However, Meyerstein and co-workers [39,58] have shown that such procedures carried out in the presence of sulphate ion yield the corresponding $[Ni(III)LSO_4]^+$ cation, which is readily isolated from solution.

D. CHARACTERISATION

(i) ESR spectroscopy

Early work [2,3,5–12] on formally nickel(III) complexes based its evidence for the tervalent state solely on microanalytical and magnetic susceptibility measurements. As noted earlier, these methods cannot distinguish between nickel(II)-stabilised ligand radicals and authentic d^7 nickel(III) complexes. In this regard, ESR spectroscopy has proven extremely successful in clarifying this ambiguous situation. Electrochemical techniques, such as cyclic voltammetry and polarography have also provided much additional information concerning the nature of the metal ion, in terms of the reversible character of electron-transfer processes of the complexes. In support, IR spectra have been used to elucidate the structure of the ligands in the oxidised complexes. Nickel(III) complexes exhibit characteristic UV/visible spectra. These have in some instances been analyzed, and used to predict ESR parameters (vide infra).

In their study of $[\mathrm{Ni(III)LX_2}]^+$ complexes (L = $\mathrm{Me_2[14]aneN_4}$), Gore and Busch [15] made extensive use of ESR. From the electronic spectra, the crystal field splitting was estimated at 15,000 $\mathrm{cm^{-1}}$. Hence, using the method of Maki et al. [4], the ESR spectrum for a low spin tetragonally distorted octahedral d^7 system, with axial symmetry, was predicted to have $g_{\parallel}$ ca. 2.00 and $g_{\perp}$ ca. 2.2. The observed ESR spectra corresponded closely (Table 2) to those calculated, establishing unequivocally the existence of Ni(III). Further, calculation of the spin-orbit coupling constants, λ, for different axial ligands, $\mathrm{X^-}$, showed the observed λ's to follow the nephelauxetic series, as expected [59]. The unpaired electron was shown to occupy principally the d_{z^2} orbital as evidenced by observed superhyperfine splitting of the $g_{\parallel}$ feature, due to interaction of the electron with the axially bound ligands. Thus, for X = $\mathrm{NCO^-}$, a quintet ($a_{\parallel} = 22$ G); $\mathrm{Br^-}$, a septet ($a_{\parallel} = 57$ G) was observed. These results are in accord with two equivalent axial ligands. The $g_{\parallel}$ values were significantly different from the predicted g value of 2.00, suggesting the ground state to contain a small admixture of $d_{x^2-y^2}$. Busch and co-workers [19] subsequently examined the ESR spectra of a wide range of nickel(III) complexes, of general formula $[\mathrm{Ni(III)L'(MeCN)_2}]^{3+}$, in frozen acetonitrile at 77 K. From Table 2, it may be seen that the two characteristic features were observed, with $g_{\perp} \simeq 2.02$ and $g_{\parallel} \simeq 2.2$ G. In these systems, interaction of the unpaired electron in the d_{z^2} orbital with the two equivalent axially-coordinated nitrogen ($I = 1$)-donor atoms from acetonitrile produces the predictable 1:2:3:2:1 intensity quintet splitting of the $g_{\parallel}$ features, with $a_{\parallel} = 21$–25 G. Splitting of the $g_{\perp}$ features was also evident, but not well resolved.

Desideri et al. [61] have studied the ESR of $[\mathrm{Ni(III)(cyclam)X_2}]^+$ cations in DMSO at liquid nitrogen temperatures. The results (Table 2) are consistent with the deductions of Busch and co-workers [19]. For the *trans*-dichloro complex a 1:2:3:4:3:2:1 septet was observed in the $g_{\parallel}$ region. This pattern is expected for coupling of a d_{z^2} electron with two equivalent axial donor chlorine ($I = 3/2$) atoms. No splitting was detectable in the $g_{\perp}$

TABLE 2
ESR parameters of Ni(III) complexes, in acetonitrile at 77 K[a]

L	X,X′[b]	$g_\perp$[c]	$g_\parallel$	$a_\parallel$(G)[d]	Ref.
(i) Octahedral complexes of type $[Ni(III)LX_2]^{n+}$					
Cyclam	MeCN	2.215	2.025		62
	Cl	2.193 (2.18)[e]	2.027(5) (2.022)[e]	(28)[e]	62 (61)
	Br	2.17	2.014 (s)	39	61
	DMSO[g]	2.242	2.026		61
	OH_2[h]	2.219	2.033		62
	NO_3	2.240	2.034		62
	$\frac{1}{2}SO_4$[h]	2.232	2.026		20
	NCS	2.208	2.048 (q)		62
Me_2cyclam[i]	MeCN	2.205	2.020 (q)	21.3	15
	Cl	2.181	2.025		15
	Br	2.171	2.022 (s)	57	15
	NCO	2.169	2.055 (q)	22	15
	NO_3	2.221, 2.182[j]	2.103		15
	$\frac{1}{2}SO_4$	2.165[k]	2.165[k]		15
Me_6cyclam	MeCN	2.215	2.029 (q)	21.3	19
	$\frac{1}{2}SO_4$[h]	2.238	2.028		20
Me_6[14]4,11-dieneN$_4$	MeCN	2.199	2.024 (q)	22.5	19
	$\frac{1}{2}SO_4$[h]	2.232	2.021		20
	OH_2	2.22	2.002		48
Me_2[14]1,3-dieneN$_4$	MeCN	2.197	2.023 (q)	23.1	19
Me_6[14]1,4,8,11-tetraeneN$_4$	MeCN	2.186	2.018 (q)	24.2	19
Me_4[14]1,3,8,10-tetraeneN$_4$	MeCN	2.172	2.023 (q)	25.4	19
Me_6[14]1,3,7,11-tetraeneN$_4$	MeCN	2.180	2.016 (q)	24.0	19
(CR + 4 H)	MeCN	2.198	2.023 (q)	22.2	19
CR	MeCN	2.175	2.023 (q)	23.9	19
TAAB	MeCN	2.198	2.031 (q)	21.6	49
DPG	Py[l]	2.162	2.034 (q)	20.1	45
(ii) $[Ni(III)(pyrone\text{-}N_5)(OH_2)]^{3+}$		2.155	2.022 (t)	23	40
(iii) Square-planar complexes $[Ni(III)L]^{-}$					
$TAAB^{2-}$		2.023	2.16		49
Me_2[15]tetraenoN$_4^{2-}$		2.012	2.144		49
$Me_2(CH_3CO)_2$[14]tetraeneoN$_4^{2-}$[m]		2.016 (2.012)	2.138 (2.144)		19
TPP^{2-}		2.295	2.116		64
$DTOA^{2-}$		2.02, 1.99[j]	2.127		74

TABLE 2 (continued)

L	X,X' [b]	$g_\perp$ [c]	$g_\parallel$	$a_\parallel$(G) [d]	Ref.
(iv) Ni(III)-peptides [n]					
$H_{-2}G_3^{3-}$	OH_2	2.242, 2.295 [j]	2.015		53
$H_{-2}G_2his^{3-}$	OH_2	2.259, 2.278 [j]	2.015		53
$H_{-3}G_4^{4-}$	OH_2	2.297, 2.278	2.010		53
$H_{-3}G_5^{4-}$	OH_2	2.340, 2.278 [j]	2.011		53
$H_{-3}G_3a^{3-}$	OH_2	2.310, 2.281 [j]	2.006		53
	OH_2, NH_3	2.217	2.011 (t)	23.4	53
	NH_3	2.178	2.019 (q)	19	53
$(H_{-2}G_3a)(H_{-1}G_3a)$	—	2.196	2.023 (t)	21.3	53
MAHH [q]	OH_2	2.264, 2.196 [j]	2.021	23.8	41
	MeIm [p]	2.175	2.025	22.4	41
	NH_3	2.168	2.025	22.4	41
ox-MAHH [q]		2.237, 2.176 [j]	2.021	23.8	41
MAGH [q]		2.274, 2.206 [j]	2.017		41
oxMAGH [q]		2.240, 2.284	2.016		41
$(oxMAGH)_2$ [q]		2.170, 2.220 [j]	2.020	23.8	41
GGH	OH_2	2.254, 2.277 [j]	2.016		41
	NH_3	2.162	2.024	22.0	41
$(GGH)_2$		2.177, 2.218 [j]	2.019	23.8	41
Bleomycin-A_2		2.169	2.027	22.4	41
P-3 A [q]		2.235, 2.163 [j]	2.022	23.5	41
(v) tris-bidentate chelates, $[Ni(III)(LL)_3]^{3+}$					
		g_{iso}			
phen		2.106			32
5-Me phen		2.107			32
5-Cl phen		2.107			32
$5-NO_2phen$		2.107			32
Bipy		2.102			32
4,4'-Me_2bipy		2.098			32

[a] Unless otherwise indicated. [b] One value given where X=X'. [c] One value where $g_{xx} = g_{yy} = g_\perp$. [d] $a_\parallel$ = superhyperfine coupling constant of $g_\parallel$ signal. [e] Values in parentheses from ref. 61. [f] Letter in parentheses refers to no. of lines observed in splitting; t = triplet, q = quintet, s = septet. [g] DMSO solvent. [h] Aqueous medium. [i] Solid sample at room temperature. [j] Non-axially symmetric, $g_{xx} \neq g_{yy}$. [k] Single broad isotropic signal. [l] In pyridine solvent. [m] In ethylene chloride. [n] See footnote b in Table 4 for abbreviations and nomenclature. [p] MeIM = *N*-methylimidazole. [q] MAHH = *N*-Mercaptoacetyl-OL-histidyl-DL-histidine, MAGH = *N*-Mercaptoacetylglycyl-L-histidine, ox-MAHH = oxidised (disulphide) form of MAHH, P-3A = biosynthetic intermediate of bleomycin A_2.

region. This observation suggests that to some extent the spin density resides on the chlorine atoms, with very little contribution from the $d_{x^2-y^2}$ orbital in the ground state. Identical results have been produced for this complex in acetonitrile solvent (Fig. 1) and in strong (ca. 0.3 M) aqueous LiCl [32]. The latter medium is necessary to prevent dissociation of the Cl^- ligands [62]. The spectrum of the *trans*-dibromo complex in DMSO [61] was found to be complicated by the presence of the two isotopes, ^{79}Br and ^{81}Br, both with nuclear spin of 3/2. The dihalo-spectra in DMSO, like those in water [32] were attainable only in high concentrations of X^-. Without these anions present, spectra consistent with mixtures of mono- and dihalo complexes were observed. In these cases, the spectra of the monohalo species exhibited three *g*-values, a phenomenon which was interpreted as a change to lower symmetry about the Ni(III) centre. Dissolution of [Ni(III)(cyclam)-$(NO_3)_2$]ClO_4 in perchloric acid [62] yields an ESR spectrum consistent with an axially symmetric (Fig. 2) low spin d^7 system at 77 K, as does the room temperature spectrum of a solid sample. The NO_3 groups are not coordinated in solution but are replaced by two solvent molecules. This is shown by the existence of a 1:2:3:2:1 quintet in the $g_\parallel$ region in acetonitrile solvent. In the reactions of halide and pseudohalide ions with the [Ni(III)(cyclam)(OH_2)]$^{3+}$, essentially an ESR "titration", analogous to those in visible spectrophotometry, at 273 K indicated only one ligand to coordinate under kinetic conditions (see later section). For thiocyanate as the incoming ligand, three lines were observed in the $g_\parallel$, consistent with formation of a mono-isothiocyanato complex, in the presence of an excess of the diaquo-nickel(III) precursor. For excess thiocyanate, five-line splittings were observed, indicating coordination of two axial ligands (Fig. 3). The [Ni(III)$(DPG)_2(py)_2$]$^+$ cation in pyridine solvent displays an analogous ESR spectrum [45] to the complexes noted above. The frozen ESR spectrum of

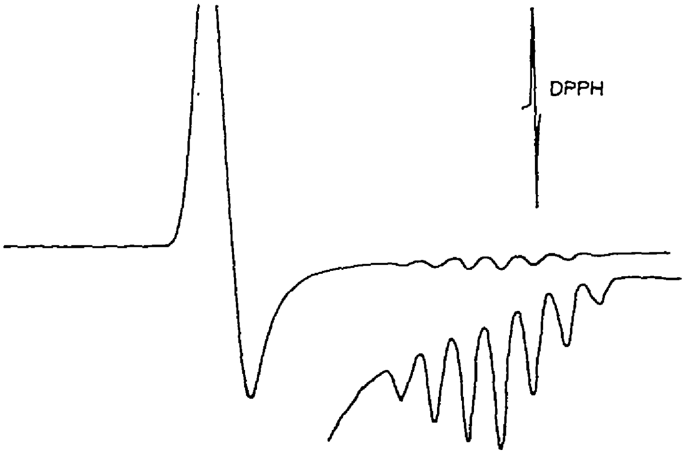


Fig. 1. ESR spectrum of Ni(cyclam)Cl_2^+ ion in MeCN, $T = 77$ K.

