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MONOVALENT, TRIVALENT AND TETRAVALENT NICKEL

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CONTENTS

A. INTRODUCTION

The known chemistry of nickel spans all oxidation states from −1 to +4. Among these the −1 state is ill-defined; a search of the literature revealed that the known examples do not far exceed those catalogued in recent text

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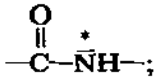
books [1,2]. The common chemistry of nickel is the chemistry of the +2 oxidation state. An extensive chemistry also exists for zero-valent nickel [3,4]. The oxidation states +1, +3 and +4 can be considered as comparatively sparse but enough is now known — mainly due to efforts during the last fifteen years or so — to merit the detailed consideration given to them in this article. In general all these oxidation states are highly reactive bringing about oxidation or reduction of a variety of organic substrates. Nickel(I) species are also prone to undergo dissociation or disproportionation particularly in solution. Historically, the first report of an uncommon oxidation state of nickel is that of Hall [5] who described a heteropolymolybdate of quadrivalent nickel in 1907. The earliest report [6] of a nickel(I) complex came in 1913 in the form of the red cyano complex, $K_4Ni_2(CN)_6$. In the same year an oxime ligand was shown to stabilise higher oxidation states of nickel [7]. Jensen isolated [8] violet-black crystals of $Ni(PEt_3)_2Br_3$ containing trivalent nickel in 1936. Nyholm's work [9] on the nickel(III) and nickel(IV) complexes using the chelating arsenic ligand, *o*-phenylenebisdimethylarsine constitutes another early landmark. Each one of these discoveries eventually led to more extensive activities which will be duly considered in this article.

The three oxidation states of nickel discussed in this article have not previously been the sole subject matter of any review paper. Some accounts of the chemistry of these oxidation states have, however, appeared separately as part of broader topics [10]. In the present article some general features of synthetic methods and structure will be considered first. This will be followed by a description of the chemistry of known systems arranged according to the principal ligand present. This arrangement is necessitated by the fact that often the same ligand type stabilises high and low oxidation states of nickel depending upon experimental conditions and companion ligands. No attempt has been made to make this compilation exhaustive. On the other hand, it is believed that much that is major, interesting and fascinating has been included.

B. GENERAL OBSERVATIONS

(i) Ligand preference, stereochemistry and structure

When a metal ion combines with a ligand, charge redistribution occurs according to the dictum of the electroneutrality principle. In the case of a metal in a high oxidation state, it is imperative that the ligand should have a high electron density and possibly one or more negative charges. Here charge will flow from the ligand to the metal but this process should not proceed to an unrestricted extent since ligand oxidation will then occur. In other words ligand electronegativity should be high [11]. In a bond description this amounts to the formation of strong metal—ligand σ-bonds. In the particular case of pseudooctahedral nickel this approach can be developed further. Strong σ-bonds here mean unstable $\sigma^*(e_g^*)$ levels which in nickel(II) are doubly occupied. Facile loss of e_g^* electron(s) can then give nickel(III) or nickel(IV) species [12]. Like many other high oxidation state metal ions, these ions have predominant class *a* character. From the above it is easy to understand why the large majority of well-characterised nickel(III) and nickel(IV) complexes have the first period donor atoms F, O and N in the primary coordination sphere. Some groups which have proved particularly effective are (the binding atom is marked by asterisk)

 ;	 $-\overset{\overset{O}{\|}}{C}-\overset{*}{N}H-$;	$>C{=}\overset{*}{N}-\bar{O}$;	O^{2-};	F^-
macrocycle	ionised amide	ionised oxime	oxide	fluoride

At the present state of development, the nitrogen donor systems — both open chain and macrocyclic — display the most extensive chemistry. The nitrogen macrocycles also stabilise nickel(I). However, ligands usually used for binding this oxidation state contain soft donors which are capable of accepting electrons through back-bonding into antibonding orbitals. By far the largest number of stable nickel(I) complexes are derived from phosphine and to a lesser extent from arsine type ligands.

Ligand preference and stereochemistry of nickel in oxidation states +1, +3 and +4 are summarily presented in Table 1. A special feature of nickel(I) chemistry is the frequent occurrence of dimeric structures (metal—metal bond)

TABLE 1

Donor groups used in stabilising nickel in the oxidation states +1, +3 and +4

Donor atom	Ligand	Oxidation state
H	Hydride	+1
B	Boranes and carboranes	+3, +4
C	Cyanide	+1, +3
	Acetylide	+1
	Cyclopentadienide	+1, +3, +4
N	Amines and amino acids	+1, +3
	Amides, peptides and related species	+3
	Oximes	+3, +4
	Macrocycles	+1, +3, +4(?)
P	Phosphines	+1, +3, +4
As	Arsines	+1, +3, +4
O	Oxide	+3, +4
	Oxo anions	+3 (?), +4
S	Dithiolenes	+1
	Dithiocarbamates	+1, +3, +4
Se	Diselenocarbamates	+4
F	Fluoride	+3, +4
Cl, Br, I	Halides [a]	+1, +3, +4

[a] Appear only as secondary ligands particularly in phosphine and arsine complexes.

both in the solid state and in solution. In the isoelectronic series, nickel(I), cobalt(0) and copper (II), the chemistry of nickel(I) is closer to that of cobalt(0). The majority of known nickel(I) compounds have tetrahedral or trigonal bipyramidal structures. Trigonal and square planar complexes are also known. In contrast, the common stereochemistry of +3 and +4 states is octahedral or distorted versions thereof. Other proven stereochemistries are four-coordinate planar and pentacoordinate trigonal bipyramidal. This does not include sandwich complexes based on delocalised cyclic π-ligands (cyclopentadiene, carboranes etc.) which now have a well-defined nickel(III) and nickel(IV) chemistry. Such systems will be discussed in due course.