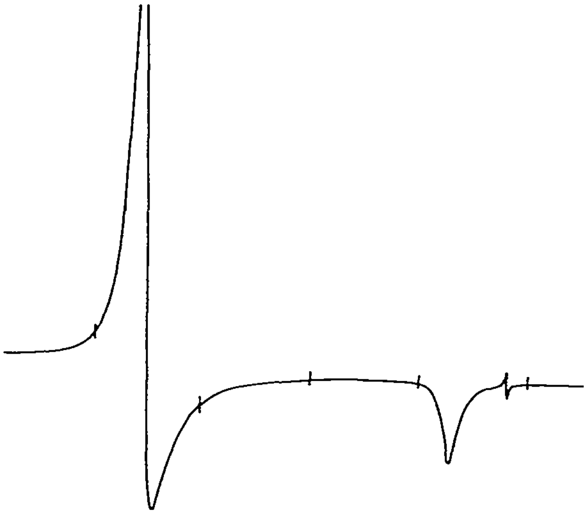


Fig. 2. ESR spectrum of Ni(cyclam)$(H_2O)_2^{3+}$ ion prepared by dissolution of [Ni(cyclam)$(NO_3)_2$][ClO_4] in 1.0 M perchloric acid.

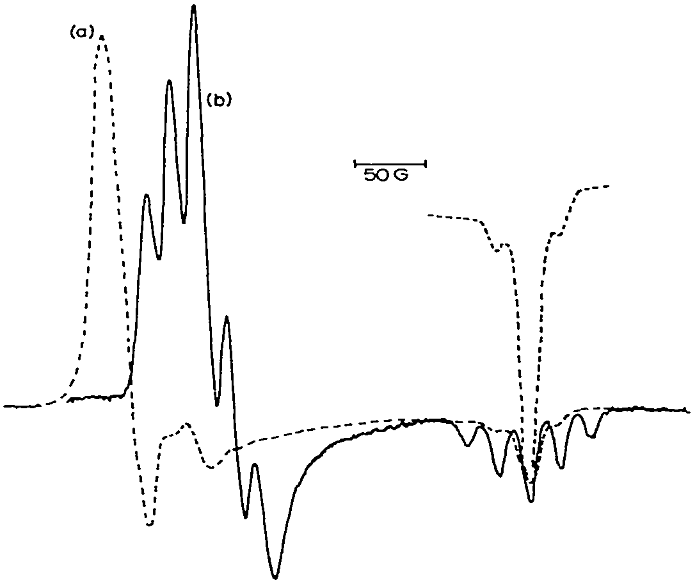


Fig. 3. ESR spectra of (a) [Ni(cyclam)NCS^{2+}] and (b) [Ni(cyclam)$(NCS)_2^+$] ions. Spectrum (a) was measured in excess Ni(III) and shows the presence of the aquo ion in addition to the monothiocyanate complex. Spectrum (b) was obtained using a large excess of NCS^- (see ref. 62).

the iodide salt, obtained either by dissolution of $Ni(DPG)_2I$ in pyridine or by oxidation of $Ni(II)(DPG)_2$ by iodine in that solvent, exhibits the typical pattern assigned to Ni(III). Superhyperfine splitting of the $g_{\parallel}$ feature at 2.034 into a 1:2:3:2:1 quintet is observed, with no resolved fine structure apparent in the $g_{\perp}$ region (2.162).

There is currently some question as to the structure of complexes of the type $[Ni(III)LSO_4]^+$. As mentioned earlier, the complex containing $Me_6[14]aneN_4$ [16] was suggested to contain bridging SO_4^{2-} ligands. Later [15], the $Me_2[14]aneN_4$ analogue was assumed to contain a bidentate SO_4^{2-} ligand with the macrocycle adopting a *cis* configuration. This is not unreasonable, since cyclam can have such a geometry in Co(III) complexes [62], in the presence of bidentate ligands such as CO_3^{2-}. In the oxidation of $[Ni(II)(pyaneN_5)]^{2+}$ (X) by peroxodisulphate, the product is characterised as a nickel(III) complex with all five nitrogen donor atoms of the macrocycle coordinated. The formula is assumed to be $[Ni(III)(pyaneN_5)(OH_2)]^{3+}$, with no mention of a sulphato adduct. If this is the case, it lends support to the bidentate SO_4^{2-} ligand, which is too weak in this complex to displace one of the strongly bound macrocyclic donors. The sulphate complexes of cyclam, $Me_6[14]aneN_4$ and its 4,11-dieneN$_4$ analogue [20] exhibit typical axially symmetric nickel(III) complex ESR spectra at 77 K in aqueous sulphate medium. Clearly, the sulphate here is not bidentate, and the complex of $Me_6[14]aneN_4$ has a formation constant [39] much larger than would be expected for a simple ion-pair (see Section E). However, the ESR spectrum of solid $[Ni(III)(Me_6[14]aneN_4)SO_4]^+$ unlike that of the corresponding dinitrato-cation [32], is a single broad isotropic signal ($g = 2.16$), atypical of an axial symmetric molecule. Hence in the solid state, the data are consistent with Gore and Busch's [15] earlier assignment of a *cis*-sulphato species. Phosphate ion has also been found to stabilise Ni(III), forming a mono-complex. Currently [54] the crystal structure of the $Me_6[14]aneN_4$-containing nickel(III) complex is being examined, in order to elucidate some of the problems outlined above.

Interestingly, whereas the above results were obtained for neutral macrocyclic ligands, anionic systems, for example $Me_2(CH_3CO)_2[14]tetraenoN_4$, (IX), form nickel(III) complexes exhibiting anisotropic ESR spectra with $g_{\parallel} > g_{\perp}$. No superhyperfine structure was observed, leading to the formulation of the species as low-spin square-planar nickel(III) complexes. The non-coordination of solvent is further supported by the independence of the ESR spectra (and redox potentials) on the nature of the solvent used. A similar situation exists in the $[Ni(III)(TAAB^{2-})]^+$ system, with $g_{\parallel}$ (2.16) being greater than $g_{\perp}$ (2.023) [49]. It is interesting to note that the fine structure in these spectra could only be resolved in the presence of added inert electrolyte. The degree of resolution was independent of the nature of the anion (for ClO_4^-, BF_4^-, or PF_6^-), but was seen to vary greatly with the cation, the degree decreasing in the order $^nPr >> Et >> Me$, for tetraalkylammonium salts. This phenomenon has been noted in other ESR studies [60]. In the case of Ni(III)edta [36], however, where $g_{\parallel} = 2.3367$ and $g_{\perp} = 2.139$, it is difficult to envisage a planar configuration. It has been suggested in this system that the species be considered as an octahedral MA_4B_2 complex with a *cis* configuration (where $A = {}^-O_2C-$ and $B = N(-CH_2-)_3$). The energy level of orbitals is then expected to differ from the *trans* configuration (d_{xz}, $d_{yz} < d_{xy} < d_{z^2} < d_{x^2-y^2}$), the order in the tetragonal distorted *cis* system being $d_{xy} < d_{xz}$, $d_{yz} < d_{x^2-y^2} < d_{z^2}$). The unpaired electron is now located in the $d_{x^2-y^2}$ orbital and no hyperfine interaction with nitrogen atoms was observed.

Bossu and Margerum [28] provided definitive evidence for the existence of Ni(III) in the oxidation product of the deprotonated tripeptide complex of (II), nickel(II), $[Ni(II)(H_{-3}G_3a)]^-$. The spectrum obtained for a pH 9.5 solution of the Ni(III) product, frozen to 77 K, exhibited characteristic $g_{\perp} = 2.166$ and $g_{\parallel} = 2.016$ features, but the latter also displayed superhyperfine splitting. Hence, the system was later reinvestigated [52]. The accurate ESR parameters are listed in Table 2. The earlier discrepancy has been explained [53] by the presence of the bis complex, $Ni(III)(H_{-2}G_3a)(H_{-1}G_3a)$, which has a much longer lifetime than the mono complex under the experimental conditions. In a detailed investigation, Lappin et al. [53] examined the ESR spectra of a series of nickel(III)–oligopeptide complexes. The results are consistent with nickel(III) in a tetragonal geometry, with four donor groups from the oligopeptide in the equatorial plane, and two axially bound water molecules. The ESR parameters are listed in Table 2. The $g_{\perp}$ features showed some distortion ($g_{xx} \neq g_{yy}$), suggesting a symmetry lower than D_{4h}. Values of g_{xx} and g_{yy} were seen to be sensitive to the nature of the donor atom. The general trend in g values reflects that in donor strength [63] of the groups. Thus g-values decrease with donor strength in the order $-N^- > -NH_2 > Im \simeq -CO_2^-$. Gradual addition of ammonia to $Ni(III)(H_{-3}G_3a)$ produces firstly a 1 : 1 : 1 and secondly a 1 : 2 : 3 : 2 : 1 splitting of the $g_{\parallel}$ signal, corresponding to axial coordination of one and two ammonia molecules respectively (structure II). Analogous studies have been made by Sugiura and Mino [41], concerning Ni(III) complexes of various histidine-containing tripeptides and bleomycin. The trend of equatorial donor strength is in the order $S^- > -NH_2$. Superhyperfine splittings indicated one axial nitrogen-donor for the complexes containing MAHH and ox-MAHH ligands. In the case of bleomycin, a five-line splitting indicated two axially coordinated nitrogens. Wolberg and Manassen [64] observed the ESR spectrum of electrochemically oxidised nickel(II) tetraphenylporphine in benzonitrile. The spectrum was consistent with the corresponding Ni(III) species, with $g_{\parallel} = 2.116$ and $g_{\perp} = 2.295$ at 77 K. These data are contrasted with those of the radical-ligand species, Ni(II)TPP$^+$ (2.031 and 2.024 respectively) under the same conditions.

(ii) Electrochemistry

Electrochemical measurements on Ni(II)-(III) systems have commonly employed acetonitrile as solvent, since it permits a wide range of potentials to be covered without decomposition and because Ni(III) complexes are stable for long periods in the anhydrous medium. In all such experiments, the usual reference electrode consists of an Ag wire in an acetonitrile solution of 0.1 M $AgNO_3$. This system has been measured [65] to have a standard potential of +0.36 V versus the standard calomel electrode (s.c.e.). All electrode potentials quoted in this review are relative to the $Ag/AgNO_3$ (0.1 M) non-aqueous reference, unless otherwise indicated.

The electrochemical studies of Busch and co-workers [19] on an extensive series of nickel(II) macrocyclic complexes have permitted a systematic separation of the electronic and structural features controlling their redox properties. It is noted that the overall redox behaviour is a composite function of degree and type of ligand unsaturation and macrocyclic ring size, as well as number and position of ring substituents, charge-type and coordination number. The electrochemical data are summarized in Table 3, together with analogous values obtained in different studies. Busch and co-workers [19] correlated the observed and theoretical half-wave potentials, $E_{1/2}$, for the Ni(II)-(III) couples for the series of ligands, from which the following empirical additive scale of structural contributions to electrode potential, $\Delta E_{1/2}$, was compiled.

Structural effect	$\Delta E_{1/2}$
(1) [14] → [15] (ring size)	+ 225 mV
(2) [14] → [16] (ring size)	+ 375 mV
(3) 2 axial Me groups in 6-membered chelate rings	+ 183 mV
(4) Delocalised charge	− 430 mV
(5) Isolated imine	+43 mV
(6) α-Diimine	+ 170 mV

For ligands containing charge-delocalised rings, ring size had no effect on the electrode potential. Importantly, Busch and co-workers [19] observed that regardless of the presence of unsaturation in certain ligands, the one-electron transfer processes of interest were essentially reversible, suggesting a change in metal oxidation state to be responsible. This characteristic behaviour had previously been reported by Olsen and Vasilevskis [47]. In the

TABLE 3
Electrode potentials [a] for Ni(II)/(III)-complex couples

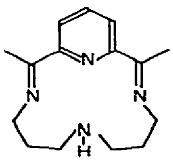
Ligand	E (V)	Ref.
Neutral ligands		
[13]aneN_4	+0.7 – +0.9	19
Cyclam	+0.67	19
[15]aneN_4	+0.90	19
Me_2cyclam	+0.68	19
Me_4cyclam	+0.71	19
Me_6cyclam	+0.87 (0.86)	19 (18)
Me_6[16]aneN_4	ca. + 1.3	19
Me_6[14]4,11-dieneN_4	+0.98	19
Me_6[14]1,4,8,11-tetraeneN_4	+ 1.05	19
Me_6[16]4,12-dieneN_4	+ 1.3	19
Me_6[16]1,4,12-trieneN_4	+ 1.3	19
Me_2[14]1,3-dieneN_4	+0.86	19
TAAB	1.24	9
(CR + 4H)	+0.89	19, 66
(CR + 2H)	+0.93	19, 66
CR	+ 1.03	19, 66
(CR − 2H)	+ 1.05	19, 66
Me_6[14]1,3,7,11-tetraeneN_4	+ 1.05	19
Me_4[14]1,3,8,10-tetraeneN_4	+ 1.00	19
Me_2[14]4,7-dieneN_4	+0.72	19
Me_2[15]8,11-dieneN_4	+0.94	19
pyroneN_5	+0.78 ± 0.01	40
isocyclam	+0.84	72
$[Ni(LL)_3]^{2+\rightarrow 3+}$ redox process [c]		
Phen	1.64	32
5-Mephen	1.61	32
5-Clphen	1.74_7	32
5-NO_2phen	1.82	32
Bipy	1.62_5	32
4,4-Me_2bipy	1.61	32
$[NiLSO_4]^{3-}$ complexes [b]		
Cyclam	+0.49	20
Me_6cyclam	+0.64	20
Me_6[14]4,11-dieneN_4	+0.93	20
Anionic ligands		
Me_2[13]dieneN_4	+0.27 (irr) [c]	19
Me_2[14]dienoN_4	+0.23 (irr) [c]	19
$Me_2(CH_3CO)_2$[14]tetraenoN_4^{2-}	+0.97 (irr) [c]	19
$Me_4(CH_3CO)_2$[14]tetraenoN_4^{2-}	+0.98 (irr) [c]	19
$Me_2(CH_3CO)_2$[15]tetraenoN_4^{2-}	+0.92 (irr) [c]	19
$Me_6(CH_3CO)_2$[14]tetraenoN_4^{2-}	+0.96 (irr) [c]	19
Me_2[15]dienoN_4^{2-}	−0.36 (irr) [c]	70, 75

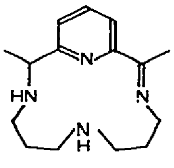
TABLE 3 (continued)

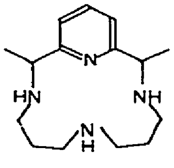
Ligand	E (V)	Ref.
$Me_2(C_2H_4CO_2C_2H_5)_2[15]dienoN_4^{2-}$ [d]	−0.39	70,75
$Me_2(CH_3CO)[15]dienoN_4^{2-}$ [d]	−0.14 (irr) [c]	70, 75
$Me_2(CONH\text{-}\alpha\text{-}C_{10}H_7)_2[15]dienoN_4^{2-}$ [d]	+0.03	70, 75
$Me_2(COC_6H_5)_2[15]dienoN_4^{2-}$ [d]	+0.21	70, 75
$Me_2(NO_2)_2[15]dienoN_4^{2-}$ [d]	+0.42	70, 75
$Me_2(CH_3CO)_2[15]dienoN_4^{2-}$	+0.22	70, 75

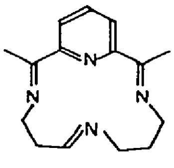
[a] Vs. ($Ag/AgNO_3$ (0.1 M) in MeCN) reference electrode. [b] In aqueous media; reference electrode is Ag/AgCl. [c] Irreversible polarograms. [d] In DMF solvent. [e] In MeCN, using sat. calomel electrode as reference (agar bridge).

case of the $Me_6[14]4,11\text{-}dieneN_4$ complex, however, these workers observed irreversible cyclic voltammograms. Barefield et al. [66] investigated the electrochemical behaviour of the nickel complexes containing various forms

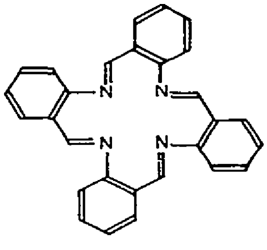

CR
III

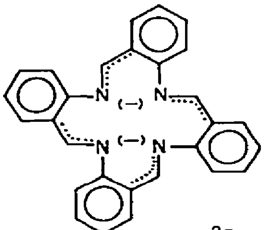

CR + 2H
IV


CR + 4H
V


CR − 2H
VI

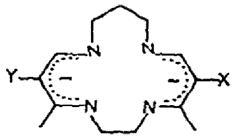
of the tetraaza macrocycle prepared by Curry [67] (structures III–VI). The one electron oxidations (Ni(II) → (III)) were found to be reversible or quasi-reversible, the electrode potential increasing with degree of unsaturation. In an investigation of the electrochemical properties of metal complexes of TAAB (VII), a quasi-reversible electron-transfer was observed, producing $[Ni(III)(TAAB)]^{3+}$, having a half-wave potential of 1.24 V. On reduction of $[Ni(II)(TAAB)]^{2+}$, an irreversible redox was seen, where instead of the expected Ni(I) product, reduction of the ligand occurs, yielding the tervalent complex $[Ni(III)(TAAB^{2-})]^+$. This phenomenon was explained by the enhanced stability of the dianionic form (VIII) of the ligand, being the


TAAB
VII


$TAAB^{2-}$
VIII

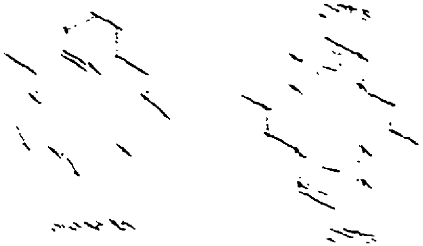
Hückel aromatic analogue to the porphyrin dianionic ring. Cyclic voltammetry has been used [64] to study electron transfer in the nickel(II) tetraphenylporphine system, $[Ni(II)(TPP^{2-})]^+$. The complex behaves in a manner similar to its $TAAB^{2-}$ analogue, in that instead of oxidising the ligand to form $[Ni(II)TPP]^{2+}$, an essentially reversible one-electron process was observed, producing the tervalent nickel complex cation, $[Ni(III)(TPP^{2-})]^+$. As noted earlier, this species was characterised by ESR. The Ni(III) complex was seen to decompose readily, forming the Ni(II)-stabilised ligand radical [68] as expected from earlier considerations of π delocalisation of electrons.

Rillema et al. [69] have compared the electrochemical behaviour of complexes of several tetraaza macrocycles with the metals Fe, Co, Ni, Cu and Zn. Their results relating to nickel were in accord with those previously reported [47]. Quasi-reversible behaviour was noted for the Ni(II)-(III) couple for the complex containing 2,9-Me_2-Me_6[14]4,11-dieneN_4 ($E_{II \to III}$ = 1.92 V, $E_{III \to II}$ = 1.22 V). For the complex containing the analogous saturated ligand, the corresponding electron-transfer process was reversible, with a half-wave potential of 1.39 V. In an electrochemical study of nickel complexes containing dianionic tetra macrocycles, Pillsbury and Busch [70] have shown that the electrode potentials for oxidation of the divalent to the tervalent state may be dramatically altered by ring-substituent changes. Experiments were performed in DMF solvent, using a reference electrode analogous to that used in acetonitrile. The ligands employed were of the type X,Y-Me_2[15]tetraenoN_4 (structure IX). Various substituents, X and Y were examined, resulting in the observation that $E_{1/2}$ changes by greater than 0.8 V from −0.44 V for X = Y = $-CH_2CH_2$-α-C_5H_5N to +0.42 V for X = Y = $-NO_2$. Values for different complexes are listed in Table 3 and a linear free energy correlation has been made between $E_{1/2}$ and σ values [71] for the substituents. Both the Ni(II) and (III) complexes of these ligands are square-planar [19]. Thus electron-transfer occurs to and from the d_{xy} orbital. Consequently, the electronic nature of the equatorial ligand is expected to influence the redox process. Sabatini and Fabbrizzi [72] have reported on the electrochemistry of a series of saturated macrocyclic nickel(II) complexes (Table 3). Account was taken of the known [73] low-spin square-planar/high-spin octahedral equilibrium $[NiLS_2]^{2+} \rightleftharpoons [NiL]^{2+} + 2\,S$. The algebraic difference, E, of the oxidation and reduction potentials was found to be



IX

constant (2.41 ± 0.08 V). Using literature data [19], Sabatini and Fabbrizzi [72] showed this behaviour to be general. The only points which do not fall on a linear plot of oxidation versus reduction potential have been characterised as Ni(II)-stabilised ligand radicals [19]. Hence, this correlation provides a rapid electrochemical test of the authenticity of proposed tervalent nickel tetraaza macrocycles. Other nickel(II) macrocycles which undergo reversible one-electron oxidations in acetonitrile include [Ni(II)-(pyaneN$_5$)(MeCN)]$^{2+}$ [40] where (pyaneN$_5$) is a pentadentate macrocycle (structure X), with $E_{1/2} = 0.78$ V and an octaaza-macrocyclic complex, [Ni(II)(C$_{30}$H$_{12}$N$_8$(CPh$_3$)$_2$)] [74]. The structure of the latter ditrityldihydrooctaaza[14]annulene dianionic ligand (XI) is shown below. $E_{1/2}$ for this system is + 0.33 V. The oxidation product was characterised as square-planar Ni(III) by ESR (Table 2).



X

XI

Several aqueous electrochemical investigations have been performed. Zeigerson et al. [20], using a gold electrode at pH [illegible] showed that whereas Ni(II)(Me$_2$[14]aneN$_4$)$^{2+}$ undergoes irreversible oxidation in aqueous perchlorate, the presence of sulphate ion (0.5 M) stabilised the tervalent state permitting reversible redox behaviour. The electrochemical data for this and the other analogues studied are listed in Table 3. Similar results have been observed for Ni(II)cyclam^{2+} [75]. Bossu and Margerum [76,77] have studied the cyclic voltammetric characteristics of a wide range of Ni(II)–(III) peptide complexes. Quasi-reversibility (peak separation [illegible] mV) was observed generally. Values of $E°$ (Table 4) were seen to decrease with the number of deprotonated peptide groups and increase with [illegible] substituents, depending on the position of the latter in the chain, and histidine-containing peptides exhibited relatively high electrode potentials.

[illegible]

In general, tervalent nickel complexes have been reported as [illegible] [illegible] [illegible] [illegible] ligands, [illegible] [illegible]. The [illegible] [illegible] has been [illegible] in a [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible]. In [illegible] [illegible] of [illegible] [illegible] [illegible]

TABLE 4
Electrode potentials of Ni(II)/(III) couples for peptide containing complexes[a], at 25°C, pH=9.6

Ligand	Δ (mV)[c]	E^0 (V)[d]	Ligand	ΔE or Δ (mV)	E^0 (V)
Tripeptides			Histidine-containing peptides[e]		
GGG	81	0.85	GGhis	90	0.96
AAA	87	0.84	GGhisG	100	0.95
AGG	78	0.85	Asp-ala-his-lys	145	0.94
VGG	79	0.85	Tetrapeptides		
IGG	73	0.85	G_3AOCH_3	75	0.84
LGG	71	0.85	G_3A	95	0.82
GGA	70	0.85	A_4	101	0.82
GGL	74	0.87	AG_3	99	0.80
GGF	89	0.89	G_4	98	0.79
GGV	78	0.89	Peptide amides and higher order peptides		
GGI	70	0.89	G_4a	73	0.84
GGβA	79	0.84	G_3a	80	0.83
GLG	72	0.86	VGGa	75	0.83
LLL	95	0.87	GGAa	75	0.82
			G_5	87	0.83
			A_5	88	0.83
			G_4AOCH_3	83	0.83
			G_6	78	0.83

[a] Taken from ref. 52. [b] Abbreviations of amino acid residues: G=glycyl; A=L-alanyl; βA=β-alanyl; V=L-valyl; L=L-leucyl; I=isoleucyl; F=L-phenylalanyl; his=L-histidyl; asp=L-aspartyl; lys=L-lysyl; G_3A=triglycinamide. [c] Peak potential separation (=59.5 mV for electrochemically reversible one-electron couple). [d] Vs. NHE. [e] pH=8.2.

Intense absorptions in the range 200–400 nm are also observed for these complexes and have been assigned to metal–ligand charge transfer. Since many of the species yield stable solutions in anhydrous acetonitrile (Fig. 4) most of the data reported refer to that solvent system. In water and other solvents more basic than acetonitrile, however, the complexes generally undergo redox decomposition which may be retarded in highly acidic media. Recently, aqueous solutions of the saturated ligand complexes have been prepared (electrochemically or by reaction with cerium(IV) or cobalt(III)) of sufficient stability that spectroscopic comparisons may be made with the acetonitrile spectra. Most of the features observed previously are retained and replacement of the axial aquo ligands by polyvalent anions (sulphate, phosphate) stabilises the species through complex formation (Fig. 5). Characterisation of transient nickel(III) complexes prepared from unsaturated macrocyclic systems has been made using pulse radiolytic-UV-visible studies with generally $\dot{O}H$ as oxidant. Some significant differences seem to persist in

TABLE 5

Electronic spectra of $[Ni(III)LX_2]^{4+}$ complexes in acetonitrile

Ligand	X	λ_{max} (nm)(ϵ_{max} (M^{-1} cm^{-1})	Ref.
Cis $Me_6[14]aneN_4$	MeCN	650 (112), 408 (12030), 327 (12 170)	47
Trans $Me_6[14]aneN_4$	MeCN	655 (116), 406 (11 600), 329 (11 800)	47
$Me_6[14]4,11\text{-diene}N_4$	MeCN	564 (76), 380 (12500), 318 (13500)	47
$Me_6[14]1,5\text{-diene}N_4$	MeCN	590 (75), 388 (8640), 318 (11 300), 195 (12600)	47
Me_2cyclam	Cl	952 (19), 775 (26), 318 (11 700)	15
	Br	1000 (17), 769 (39), 360 (3 540), 305 (5 120))	15
	NCO	964 (9), 673 (16), 304 (1 888)	15
	NO_3	714 (42), 313 (11 100)	15
	$\frac{1}{2}SO_4$ [a]	629 (43), 370 (2460), 307 (4260)	15
Cyclam	$\frac{1}{2}SO_4$ [a]	370 (6 000), 295 (11 000)	20
Me_6cyclam	$\frac{1}{2}SO_4$ [a]	410 (7000), 310 (11 000)	20
$Me_6[14]4,11\text{-diene}N_4$	$\frac{1}{2}SO_4$ [a]	319 (12000), 262 (7000)	20
$TAAB^{2-}$	[b]	990 (7000), 530 (1 700), 440 (4560), 372 (16380), 312 (31200)	49
$(DPG)_2$	Py [c]	682 (100)	45
$H_{-3}GGAa$ [a]		325 (5820 ± 100), 238 (11 300 ± 600)	52
$H_{-3}G_3a$ [a]		325 (5360 ± 150), 235 (10700 ± 500)	28, 52
$H_{-3}G_5$ [a]		325 (5820 ± 130), 214 (11 300 ± 400)	52
$H_{-3}G_4$ [a]		327 (5240 ± 240), 250 (sh)	52
$H_{-2}GGG$ [a]		340 (4500 ± 150), 250	52
$H_{-2}VGG$ [a]		340 (4330 ± 100), 254 (10200 ± 400)	52
$H_{-2}AAA$ [a]		345 (4270 ± 200), 260 (10600 ± 300)	52
$H_{-2}GGV$ [a]		355 (4740 ± 100), 255 (11 300 ± 600)	52

[a] In aqueous medium. [b] Square planar, see text. [c] In pyridine.