(ii) Methods of study

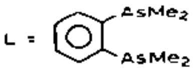
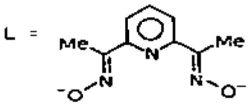
Structures of a limited number of complexes are now accurately known from three-dimensional diffraction work [13—25]. These are collected in Table 2. Even though the known chemistry of nickel(III) is dominated by

TABLE 2

Crystal structure data of discrete complexes

Compound	Structural detail and comments	Ref.
Nickel(I)		
$K_4Ni_2(CN)_6$	The dinuclear anion contains two almost planar $Ni(CN)_3$ units which are linked by a short Ni—Ni bond of length 2.32 A about which the two units are twisted by 82° with respect to each other; Ni—C(av), 1.91 A. The same molecular structure obtains in $Rb_4Ni_2(CN)_6$.	13,14
$[NiL_4]BPh_4$ $L = PMe_3$	The geometry of nickel is a slightly distorted tetrahedron; <PNiP, 120—105°; Ni—P(av), 2.22 A.	15
$[NiLI]$ $L = MeC(CH_2PPh_2)_3$	The $[NiP_3I]$ coordination unit is a distorted tetrahedron; <PNiP, 92—97°, <PNiI 116—125°; Ni—P (av), 2.22 A; Ni—I, 2.546 A.	16
$[Ni_2L_4Br_2]BPh_4$ L = 	Each ligand bridges the two metal atoms through the two nitrogen donors and each nickel atom is square pyramidal having four nitrogen atoms at the base and one bromine atom at the apex. The two equivalent NiN_4Br chromophores together constitute a distorted bicapped tetragonal antiprism. The average twist angle between the two tetragonal pyramids is 25°; Ni—Ni, 2.415 A; Ni—N(av), 2.01 A; Ni—Br(av), 2.61 A.	17
$[NiLH_{0.5}]BF_4$ $L = N(CH_2CH_2PPh_2)_3$	The nickel atom lies at the centre of an almost regular trigonal bipyramid. The three phosphorus atoms form the basal equilateral triangle and the nitrogen atom lies at one of the apices; Ni—P (av), 2.20 A, <P—Ni—P, 120°. The other apex holds a	18

TABLE 2 (Continued)

Compound	Structural detail and comments	Ref.
	hydrogen atom in only half of the molecules ($<$N—Ni—H, 171°). Among the coordination spheres NiP_3NH and NiP_3N the latter has a vacant site and the nickel atom is in the formal oxidation state +1.	
$[Ni_2L_2I]BPh_4 \cdot 3$ THF $L = N(CH_2CH_2AsPh_2)_3$	Each nickel atom has a $NiAs_3NI$ coordination sphere which is grossly trigonal bipyramidal. The three arsenic atoms form the basal plane ($<$As—Ni—As ~ 120°) and the two trigonal bipyramids have a common I vertex ($<$Ni—I—Ni = 180°); the other vertex is occupied by the nitrogen atom. Ni—I, 2.994 Å; Ni—N(av), 2.31 Å; Ni—As(av), 2.35 Å.	19
$[NiLL'_2]$ $L = N(SiMe_3)_2$ $L' = PPh_3$	The NiP_2N coordination sphere has a triangular geometry in which the two Ni—P bonds are almost equal (2.22 Å) and the Ni—N distance (1.88 Å) is rather short. $<$P—Ni—P, 170°; $<$P—Ni—N, 122.5 and 130.4°.	20
Nickel(III)		
$NiL_2Br_3 \cdot 0.5\ NiL_2Br_2 \cdot C_6H_6$ $L = PMe_2Ph$	The crystal contains well-separated NiL_2Br_2 (centrosymmetric *trans* planar) and NiL_2Br_3 units in which Ni(III) is grossly trigonal bipyramidal with L at axial and Br at equatorial positions. $<$P—Ni—P, 178.8°; Ni—Br(av), 2.36 Å; Ni—P(av), 2.27 Å.	21
$[NiL_2Cl_2]Cl$ L = 	The $NiAs_4Cl_2$ coordination sphere is centrosymmetric *trans* octahedral (~C_{2h}); distortion from ideal D_{2h} symmetry is reflected in the displacement of Cl atoms from axial positions by ~3°. Ni—As, 2.342 Å; Ni—Cl, 2.425 Å. The Co(III) complex [Co(diars)$_2$Cl$_2$]Cl is isostructural.	22
Nickel(IV)		
$[NiL_3]Br$ $L = (n\text{-}Bu)_2NCS_2^-$	Pseudo-octahedral complex cation of approximate D_3 symmetry; the NiS_6 core is twisted by 14.6° towards trigonal prismatic geometry. Crystal can be considered as close packed columns of S atoms forming octahedra with Ni atoms occupying half the octahedral interstices (similarity to NiAs structure). Ni—S, 2.261 Å; S—C, 1.708 Å; C—N, 1.318 Å; S—S bite, 2.794 Å, Ni—Ni (along column), 5.384 Å.	23
$[NiL_3]Br$ $L = (n\text{-}Bu)_2NCSe_2^-$	Isomorphous with the sulfur analogue; the $NiSe_6$ core is a trigonally distorted octahedron with Ni—Se distance 2.391 Å.	24
NiL_2 L = 	Pseudo-octahedral NiN_6 coordination sphere has a tetrahedrally distorted (D_{2d}) basal plane and the tridentate ligand spans meridionally; all atoms of one ligand (except Me protons) lie very nearly in a plane (molecular symmetry S_4). Ni—N (pyridine) 1.837 Å; Ni—N(oxime), 1.937 Å.	25