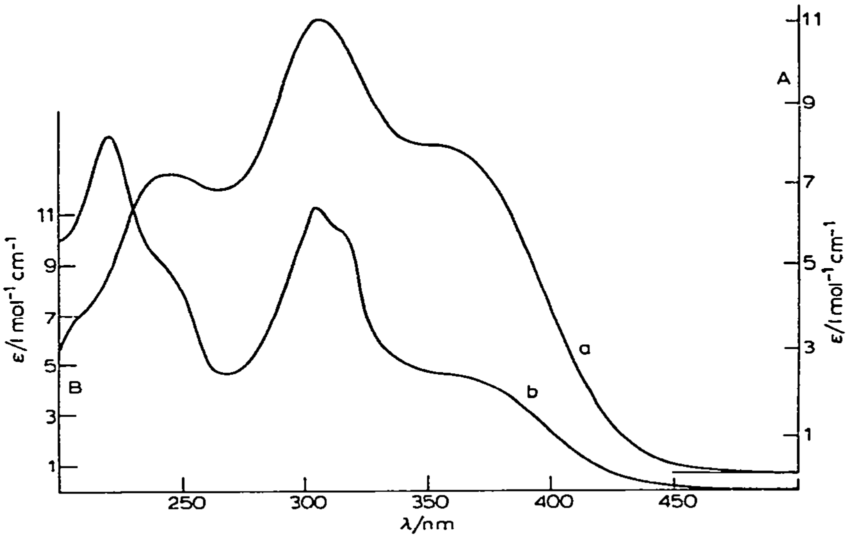


Fig. 4. UV/visible spectra of Ni(cyclam)[NiL_1^{3+}], in (a) 1.0 M $HClO_4$, $\lambda_{max} = 308.6$ and 246.5 nm; (b) anhydrous CH_3CN, $\lambda_{max} = 307.3$ and 221.9 nm.

the reaction products from the electrochemical and radical oxidations. These studies were, however, carried out under different pH and ionic strength conditions.

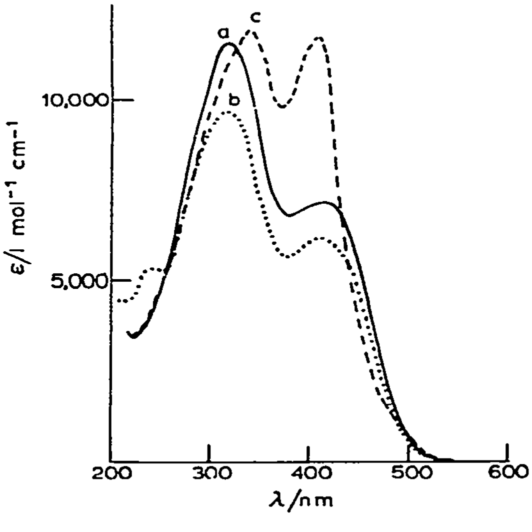


Fig. 5. Electronic absorption spectrum of the oxidation product of complex A measured by a Cary 17 spectrophotometer: (a) immediately after preparation in aqueous 0.5 M Na_2SO_4 solution at pH 1.6; (b) 3.5 months after preparation, solution as in (a); (c) in acetonitrile. (From ref. 18.)

Recently, Czarnecki and Margerum [51] investigated the CD spectra of di- and tervalent peptide complexes of nickel and copper. The data reported on the tervalent complexes result from ligand–metal charge transfer bands centred at 365 nm. Substantial changes in the spectra with peptide have suggested an application of this technique to redox kinetics and equilibria involving metal oligopeptide complexes. For example

$$M(III)L^* + M(II)L \rightleftharpoons M(II)L^* + M(III)L$$

where M = Ni or Cu and L* and L represent optically active and inactive deprotonated peptides respectively. Changes in the visible CD may then be followed whereas M(III)L* and M(III)L frequently exhibit almost identical UV/visible spectra.

E. KINETIC STUDIES

(i) Rates of complex formation

There are, to date, relatively few data available on the kinetics of complex formation. This, in part, reflects the fact that whereas many of the nickel(III) complexes are stable in non-aqueous media, they exhibit ready reduction in basic solvents. In the case of nickel(III)cyclam, however, it has been found that in > 1 M $HClO_4$, solutions of this ion prepared electrochemically are stable for several hours. This has enabled the study of complexation by Cl^-, Br^- and NCS^- using stopped-flow methods [62]. In the reaction with iodide, however, oxidation of the halide was observed.

Using an excess of Cl^- or Br^- in reaction with Ni(III)cyclam, $[Ni(III)L(OH_2)_2]^{3+}$, absorbance changes in the UV, monitored over the range 250–380 nm enabled evaluation of equilibrium constants (K_1) for the reaction

$$[Ni(III)L(OH_2)_2]^{3+} + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Ni(III)L(OH_2)X]^{2+} + H_2O \quad K_1 = \frac{k_1}{k_{-1}} \qquad (1)$$

In conditions of excess thiocyanate, however, there is evidence for 1 : 2 complexation and in this system, rates and spectra were measured in an excess of metal ion.

First order formation rate constants, k_{obs}, were found to vary linearly with anion concentration, the curves for Cl^- and Br^- showing intercepts consistent with the rate law

$$\frac{d[Ni(III)LX]^{2+}}{dt} = k_{obs}[Ni(III)LX]^{2+} = \{k_1[X^-] + k_{-1}\}[Ni(III)LX]^{2+} \qquad (2)$$

From such plots, both formation and dissociation rates were derived

TABLE 6

Complex formation rates and equilibrium constants for reactions of Ni(III) species with anions $I = 1.0$ M

Reaction	k_1 (M^{-1} s^{-1})	k_{-1} (s^{-1})	K (M^{-1})	Ref.
$[Ni(III)L]^{3+} + Cl^-$ [a]	902 ± 7 [c]	4.3 ± 0.2	210 ± 40	62
$[Ni(III)L]^{3+} + Br^-$	207 ± 20 [c]	6.1 ± 0.2	34 ± 10	62
$[Ni(III)L]^{3+} + NCS^-$	1160 ± 20 [c]			62
$[Ni(III)L']^{3+} + SO_4^{2-}$ [b,c]	1×10^6 [d]	33		39
$[Ni(III)L']^{3+} + SO_4^{2-}$ [f]			3×10^3	39
$[Ni(III)L]^{3+} + SO_4^{2-}$ [f]			ca. 5×10^4	58

[a] $[Ni(III)cyclam]^{3+}$. [b] $[Ni(III)$-*meso*$Me_6[14]aneN_4]^{3+}$. [c] Use of $K_{os} = 1$ (see text) leads to similar values of k_f(s^{-1}) (exchange rate on Ni(III)L, eqn. (3)), $T = 25$°C. [d] Use of $K_{os} = 90$ M^{-1} yields $k_f = 1.1 \times 10^4$ s^{-1} for exchange rate on [Ni(III)L′]. [c] $I = 0.03$ M correction for ionic strength leads to $k_f = 3\text{–}5 \times 10^2$ s^{-1}. [f] $I = 0.3$ M, $T = 22 \pm 2$°C.

(Table 6). For thiocyanate, however, where K_1 is at least an order of magnitude greater, only the formation rate was obtained experimentally. Replacement of a solvent molecule is generally considered to proceed via an outer sphere species

$$[Ni(III)L]^{3+} + [X^-] \overset{K_{os}}{\rightleftharpoons} [Ni(III)L,X]^{2+} \xrightarrow{k_f} [Ni(III)LX]^{2+} + H_2O \tag{3}$$

Under the experimental conditions used ($I = 1.0$ M) for a reaction of this type (+3, −1) values of K_{os} are ≈ 1 [76], leading to values of $k_f = 902$, 207 and 1160 s^{-1} for Cl^-, Br^- and NCS^- respectively. Although only three substitution reactions have been studied, the spread of rate constants is less than an order of magnitude suggesting a dissociative mechanism. The nickel(III) ion being a d^7 low-spin system, it would be smaller than the corresponding cobalt(III) species which reacts via an I_d process.

A feature of the halide complexes is the considerable increase in kinetic stability in halide media of the $[Ni(III)LX_2]^+$ ions over the bis aquo complexes. Whereas the latter decomposes fairly rapidly (ca. 1 h) at pH > 2, the dichloro complex is stable for a period of days. In perchlorate media, however, there is evidence [38] for a rapid dissociation of one chloride ligand and solutions of $Ni(cyclam)Cl_2^+$ are present only in solutions of > 0.5 M Cl^-. A similar effect has been noted recently by Meyerstein and co-workers [20] with $[Ni(III)Me_6[14]aneSO_4]^+$ where coordination by an anion appears to impart increased thermodynamic and kinetic stability. The formation of the latter species has been determined in a pulse radiolytic study [39]. Although $Ni(III)[meso Me_6[14]ane]^{3+}$, $(Ni(III)L')^{2+}$ hydrolyses (with $pK = 3.7 \pm 0.2$), the substitution by SO_4^{2-} occurs only on the unhydrolysed complex with a rate constant $k_2 = 1 \times 10^6$ M^{-1} s^{-1}. A rate expression similar to eqn. (2) is observed and $K_1 = 3 \times 10^4$ M^{-1}. If it is assumed that the formation reaction proceeds via an ion-pair, the value of K_{os} computed in this instance is ca. 90 M^{-1}, leading to a first order exchange constant (k_f eqn. (3)) of 1.1×10^4 s^{-1} (at $I = 0.03$ M). An ionic strength dependence study of the formation rate has been made [39] and extrapolation to $I = 1.0$ M leads to $k = 3\text{–}5 \times 10^2$ s^{-1}, a value very similar to that obtained for the nickel(III)cyclam systems suggesting that again an I_d mechanism may be operating. The fact that the equilibrium constant $K_{SO_4^{2-}} = 3 \times 10^4$ M^{-1}, is over 300 times that expected for a contact ion pair, together with the marked spectroscopic changes, is taken as evidence for true inner sphere complex formation. Recently the corresponding $[Ni(III)cyclamSO_4]^+$ complex has been characterised [54] with $K_{SO_4^{2-}} = (5 \pm 2) \times 10^4$ M^{-1} ($I = 0.1$ M Na_2SO_4).

Further studies have been made [84] on the formation of the $Ni(cyclam)NCS^{2+}$ complex. Using solutions of nickel(III)cyclam prepared electrolytically in aqueous $HClO_4$, investigations have been carried out over the range pH = 1–3. Under these conditions there is evidence for a reaction pathway involving the ion $Ni(L)(NCS)OH^+$.

(ii) Electron transfer reactions

(a) Oxidation of nickel(II) complexes

Pulse radiolysis—flash photolysis studies. Although there have been studies published previously [34,35] on transient nickel(III) species, the current interest in this area is confirmed by the almost simultaneous publication of results from three laboratories on virtually identical studies on macrocyclic systems.

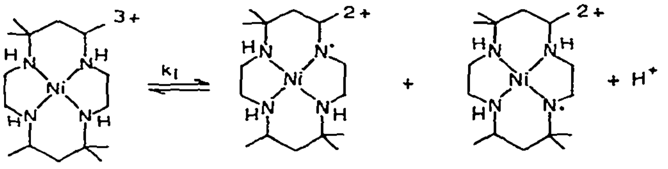
The kinetics of formation and decay of the short-lived nickel(III) complexes of ammonia [34], ethylenediamine [77], glycine [77], edta [36] and dimethylglyoxime [78] have been described by Lati and Meyerstein. The oxidation of $Ni(II)(NH_3)_n$ ($n = 4$, 5, 6) by $NH_2^{\cdot}$ in 0.67 M NH_3 solutions (pH = 11.3) leads to the formation of the transient species $[Ni(III)(NH_3)_q]^{3+}$. The number of ammonia ligands complexed is not known. The spectrum of the intermediate shows a maximum at 295 ± 5 nm with $\epsilon_{max} = 1400 \pm 300$ M^{-1} cm^{-1}. The species decays via the second order process $2\ Ni(III)(NH)_3)_q \xrightarrow{k_2} 2\ Ni(II)(NH_3)_n$ + oxidation products with $2k_2 < 3.5 \times 10^7$ M^{-1} s^{-1} under the conditions described above. The oxidised products may be either H_2O_2 or $H_2N{\cdot}NH_2$. From separate experiments it was concluded that oxidation of the solvent H_2O or of the NH_3 ligand by the Ni(III) centre is slower than 2×10^2 s^{-1}. In the reactions with Ni(II) ethylenediamine and glycine complexes [77], the oxidant $\dot{\mathrm{O}}\mathrm{H}$ is involved, the site of oxidation being the nickel centre. Spectra of the transients are similar to that for the ammine complex and do not show the absorption bands at 300 nm, ca. 400 and 650 nm reported for the complexes of the cyclic ammine complexes in acetonitrile. No pH effects are observed in the formation rate studies. The disappearance of $\mathrm{Ni(III)(en)}_n$ was found to follow a second order rate law, the increasing rate with increasing pH being ascribed to either an acid–base equilibrium involving coordinated water molecules or a redox equilibrium of the type

$$\mathrm{Ni(III)(en)}_n + \mathrm{OH}^- \rightleftharpoons \mathrm{Ni(en)}_n^{2+} + \dot{\mathrm{O}}\mathrm{H} \qquad (4)$$

Hydroxyl ions also oxidise Ni(II)edta to the nickel(III) complex [36,77] which is stable for several days in deoxygenated solutions at pH 4.3. Oxygen, however, reacts with this complex ($k_2 = 6.5 \times 10^2$ M^{-1} s^{-1}). From an examination of the ESR spectrum of the nickel(III) species it is concluded that the electron resides in the $d_{x^2-y^2}$ orbital, the complex having a tetragonally distorted *cis* configuration.

In the case of macrocyclic ligand complexes, however, the stability of the transient intermediates produced in aqueous media on pulse radiolysis varies with the degree of unsaturation of the ring system. Studies have been undertaken using both hydroxyl and dihalogen radical ions, X_2^-, (X = Cl, Br) and $[(\mathrm{NCS})_2]^-$. Since some differences in interpretation arise in the results presented, these oxidants will be treated separately.

Reactions with hydroxyl radicals. Recently, details of investigation of the reaction of $\dot{\mathrm{O}}\mathrm{H}$ with $[\mathrm{Ni(II)Me_6[14]aneN_4}]^{2+}$ (A) [39,56,80], $[\mathrm{Ni(II)Me_6[14]4,11\text{-}dieneN_4}]^{2+}$ (B) [56,79–81] and $[\mathrm{Ni(II)Me_6[14]1,4,8,11\text{-}tetraeneN_4}]^{2+}$ (C) [56,80,81] have been published. Although the rate data show a broad measure of agreement, there are some areas, especially in mechanism, where discrepancies arise. In an earlier study of the stability of the $[\mathrm{Ni(III)Me_6[14]aneN_4}]^{2+}$ ion in aqueous media, Barefield and Mocella [50] suggested that a nickel(II) ligand radical species, with an absorption maximum at 540 nm was formed according to the reaction



XII XIII

(5)

The transient with the 540 nm absorption band was identified using ESR techniques as roughly a 1.1 : 1 mixture of the radicals (XII) and (XIII).

Formation appeared to be via the reversible reaction at pH ~ 5–7.

Whitburn and Laurence [56] have shown that on reaction of complexes (A) and (B) with $\mathrm{O\dot{H}}$, in addition to the characteristic absorbance due to Ni(III) over the range 300–450 nm, a second absorbance ($\lambda_{max} = 550$ nm) was also formed. The spectra and initial yields of both species were pH dependent. Comparison of the rates of decay of (XII) or (XIII) showed them to be similar to the observed absorbance decrease at 550 nm. Also at pH 5 the conversion (k_i above) took place with k_i = ca. 150 s^{-1}. This reaction was so slow that the initial yield of $\mathrm{Ni(II)\dot{L}}$ observed in the $\mathrm{O\dot{H}}$ reaction with nickel(II) could not arise from eqn. (5). From a detailed analysis of the pH profile of the λ_{546} absorbance, it is suggested that the Ni(III) and $\mathrm{Ni^{II}\dot{L}}$ species were not in equilibrium at the time at which the measurements of the initial yields were made (< 100 μs). The formation of $\mathrm{Ni^{II}\dot{L}}$ species in reactions with $\mathrm{O\dot{H}}$ radicals contrasted with the corresponding reactions with Cl_2^- and Br_2^- where no initial absorbance increase at 550 nm was observed. Also reaction of $OH^{\cdot}$ with the tetraene (C) yielded only the nickel(III) complex. The rate constants for reactions of $OH^{\cdot}$ with (A) and (B) were pH independent despite the differences in the initial yields of [Ni(III)] and [$Ni(II)L^{\cdot}$] in the pH range 1–5 suggesting that both species are formed from an initial precursor which is the initial product of $OH^{\cdot}$ radical attack. A reaction scheme consistent with the findings involves $H^{\cdot}$ atom abstraction at a C-atom site on the ligand at a pH independent rate. A proton-catalysed intramolecular transfer yields the Ni(III) complexes. Rearrangement takes place from a $C^{\cdot}$ to an $N^{\cdot}$ centered radical which is the species responsible for the 550 nm absorbance.

$$\mathrm{\dot{O}H^{\cdot} + Ni(II)L \rightarrow Ni(II)L'\dot{C}H + H_2O}$$

$$\mathrm{Ni(II)L'C^{\cdot}H + H^+ \rightleftharpoons Ni(III)L}$$

$$\mathrm{Ni(II)L''\dot{N} + H^+ \rightarrow Ni(II)L''\dot{N}H^+}$$

(L′ and L″ represent parts of the macrocyclic ligand.)

Similar reaction with the free diene ligand gave rise to a small transient absorbance at 300–400 nm at a rate similar to that for the Ni(II) complex systems. The transient did not absorb at 550 nm, however. From studies of the interconversion (5) above, a proton equilibrium of Ni(III) ($pK = 8.8$) is indicated, with a second less well defined base-dependent pathway for which pK_a = ca. 6.0.

The above interpretation differs somewhat from those of Jaacobi et al. [81] and Patterson and co-workers [79,80]. In the reaction of $OH^{\cdot}$ with (C) (pH ca. 5), no longer wavelength absorbance was observed but with (A) there was no evidence for a large transient absorbance in the UV region. By contrast, the reaction of the diene (B) exhibited spectroscopic features with both the 300–400 and 500–600 nm bands present and a complex kinetic pattern. An isosbestic point at ca. 490 nm indicates the interconversion of two intermediates involved. (A pH profile of the same reaction by Whitburn and Laurence [56] shows an isosbestic point at $\lambda =$ ca. 470 nm.) There is some evidence for interconversion between two intermediates, in that decay in the UV region is concurrent with growth in the 500–600 nm range. Under conditions of nanosecond resolution, however, it is suggested that the two intermediates, one of which is long-lived, are produced simultaneously from the initial OH· attack. Reactions with nickel(I) complexes and rate variations with ionic strength indicate an overall charge of +3 for the longer lived transient. Also, the rate of decay of this species (half-life ca. 40 s at pH 4) is markedly pH dependent. Differences are observed in the extinction coefficients of the transients found for the $[\mathrm{Ni(II)Me_6[14]aneN_4}]^{2+}$ intermediate and the shift in equilibrium (5) toward the Ni(III) complex with increasing $[\mathrm{H^+}]$ was not observed. It is suggested that the data on the long-lived oxidation products are inconsistent with a free radical and that the assignment of the 530–540 nm band be made on the basis of a nickel(III) complex in which there is distortion from planarity of the macrocyclic ligand contributing to removal of the inversion centre. Support for this suggestion comes from the observations, confirmed by Whitburn and Laurence [56], that reaction of the tetraene (C) leads solely to the Ni(III) complex. It is considered that planarity is maintained owing to the presence of the four double bonds. The assignment of the longer-lived species as a nickel(III) complex has also been proposed by Meyerstein and co-workers [81]. From variations of its absorption spectrum with pH, it is suggested that for (B) the species undergoes a proton dissociation ($\mathrm{p}K_a = 3.45$) leading to the complex $[\mathrm{Ni(III)L(OH)}]^{2+}$ and that this reaction is accompanied by major stereochemical rearrangement of the complex. Additional evidence presented against a radical is that in reaction between the transient and O_2, the rate constant (ca. 20 $\mathrm{M^{-1}\ s^{-1}}$) is more similar to that for Ni(III)(edta) + O_2 (ca. 650 $\mathrm{M^{-1}\ s^{-1}}$) than to that expected for reaction of aliphatic free radicals. Also, the observed $\mathrm{p}K_a$ is as expected for dissociation from a water molecule in a trivalent metal complex (for Co(III) the corresponding value is 4.2). Evidence that the transient Ni(II) ligand radical may be photogenerated in the flash photolysis of the $[\mathrm{NiMe_6[14]dieneN_4}](\mathrm{CH_3CN})_2^{3+}$ complex has been presented recently [48]. Two pathways for photoreaction are indicated, one involving oxidation of coordinated acetonitrile. At excitation energies lower than the threshold energy for the latter process, charge transfer from the amino groups to the nickel *d* orbitals takes place leading to the radical intermediate which has an absorption spectrum (in 2×10^{-3} M H_2SO_4) with $\lambda_{max} = 530–540$ nm.

Reactions with radical anions: Cl_2^-, Br_2^- *and* $(NCS)_2^-$. In their study, Maruthanutha et al. [80] have monitored three steps in the reactions of these anion radicals (X_2^-) with nickel(II) macrocycles. The sequence is (i) formation of X_2^- from $^{\cdot}OH$, (ii) disappearance of X_2^- by reaction to form a transient oxidation product and (iii) transformation of this transient intermediate into a longer-lived species. The former has been identified and comparison made with the normalised spectrum of the corresponding nickel(III) complex in acetonitrile. In each case, however, the apparent extinction coefficient for the transient in (ii) was found to be half the value found previously. The rates for halogen ion oxidations were found to be comparable with those observed for $OH^{\cdot}$ attack, the reactions of $(NCS)_2^-$ proceeding with the rate constants about an order of magnitude slower (Table 7). Although the transient oxidation product spectra generated by the various anion radicals were found to be the same for a given macrocycle, the kinetics of subsequent transformations into longer lived intermediates varied markedly with oxidant. This observation has been attributed to the reaction of the anions with the transient oxidation product. If oxidation took place via an inner-sphere mechanism

$$Ni(II)N_4 + X_2^- \rightarrow Ni(III)N_4X + X^- \qquad (6)$$

then the anion X^- could remain axially coordinated after electron transfer. Dissociation or aquation of the halide ligand may then make a significant contribution to the rate of conversion of the short-lived to the longer-lived intermediate. Support for this interpretation has been provided from studies

TABLE 7

Second order rate constants, k_2, for radical oxidations of nickel(II) macrocyclic complexes

Radical	$k_2 \times 10^{-9}$ (M^{-1} s^{-1})			Ref.
	Complex (A)	(B)	(C)	
$OH^{\cdot}$	4.3 ± 1.5 [a]	6.0 ± 0.2 [a]	12 ± 2 [a]	56
	1.9	3.0	4.1	80 [d]
		2.5 [b]		81
$[Cl_2^{\cdot}]$		10.2 [a]	12 ± 2 [a]	56
	2.0	9.6	8.7	80
$[Br_2^{\cdot}]$	4.0 ± 1 [a]	2.2 ± 0.7 [a]	2.6 ± 0.6 [a]	56
	3.4	9.8	9.5	80
		9.0 ± 1.5 [c]		81
$[(NCS)_2^{\cdot}]$	0.1 [a]	0.6 [a]	$\leqslant 0.05$ [a]	56
	1.0			80
$[\dot{H}O_2]$	0.011 [a]			56

[a] $T = 22 \pm 2$°C, pH = 1. [b] pH = 5.7. [c] Rate independent of pH in range pH 3–10. [d] Rates constant in the range pH 4–9; halide concentrations used were in range $(5-20) \times 10^{-3}$ M, with $[Ni(II)L]^{2+}$ = ca. 10^{-4} M.

of Br_2^- with the macrocyclic-diene (B) [81]. Conductance measurements indicate that (ii) may be represented as reaction (6) to yield $Ni(III)L-Br^{2+}$. Also the reaction (7)

$$Ni(III)L-Br^{2+} \xrightarrow{k_7} Ni(III)L + Br^- \tag{7}$$

has been shown to be base-catalysed with $k_7 \approx 120\ s^{-1}$ in weakly acidic solutions, rising to ca. $2.5 \times 10^5\ s^{-1}$ at pH 8.2. It is of interest that the rate constants k_7 are several orders of magnitude lower than for similar complexes of Co(II)L–X which have the same low-spin d^7 configuration. This may be attributed to charge effects on the ligand substitution rates in complexes of this type.

Working in somewhat more acidic conditions, Whitburn and Laurence [56] have shown that at pH 1 oxidation of (A), (B) and (C) by Cl_2^- leads to the formation of transients with spectra (taken with 50 μs of reaction) almost identical to those of the nickel(III) complexes produced electrochemically in acetonitrile. The spectra are in general very similar to those presented [80] at 30 μs after the pulse. Rate constants were determined by a competition method between the known reaction of Cl_2^- with Fe(II)aq and the oxidation of the nickel(II) macrocycles. The free diene ligand reacted only slowly with Cl_2^-. Also at concentrations of [Ni(II)L] up to $2-3 \times 10^{-4}$ M there was no detectable change in the rate of the I_2^- disproportionation reaction, indicating that the rate constants with I_2^- ions must be $< 10^7\ M^{-1}\ s^{-1}$. Any oxidation of the nickel(II)–tetraene, (C), by $(NCS)_2^-$ must also be slow ($k \leqslant 5 \times 10^7\ M^{-1}\ s^{-1}$). Complexes (A) and (B), however, reacted with $(NCS)_2^-$ to yield transient intermediates. Unlike the previous authors [80,81], Whitburn and Laurence suggest that the reactions involving (Cl_2^-) and (Br_2^-) are diffusion controlled, the rates being independent of both macrocyclic complex and radical anion despite the large differences between the standard reduction potentials of the two oxidants.

The rates of decay of the nickel(III) complexes are dependent on the other species present in solution. The strong dependence of the lifetime of the Ni(III) macrocycle on pH indicates that oxidation of the ligand to yield a more unsaturated ligand system proceeds predominantly via a deprotonated form of the macrocyclic complex. At low concentrations of halide ion ($\leqslant 10^{-3}$ M) nickel(III) complexes decay by first order reactions over the range pH 1–9 and at all pH's studied the relative rates of decay are (C) > (B) > (A). In acid solutions, the rate of disappearance of (A) is sufficiently slow that independent studies may be made of the reduction reactions with Br^-, I^-, $[SCN]^-$ and H_2O_2. Where areas of overlap do occur, the agreement between these studies appears to be good.

From the foregoing discussion it is clear that further studies are required over a variety of pH conditions to clarify the situation regarding transients formed in the reactions of nickel(II) macrocycles with radicals and radical anions.

Reaction of Ni(II) macrocycles with Ce(IV) and Co(III). In addition to the oxidation described above, the facile preparation of nickel(III)cyclam has been observed in the oxidation of the nickel(II) ion with aquo cerium(IV) and cobalt(III) ions in acid perchlorate media [38]. The ESR spectra of frozen glass samples of the product ions are identical to those prepared from solid nickel(III) complexes. Stopped-flow studies have been made over the range 10–35° and $[H^+] = 0.2–1.50$ M. Spectrophotometric titrations are consistent with the overall reaction

$$M_{aq}^{n+} + Ni(II)L \rightarrow Ni(III)L + M_{aq}^{(n-1)} \tag{8}$$

From rate studies (Table 8) it is proposed that the hydroxo cation $CoOH^{2+}$ is the reactive species in these outer-sphere reactions. There are no protolytic equilibria associated with the nickel(II)cyclam complexes in the acidity range studied, and the hydrogen ion dependence may be attributed to hydrolysis of the aquo cation. In the case of $CoOH^{2+}$, the rate law $d[Ni(III)]/dt = k_8 K_h [Co(III)][Ni(II)]/[H^+]$ is observed.

It is of interest that no reaction is observed between Ce(IV) and the tetra-*N*-methylated t-$[Ni(II)Me_6[14]aneN_4Me_4]^{2+}$ ion. On mixing with cobalt(III), however, a transient absorbance was observed in the flow system. Consumption of cobalt(III) took place, indicating a redox process, possibly

TABLE 8

Rate constants and thermodynamic parameters for oxidation [84] of $[Ni(II)L]^{2+}$ complexes by aquo cobalt(III) species [a,b]

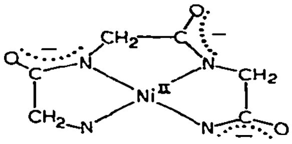
$$CoOH^{2+} + Ni(II)L^{2+} \xrightarrow{k_8} Co(II) + Ni(III)L^{3+}$$

Ligand (L)	$10^{-5}\,k_8$ ($M^{-1}\,s^{-1}$)	$\Delta H^{\ddagger}$ [c]	$\Delta S^{\ddagger}$ [d]	Ref.
Cyclam	3.8	4.8	−17	38
Tet-*a*	0.33	4.5	−23	84
Tet-*c*	0.31	5.4	−20	84
CRH	1.50	3.8	−22	84
$Me_6[14]4,11\text{-dieneN}_4$	1.95	5.9	−15	84

[a] $I = 1.50$ M, $T = 25$°C. [b] Calculated using $K_h = 2 \times 10^{-3}$ M, $\Delta H = 10$ kcal mol^{-1}, $\Delta S = 22$ cal mol^{-1} K^{-1} for the hydrolysis constant of aquo cobalt(III) ion. [c] kcal^{-1} mol^{-1}. [d] cal mol^{-1} K^{-1}. [e] Reaction of Ni(II) cyclam^{2+} with Ce(IV) ($I = 1.0$ M, $T = 25$°C) shows only a slight hydrogen ion dependence, with possible evidence for a pathway involving the aquo cation $Ce(H_2O)_n^{4+}$ ($k_8' = 3.1 \times 10^3$ M^{-1} s^{-1}).

involving a ligand oxidation. This ligand, however, is not capable of the usual modes of chelation and is probably not directly comparable with the other tetraamines. Reaction of aquo-cerium(IV) with (A) did produce evidence for nickel(III) complex formation but did not exhibit the same first-order kinetic behaviour as the cyclam complex. Reaction stoicheiometry was again consistent with a degree of ligand oxidation. The unsaturated macrocycles of nickel(III) are much less stable in aqueous acidic media, and the low concentrations of reactants precluded a detailed analysis of reaction products.

Reaction of nickel(II) peptides. Molecular oxygen reacts with nickel(II)–peptide complexes in aqueous solution in a facile autocatalytic process in which nickel(III) intermediates are formed. In the reaction [82] of nickel(II)tetraglycine(XIV) ($Ni(II)H_{-3}G_4^{2-}$) rapid oxygen uptake occurs



XIV

after a short induction period. A similar observation is made for other nickel(II) complexes with peptides containing four or more potential N-donor sites. The reactive species has been shown to be the anion XIV, and there is no evidence for any H_2O_2 formation. A mechanism consistent with these observations involves the formation of $[Ni(III)(H_{-3}G_4)]^-$ initiating the reaction resulting in the production of principally CO_2, triglycyl-*N*-(hydroxymethyl)amide and glycinamide. The presence of a free carboxylate group adjacent to a deprotonated peptide nitrogen promotes decarboxylation and the auto-oxidation reactions are more rapid than for other peptide complexes.

The oxidising intermediate is a nickel(III)–peptide, rather than a peroxide, with an absorption maximum at 327 nm ($\epsilon = 5600 \pm 200\ M^{-1}\ cm^{-1}$) and a shoulder at 245 nm. The fully deprotonated species $[Ni(III)H_{-3}G_4]^-$ has been prepared by mild electrolysis or chemical oxidation. The electrode potential of the $[Ni(II),(III)(H_{-3}G_4)]^{2-/1-}$ couple has been evaluated as 0.79 V vs. NHE. The nickel(III) complex which is slightly more stable in acid than in base decays with a first-order rate constant of $7.1 \times 10^{-3}\ s^{-1}$. In the decomposition, half the peptide is oxidized and half may be recovered intact.

The reaction of the nickel(II) peptide with O_2 is sensitive to radical inhibitors and reducing agents, the latter reacting with the nickel(III) intermediate. Using nickel(III)–peptide complexes prepared electrolytically, the reaction order at low concentrations was shown to be first order in $[\mathrm{Ni(II)G_4}]_{\mathrm{tot}}$, $[\mathrm{Ni(III)H_{-3}G_4)}]^-$ and $[\mathrm{O_2}]$ although at higher concentrations the order in each approaches zero.

Reduction of nickel(III)

Reactions of tris(2,2′-bipyridine)nickel(III). Solutions of the lime-green $[\mathrm{Ni(bipy)_3}]^{3+}$ ion have been prepared by anodic oxidation under nitrogen of a suspension of the corresponding nickel(II) perchlorate in 2.00 M $HClO_4$ at 5°C. The ion is stable in solutions of concentrated acid and oxidises water only at lower $[H^+]$ (>2.0 M). Solutions show a weak absorbance at ca. 550 nm, with absorbance increasing continuously from 450–325 nm. Rate measurements were made at 350 nm where $\epsilon =$ ca. $7 \times 10^3\ \mathrm{M^{-1}\ cm^{-1}}$ and ca. $370\ \mathrm{M^{-1}\ cm^{-1}}$ for the nickel(III) and (II) complexes respectively.

In the reaction with hydrogen peroxide [33]

$$2\ \mathrm{Ni(III)} + \mathrm{H_2O_2} \rightarrow 2\ \mathrm{Ni(II)} + \mathrm{O_2} + 2\ \mathrm{H^+} \tag{9}$$

stopped-flow studies indicate the rate law $R = k_9[\mathrm{Ni(III)}][\mathrm{H_2O_2}]$ with a zero-order dependence in $[H^+]$ over the range 0.5–2.00 M. No specific ion effects were observed at $I = 2.0$ M, although differences in rate were observed on changing Li^+ for Na^+, as the counter ion at $I = 3.60$ M.The lack of a term in $[H^+]$ is considered as evidence that oxidation is not preceded by substitution of H_2O_2 into the inner sphere of Ni(III). In this regard the oxidation differs from that of hydrogen peroxide by aquo cations.

In the corresponding reaction with bromide [82], the 1 : 1 reaction stoicheiometry leading to Br_2 formation has been determined. The rate law is first order with respect to both oxidant and reductant and also shows no term in $[H^+]$. Again data have been compared with those for the highly oxidising cations, Ce(IV), Mn(III), V(V) and Co(III) where intermediate complexes have been observed previously.

A hydrogen ion dependence observed in the reaction with hydrazoic acid [83] has been ascribed to the proton dissociation of the ligand. In this system the kinetic rate law, $\mathrm{Rate} = kK_a[\mathrm{Ni(III)(bipy)_3}][\mathrm{HN_3}][\mathrm{H^+}]^{-1}$ is consistent with the reaction scheme

$$\mathrm{HN_3} \rightleftharpoons \mathrm{H^+} + \mathrm{N_3^-} \quad K_a$$

$$[\mathrm{Ni(bipy)_3}]^{3+} + \mathrm{N_3^-} \xrightarrow{k_{10}} [\mathrm{Ni(bipy)_3}]^{2+} + \mathrm{N_3^{\cdot}} \tag{10}$$

$$2\ \mathrm{N_3^{\cdot}} \xrightarrow{\text{fast}} 3\ \mathrm{N_2}$$

An interesting analysis has been made of the thermodynamic parameters associated with these reactions (Table 9). The higher $\Delta H^\ddagger$ (60 kJ mol^{-1}) for

TABLE 9

Rate constants and thermodynamic parameters for reduction of $\mathrm{Ni(bipy)_3^{3+}}$ ions, $I = 2.0$ M ($\mathrm{LiClO_4/HClO_4}$)

Reaction	$k_9(\mathrm{M^{-1}\,s^{-1}})$	$\Delta H^{\ddagger\,a}$	$\Delta S^{\ddagger\,a}$	Ref.
$\mathrm{Ni(bipy)_3^{3+} + H_2O_2}$	0.34	37.5	-126 ± 7	33
$\mathrm{Ni(bipy)_3^{3+} + Br^-}$	101 ± 9	60 ± 4	-3 ± 11	82
$\mathrm{Ni(bipy)_3^{3+} + N_3^-}$ [b]	1.04×10^6	36 ± 3	-3 ± 10	83

[a] ΔH, kJ $\mathrm{mol^{-1}}$; ΔS, J $\mathrm{K^{-1}\,mol^{-1}}$.

[b] Values (K_{10}) derived using dissociation constant $K_a = 1.0 \times 10^{-4}$ M, $\Delta H^0 = 15.1$ kJ $\mathrm{mol^{-1}}$, $\Delta S^0 = -32.6$ J $\mathrm{K^{-1}\,mol^{-1}}$.

the oxidation of $\mathrm{Br^-}$ compared to that for the reaction with $\mathrm{H_2O_2}$ (37.5 kJ $\mathrm{mol^{-1}}$) reflects the higher redox potential of the bromide ion (1.087 V) compared with that (0.682 V) of hydrogen peroxide. The value ($\Delta H^{\ddagger} = 51$ kJ $\mathrm{mol^{-1}}$) for reaction with hydrazoic acid (−3.1 V) does not, however, follow this trend. Also, the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ relate to the rearrangement of the system, including solvation effects, in the transition state sufficient to enable electron tunnelling to occur between cation and ligand. A major contribution arises from changes in solvent molecules adjacent to oxidant and reducing ligand attendant on the changes in charge occurring with the redox process. Whereas a positive $\Delta S^{\ddagger}_{\mathrm{elec}}$ is associated with release of solvent molecules on reduction of charge on oxidant, a negative $\Delta S^{\ddagger}_{\mathrm{prot}}$ may be observed where increased restriction is imposed on the solvent by protons released. The high negative overall $\Delta S^{\ddagger}$ observed for the $\mathrm{H_2O_2}$ (−126 J $\mathrm{K^{-1}\,mol^{-1}}$) reaction may be attributed to the dominance of the latter effect whereas the low value $\Delta S^{\ddagger} = -3$ J $\mathrm{K^{-1}\,mol^{-1}}$ for $\mathrm{Br^-}$ indicates no substantial charge reduction in the transition state and no release of $\mathrm{H^+}$. An identical low $\Delta S^{\ddagger}$ is consistent with reaction of the dissociated anion in the reaction with azide [83], confirming the absence of any proton release on electron transfer.

Reactions of Ni(III) macrocycles. To date relatively few kinetic studies have been made on the oxidation of ligands by these nickel(III) complexes. It is of interest, however, to investigate whether these d^7 ions will oxidise via inner sphere (coordination of an axially substituted ligand) or outer sphere pathways. Using solutions of nickel(III)cyclam and *cis* and *trans*[Ni(III)-$\mathrm{Me_6[14]aneN_4]^{3+}}$ prepared from crystalline samples of the complexes, the stability (where $[\mathrm{H^+}] > 0.2$ M) is sufficient to enable stopped-flow studies to be made. The reactions of these oxidants with hydroquinone, catechol and ascorbic acid have been studied [84]. In all systems examined the overall reaction may be written as

$$\mathrm{2\,Ni(III) + H_2A \rightarrow 2\,Ni(II) + A + 2\,H^+} \qquad (11)$$

From a comparison of the rate data (Table 10) with those for complex formation (Table 6) it is apparent that the spread of reaction rates is much greater and is consistent with an outer-sphere process. In the reactions of $\mathrm{Ni(cyclam)^{3+}}$ with hydroquinone and catechol ($\mathrm{H_2X}$) there is evidence for two pathways.

$$\mathrm{NiL_1^{3+} + H_2X \xrightarrow{k_{12}} Ni^{II}L_1 + HX + H^+} \qquad (12)$$

$$\mathrm{NiL_1(OH)^{2+} + H_2X \xrightarrow{k_{13}} Ni^{II}L_1 + HX} \qquad (13)$$

The acid dissociation involving a coordinated water molecule (pK_a = ca. 3.5) is favoured over any proton equilibrium of the organic substrate ($pK \geq 10$) where the rate constants would be greater than the diffusion controlled limit. Complexing of the nickel(III) species with sulphate (Fig. 6) produces a marked deceleration in rate. The equilibrium constant for the inner sphere complex $\mathrm{NiL_1SO_4^+}$ is ca. 10^3 M and the redox potential of this species is too low to act as a contributor in the oxidation process.

In reactions with ascorbic acid ($\mathrm{H_2A}$), however, the rate law

$$\mathrm{Rate} = (k_{15} + k_{16}K_a[\mathrm{H^+}]^{-1})[\mathrm{Ni(III)L}][\mathrm{H_2A}] \qquad (14)$$

is consistent with a reaction scheme where both the protonated and dissociated forms of the reductant are involved, although reaction of NiL(OH) cannot be excluded.

$$\mathrm{H_2A \rightleftharpoons HA^- + H^+} \qquad K_a$$

$$\mathrm{Ni(III)L + H_2A \xrightarrow{k_{15}} Ni(II)L + H_2A^+\ (HA + H^+)} \qquad (15)$$

$$\mathrm{Ni(III)L + HA^- \xrightarrow{k_{16}} Ni(II)L + HA} \qquad (16)$$

$$\mathrm{Ni(III)L + HA \xrightarrow{k_{17}} Ni(II)L + H^+}$$

For all these reagents the rate-determining step [illegible] is the formation of radicals which react very rapidly with a second mole of oxidant. Differences in rate observed in the reactions of the [illegible] complexes compared to the [illegible] result from differences in the [illegible] potentials.

The reduction of nickel(III) [illegible] proceeds via a [illegible] outer sphere [illegible] $\mathrm{Ni(III)L}$ [illegible] with no evidence [illegible] of higher order in oxidant. Rate constants [illegible] under conditions where [illegible]

TABLE 10
Rate constants for redox reactions of nickel(III) macrocycles ($T=25°C$) [84]

Reaction	$k_{25}(M^{-1}\ s^{-1})$
$NiL_1^{3+} + H_2Q$ [c]	1 $\times 10^4$
$NiL_1OH^{2+} + H_2Q$	ca. 5 $\times 10^{4a}$
$NiL_1^{3+} + H_2cat$ [d]	6.5 $\times 10^2$
$NiL_1OH^{2+} + H_2cat$	1.5 $\times 10^{3a}$
$NiL_2^{3+} + H_2cat$	2.25×10^3
$NiL_2^{3+} + H_2$ ascorbic	$2.5_2 \times 10^{4b}$

[a] Calculated using $pK_a[NiL_1(OH_2)_2] = 3 \times 10^{-4}$ M. [b] Accompanying reactions showing hydrogen ion dependences yield composite rate constants. [c] H_2Q = hydroquinone. [d] H_2cat = catechol.

nickel(III) or iodide are in excess. The rate constant ($k_2(26°) = 3.08 \times 10^3$ $M^{-1}\ s^{-1}$) is somewhat greater than for the substitution processes described earlier and the electron transfer is considered outer sphere.

Reduction reactions of other macrocycles have also been studied following pulse-radiolysis/flash photolysis oxidation studies. Laurence [56] has found that in acid solution the decay of (A), formed by reaction of ·OH with the nickel(II) species, is so slow that it is possible to add reducing substrates (Br^-, I^-, NCS^-) and H_2O_2 (0.01–0.1 M) to determine rates and mecha-

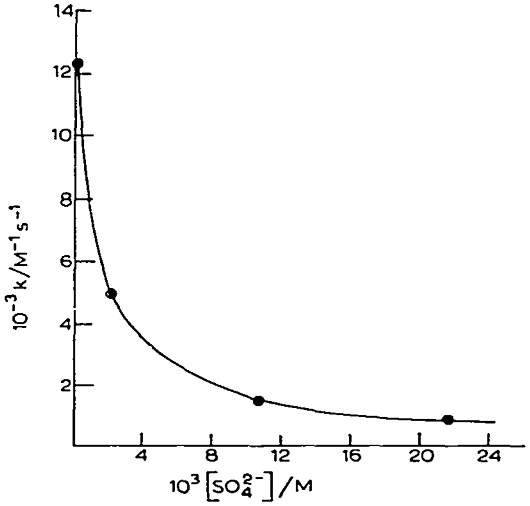


Fig. 6. Decrease in second order rate constant on addition of Li_2SO_4 in reaction of $Ni(cyclam)^{3+}$ with catechol, pH = 3.27, $T = 25°C$. $[Ni(III)] = 2 \times 10^{-5}$ M, $[catechol] = 5.93 \times 10^{-4}$ M.

nisms of decay of the nickel(III) ions. Study at low pH also removes complicating competing reactions involving nickel(II)–ligand radical species observed at higher pH. No reaction of (A), (B) or (C) was observed with Cl^- at low concentrations and at pH 1 even at $[Cl^-] = 0.1–0.5$ M, only the tetraene (C) was found to react. Under these conditions a second-order process was observed, the rate constant being dependent on chloride ion concentration. With Br^-, however, all three complexes reacted in a sequence similar to that for chloride. A suggested mechanism may be written as

$$[Ni(III)L]^{3+} + X^- \rightleftharpoons [Ni(III)LX]^{2+} \tag{17}$$

$$[Ni(III)LX]^{2+} + X^- \rightleftharpoons [Ni(II)L]^{2+} + X_2^- \tag{18}$$

$$[Ni(III)L]^{3+} + X_2^- \rightarrow [Ni(II)L]^{2+} + X_2 \tag{19}$$

leading to the rate expression

$$\frac{-d[Ni(III)L]}{dt} = \frac{2k_{18}k_{19}[Ni(III)]^2}{k_{-18}[Ni(II)] + k_{19}[Ni(III)]} \cdot \frac{K_{17}[X^-]^2}{K_{17}[X^-] + 1} \tag{20}$$

The linear dependence of the second order rate constant on $[Cl^-]$ implies that at 0.1 M $[Cl^-]$ a high proportion of complex (A) has at least one Cl^- axially coordinated. The observed second order dependence on [Ni(III)] also implies that $k_{-18}[Ni(II)] > k_{19}[Ni(III)]$. In an independent study on the bromide oxidation by complex (B), Meyerstein and co-workers [81] have proposed an almost identical mechanism, δ having also observed the second order rate law, linear dependence on $[Br^-]$, and the slight decrease on increasing [Ni(II)L]. (At higher $[Br^-]$, $K_{17} \cdot [Br^-] > 1$, eqn. (20)). Although Whitburn and Laurence [56] have chosen to present only composite constants, using the relative concentrations of the Ni(II) and Ni(III) complexes present in solution, Meyerstein and co-workers [81] have provided estimates for the individual reaction rate constants. At pH 3.0, $k_{17} = $ ca. 1300 M^{-1} s^{-1}, $k_{-17} = $ ca. 120 s^{-1}, $k_{18} = $ ca. 40 M^{-1} s^{-1} and $k_{-18} = 9 \times 10^9$ M^{-1} s^{-1}. Where comparisons are possible it appears that the value for $k_{17} \cdot k_{18}$ (ca. 1.9×10^{13} M^{-2} s^{-2}) at pH 3 is about an order of magnitude ($(2 \pm 0.3) \times 10^{12}$ M^{-2} s^{-2}) greater than at pH 1.

Under conditions of relatively low ratios of $[H_2O_2]$:[Ni(II)L], the reaction of nickel(III), complexes (A), (B) and (C) showed first order behaviour, the rate constants [56] being linear functions of $[H_2O_2]$. Whereas for complexes (B) and (C) the rates were pH independent (pH 1–4), for species (A) the rate constants increased with pH in this range. Below pH 1, the latter reaction was complicated by a second order process and at pH ca. 0.3, the kinetic behaviour resembled that of the halide ions above. No evidence was found for coordination of HO_2^- ion although this is a feature of many aquo metal ions [85].

Studies have also been undertaken on the reaction with reduced metal ions [56]. Using conditions in which relative concentrations of nickel(II) complexes and metal ions were such that >90% of the oxidising radicals reacted to yield nickel(III) species, the second order rate constants for the reactions

$$[\mathrm{Ni(III)L}]^{3+} + \mathrm{M}^{2+} \xrightarrow{k_{21}} [\mathrm{Ni(II)L}]^{2+} + \mathrm{M}^{3+} \tag{21}$$

were determined. All nickel(III) complexes (A), (B), (C), oxidise Fe(II) ions with rate constants k_{21} = ca. 10^4 M^{-1} s^{-1}, but only for (C) was the oxidation of Mn^{2+} measurable ($k_{21} = 1.5 \times 10^2$ M^{-1} s^{-1}). None of the nickel(III) species oxidised cobalt(II) aquo ions. In view of the similarity of the rates for the complexes where a Marcus treatment of outer sphere reactivity would indicate an expected difference of ca. 10^2 in the rate between (A) and (C) and since for (C) the rate with Mn(II) is only ca. 200 times smaller than for Fe(II) it is suggested that the reactions may be inner sphere in nature.

F. ADDENDUM

Since the preparation of this review, the results of two important investigations have been published. Single crystal EPR studies have been reported [87] on $[Ni(DP)_2X_2]Y$ (DP = *o*-phenylenebis(dimethylphosphine); $X^- = Cl^-$, Br^-; $Y^- = ClO_4^-$, PF_6^-) doped in the corresponding cobalt(III) lattices. In the $[Co(III)(DP)_2Cl_2]ClO_4$ matrix, the spectrum of magnetically dilute polycrystalline $[Ni(DP)_2Cl_2]ClO_4$ shows an orthorhombic g tensor with the high-field g component containing 17 strong intensity lines (within which are spaced a set of lines of lower intensity), with the lowest field lines overlapping the higher field lines of the low-field g component. The origin of the signal is a quintet hyperfine feature from four equivalent ^{31}P centres being further split by ^{35}Cl and ^{37}Cl such that $A(^{31}P) \approx 2.5\,A(^{35}Cl)$. The principal values of g obtained together with those of the ligand superhyperfine tensors are $g_{xx} = 2.1123$, $g_{yy} = 2.1157$ ($g_\perp$ calculated = 2.11048), g_{zz} = 2.0089; for ^{35}Cl $A_{xx} = 18.3 \pm 1$ G, $A_{yy} = 15.3 \pm 1$ G, $A_{zz} = 17.6 \pm 1$ G; for ^{31}P, $A_\sigma = 13 \pm 1$ G, $A_\pi = 5 \pm 1$ G, $A_{zz} = 43.6 \pm 1$ G. For the dibromo complex $[Ni(DP)_2Br_2]PF_6^-$, $g_{xx} = 2.0961$, $g_{yy} = 2.1413$, $g_{zz} = 1.9936$; for ^{81}Br $A_{xx} = 61 \pm 1$ G, $A_{yy} = 26 \pm 1$ G, $A_{zz} = 169 \pm 1$ G and for ^{31}P the value of A is nearly isotropic (20 ± 2 G). In this system the spectrum is complicated owing to isotopic effects of the bromine. Both complexes studied, however, indicate considerable delocalisation of the electron density for nickel(III) complexes with Group V donor ligands. In the bromo complex there is a high degree of σ delocalisation onto the axial bromine centres leading to a net higher covalency than for the corresponding dichloro complexes ions $[Ni(DP)_2Cl_2]^+$ or the ditertiary arsine analogue [88] $[Ni(DAs)_2Cl_2]^+$.

Nickel(II) complexes of novel penta-azamacrocycles have been shown to be easily oxidised both chemically and electrochemically [89]. In contrast to the tetra-aza systems, the $E_{1/2}$ values are only slightly dependent on the macrocyclic ring size. Nickel(III) complexes with unsubstituted penta-aza ring systems of the type $N_5[15]$ane, $N_5[16]$ane and $N_5[17]$ane have been prepared. The lowest energy absorption band decrease in energy in the order Ni[15]ane > Ni[16]ane > Ni[17]ane for the divalent metal centres indicating a progressive weakening of the Ni–N interactions on enlarging ring size. In the nickel(III) systems, the macrocycle is considered quinquidentate with the sixth octahedral site occupied by a solvent molecule ($g_\perp = 2.17$, $g_\parallel = 2.03$). The half wave potentials (vs. $Ag/AgNO_3$ (0.01 M) in CH_3CN containing 0.1 M Et_4NBF_4) are Ni[15]ane$^{2+/3+}$, 0.737 V; Ni[16]ane$^{2+/3+}$, 0.772 V; and Ni[17]ane$^{2+/3+}$, 0.817 V. For the tetra-aza macrocycles variation of ring size from [12]ane to [16]ane shows an increase of ca. 0.4 V in $E_{1/2}$. The presence of a nitrogen donor in the apical coordination site is considered to help the attainment of the nickel(III) state and release the redox (Ni(III)/(II)) process from inplane ring size effects. This view is substantiated by the ready chemical oxidation of the penta-aza systems (by NO^+ in CH_3CN or $S_2O_8^{2-}$ in MeOH).

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REFERENCES

1 Gmelin's Handbuch der Anorganischen Chemie, Part C, No. 2. Verlag Chemie, GmbH, Weinheim/Bergstr., 1969.
2 K.A. Jensen, Z. Anorg. Allg. Chem., 229 (1936) 265.
3 K.A. Jensen, B. Nygaard and K.T. Pedeygen, Acta Chem. Scand., 17 (1963) 1126.
4 A.H. Maki, N. Edelstein, A. Davison and R.H. Holm, J. Am. Chem. Soc., 86 (1964) 4580.
5 J.A. McCleverty, Prog. Inorg. Chem., 10 (1968) 49.
6 A.L. Balch, F. Rohrscheid and R.H. Holm, J. Am. Chem. Soc., 87 (1965) 2301.
7 A. Davison, N. Edelstein, A.H. Maki and R.H. Holm, Inorg. Chem., 2 (1963) 1227.
8 R.S. Nyholm, J. Chem. Soc., (1950) 2061; (1951) 2602; (1952) 2906; Nature (London), 165 (1950) 154.
9 F.H. Burstall and R.S. Nyholm, J. Chem. Soc., (1952) 3570.

10 G.A. Barclay and R.S. Nyholm, Chem. Ind. (London), (1953) 378.
11 P. Kreisman, R. Marsh, J.R. Preer and H.B. Gray, J. Am. Chem. Soc., 90 (1968) 1967.
12 N.C. Stephenson, Acta Crystallogr., 17 (1964) 592.
13 S.I. Shupack, E. Billig, R.J.H. Clark, R. Williams and H.B. Gray, J. Am. Chem. Soc. 86 (1964) 4594.
14 E.I. Stiefel, J.H. Waters, E. Billig and H.B. Gray, J. Am. Chem. Soc., 87 (1965) 3016.
15 E.S. Gore and D.H. Busch, Inorg. Chem., 12 (1973) 1.
16 C.F. Cook and N.F. Curtis, Chem. Commun., (1967) 962.
17 E.K. Barefield and D.H. Busch, Chem. Commun., (1970) 523.
18 D.C. Olsen and J. Vasilevskis, Inorg. Chem., 8 (1969) 1611.
19 F.V. Lovecchio, E.S. Gore and D.H. Busch, J. Am. Chem. Soc., 96 (1974) 3109.
20 E. Zeigerson, G. Ginsburg, N. Schwartz, Z. Luz and D. Meyerstein, Chem. Commun., (1979) 241.
21 R.S. Drago and E.I. Baucom, Inorg. Chem., 11 (1972) 2064.
22 R.S. Drago, G.C. Vogel and T.E. Needham, J. Am. Chem. Soc., 93 (1971) 6014.
23 B. Bosnich, M.L. Tobe and G.A. Webb, Inorg. Chem., 4 (1965) 1102, 1109; B. Bosnich, C.K. Poon and M.L. Tobe, Inorg. Chem., 5 (1966) 1514.
24 W. Levason and C.A. McAuliffe, Coord. Chem. Rev., 12 (1974) 151.
25 See for example, L.F. Lindoy, Chem. Soc. Rev., 4 (1975) 421.
26 L.F. Lindoy and D.H. Busch, in W.L. Jolly (Ed.), Preparative Inorganic Reactions, Vol. 6, Interscience, New York, 1971.
27 N.F. Curtis, Coord. Chem. Rev., 3 (1968) 33; D.H. Busch, Acc. Chem. Res., 11 (1978) 392.
28 F.P. Bossu and D.W. Margerum, J. Am. Chem. Soc., 98 (1976) 4003.
29 D.W. Margerum, K.L. Chellappa, F.P. Bossu and G.L. Burce, J. Am. Chem. Soc., 97 (1975) 6894.
30 H.C. Freeman, J.M. Gauss and R.L. Sinclair, Chem. Commun., (1968) 485.
31 R.H. Felton, D. Dolphin, D.C. Borg and J. Fajer, J. Am. Chem. Soc., 91 (1969) 196; 92 (1970) 743, 3451, and references therein.
32 J.C. Brodovitch, R.I. Haines and A. McAuley, Can. J. Chem., in press.
33 D. Fox and C.F. Wells, J. Chem. Soc., Dalton Trans., (1977) 1498.
34 J. Lati and D. Meyerstein, Inorg. Chem., 11 (1972) 2393.
35 J. Lati and D. Meyerstein, Inorg. Chem., 11 (1972) 2397.
36 J. Lati, J. Koresh and D. Meyerstein, Chem. Phys. Lett., 33 (1975) 286.
37 N.F. Curtis, Chem. Commun., (1966) 881; J. Chem. Soc. A, (1971) 2835.
38 J.C. Brodovitch and A. McAuley, Inorg. Chem., in press.
39 H. Cohen, L.J. Kirschenbaum, E. Zeigerson, G. Ginsburg, M. Jaacobi, E. Fuchs and D. Meyerstein, Inorg. Chem., 18 (1979) 2763.
40 M.C. Rakowski, M. Rycheck and D.H. Busch, Inorg. Chem., 14 (1975) 1194.
41 Y. Sugiura and Y. Mino, Inorg. Chem., 18 (1979) 1336.
42 F.P. Bossu, E.B. Paniago, D.W. Margerum, S.T. Kirksey Jr. and J.L. Kurtz, Inorg. Chem., 17 (1978) 1034.
43 E.K. Barefield and D.H. Busch, Chem. Commun., (1970) 523.
44 L.E. Edelman, J. Am. Chem. Soc., 72 (1950) 5765; A.S. Foust and R.H. Soderberg, J. Am. Chem. Soc., 89 (1967) 5507.
45 L.F. Mehne and B.B. Mayland, Inorg. Chem., 14 (1975) 881.
46 P. Spacu, C. Gheorghiu and A. Nicolaescu, Inorg. Chim. Acta, 2 (1968) 413.
47 D.C. Olsen and J. Vasilevskis, Inorg. Chem., 8 (1969) 1611.
48 G. Ferraudi, Inorg. Chem., 18 (1979) 3230; G. Ferraudi and L. Patterson, Chem. Commun., (1977) 755.

49 N. Takuoryan, F. Farmery, V. Katovic, F.V. Lovecchio, E.S. Gore, L.B. Anderson and D.H. Busch, J. Am. Chem. Soc., 96 (1974) 731.
50 E.K. Barefield and M.T. Mocella, J. Am. Chem. Soc., 97 (1975) 4238.
51 J.J. Czarnecki and D.W. Margerum, Inorg. Chem., 16 (1977) 1997.
52 F.P. Bossu and D.W. Margerum, Inorg. Chem., 16 (1977) 1210.
53 A.G. Lappin, C.K. Murray and D.W. Margerum, Inorg. Chem., 17 (1978) 1630.
54 L.J. Kirschenbaum and D. Meyerstein, 1980, personal communication.
55 R.I. Haines and A. McAuley, 1980, unpublished observations.
56 K.D. Whitburn and G.S. Laurence, J. Chem. Soc., Dalton Trans., (1979) 139.
57 A.T. Thornton and G.S. Laurence, J. Chem. Soc., Dalton Trans., (1973) 804.
58 E. Zeigerson, G. Ginsburg, D. Meyerstein and L.J. Kirschenbaum, J. Chem. Soc., Dalton Trans., (1980) 1243.
59 B.N. Figgis, Introduction to Ligand Fields, Interscience, New York, 1966, p. 242.
60 S. Cockle, H.A.O. Hill, S. Ridsdale and R.J.P. Williams, J. Chem. Soc., Dalton Trans., (1972) 297.
61 A. Desideri, J.B. Raynor and C.K. Poon, J.Chem. Soc., Dalton Trans., (1977) 2051.
62 R.I. Haines and A. McAuley, Inorg. Chem., 19 (1980) 719.
63 E.J. Billo, Inorg. Nucl. Chem. Lett., 10 (1974) 613.
64 A. Wolberg and J. Manassen, Inorg. Chem., 9 (1970) 2365.
65 J.L. Mills, R. Nelson, S.G. Shore and L.B. Anderson, Anal. Chem., 43 (1971) 157.
66 E.K. Barefield, F.V. Lovecchio, V.E. Tokel, E. Ochiai and D.H. Busch, Inorg. Chem., 11 (1972) 283.
67 J.D. Curry, Ph.D. Dissertation, The Ohio State University, 1964.
68 A. Wolberg and J. Manassen, J. Am. Chem. Soc., 92 (1970) 2982.
69 D.P. Rillema, J.F. Endicott and E. Papaconstantinou, Inorg. Chem., 10 (1971) 1739.
70 D.G. Pillsbury and D.H. Busch, J. Am. Chem. Soc., 98 (1976) 7836.
71 J. Gordon and R.A. Ford, The Chemist's Companion, Wiley, New York, 1972, pp. 144–153.
72 L. Sabatini and L. Fabbrizzi, Inorg. Chem., 18 (1979) 438.
73 A. Anichini, L. Fabbrizzi, P. Paoletti and R.M. Clay, Inorg. Chim. Acta, 24 (1977) L21.
74 G.C. Gordon, S.-M. Peng and V.L. Goedken, Inorg. Chem., 17 (1978) 3578.
75 D.H. Busch, D.G. Pillsbury, F.V. Lovecchio, A.M. Tait, Y. Hung, S. Jackels, M.C. Rakowski, W.P. Schammel and L.Y. Martin, A.C.S. Symp. Ser. No. 30, (1977) 32.
76 C. Postmus and E.L. King, J. Phys. Chem., 59 (1955) 1208.
77 J. Lati and D. Meyerstein, Int. J. Radiat. Phys. Chem., 7 (1975) 611.
78 J. Lati and D. Meyerstein, Isr. J. Chem., 10 (1972) 735.
79 G. Ferraudi and L. Patterson, J. Chem. Soc., Chem. Commun., (1977) 755.
80 P. Maruthanutha, L.K. Patterson and G. Ferraudi, Inorg. Chem., 17 (1978) 3157.
81 M. Jaacobi, D. Meyerstein and J. Lilie, Inorg. Chem., 18 (1979) 429.
82 C.F. Wells and D. Fox, J. Chem. Soc., Dalton Trans., (1977) 1502.
83 J.K. Brown, D. Fox, M.P. Heyward and C.F. Wells, J. Chem. Soc., Dalton Trans., (1979) 735.
84 R.I. Haines, A. McAuley and T. Oswald, to be published.
85 C.F. Wells and M. Husain, Trans. Faraday Soc., 67 (1971) 706.
86 F.P. Bossu, E.P. Paniago, D.W. Margerum, S.T. Kirksey and J.L. Kurtz, Inorg. Chem., 17 (1978) 1034.
87 C.N. Sethulakshmi, S. Subramainan, M.A. Bennett and P.T. Manoharan, Inorg. Chem., 18 (1979) 2520.
88 P.K. Bernstein and H.B. Gray, Inorg. Chem., 11 (1972) 3035.
89 L. Fabrizzi, J. Chem. Soc., Chem. Commun., (1979) 1063.