nitrogen ligands, the structure of only one such complex has been carefully worked out so far.

For detailed structure determination the X-ray diffraction technique is evidently the most reliable. However, considerable structural information can be obtained using other techniques. For example, nickel(III) species are almost invariably paramagnetic with one unpaired electron (low-spin). Bulk susceptibility and EPR data, particularly the latter, are thus of prime importance in the characterisation of the electronic structure of such species. In the first place EPR data can help to establish whether an unpaired electron in the complex belongs primarily to the metal ion or to the ligand. Ambiguities of the type

$\dot{\mathrm{N}}\mathrm{i(III)L}$ or $\mathrm{Ni(II)(L^{\dot{+}})}$?

$\dot{\mathrm{N}}\mathrm{i(I)L}$ or $\mathrm{Ni(II)(L^{\dot{-}})}$?

where the dot represents an unpaired electron can thus be removed. The average g-tensor of a metal bound electron is substantially different from the free electron value due to spin-orbit contribution while in the ligand radical description this is not so.

For genuine low-spin nickel(III)(d^7) in a tetragonal ligand field, the ground state is usually $(d_{xz}, d_{yz})^4(d_{xy})^2(d_{z^2})^1(d_{x^2-y^2})^0$ which is often simply stated as $(d_{z^2})^1$. In the more general case of rhombic symmetry (d_{xz}, d_{yz} not degenerate) the EPR g-tensors can be written as [26]

$$g_{xx} = 2 - 6\lambda/\epsilon_1 \tag{1}$$

$$g_{yy} = 2 - 6\lambda/\epsilon_2 \tag{2}$$

$$g_{zz} = 2 \tag{3}$$

where λ is the spin-orbit coupling constant ($-715\ \mathrm{cm}^{-1}$, in the free ion) and ϵ_1 and ϵ_2 are respectively the energy gaps $d_{z^2} - d_{yz}$ and $d_{z^2} - d_{xz}$. In tetragonal symmetry these energy gaps are equal ($\epsilon_1 = \epsilon_2 = \epsilon$) and

$$g_{\perp} = 2 - 6\lambda/\epsilon \tag{4}$$

$$g_{\parallel} = 2 \tag{5}$$

Equations (4) and (5) mean $g_{\perp} > g_{\parallel}$, a result which is often used as evidence for $(d_{z^2})^1$ ground state. On the other hand, many paramagnetic $S = \frac{1}{2}$ nickel(I) d^9 species have $g_{\parallel} > g_{\perp}$ suggesting an axial ligand field with $(d_{x^2-y^2})^1$ ground state. However, nickel(I) species can also be diamagnetic due to the presence of nickel—nickel bond in a dimeric structure whose gross presence can be established from molecular weight measurements. The nickel(IV) complexes (d^6) are invariably spin-paired resulting in diamagnetic or very weakly paramagnetic (temperature independent) behaviour. The characterisation of such complexes can be based on stoichiometry, redox studies and use of spectroscopic techniques.

When complex formation occurs, charge is transferred such that each atom approaches electroneutrality. The effective charge on a metal atom in a complex is therefore quite different from the formal oxidation state or number which merely is the charge left on the metal atom after all attached ligands have been hypothetically removed in their closed shell configuration. Photoelectron spectroscopy provides a powerful technique for probing the variation of the effective charge in going from complexes of one oxidation state to those of another. The ${}^2P_{3/2}$ binding energies of a number of nickel complexes have been investigated [27—29]. Some selected results are tabulated below.

Substance		Binding energy (eV)
Ni(powder)		852.8
NiO		856.2
$K_2Ni(CN)_4$		855.6
$K_4Ni_2(CN)_6$		852.8
K_2NiF_6		861.2
$Ni(S_2C_2Ph_2)_2^{z-}$	$z = 0$	852.9
	$z = 1$	852.5
	$z = 2$	852.8
$Ni(\eta\text{-}B_9C_2H_{11})_2$		857.2
$Ni(\eta\text{-}B_9C_2H_9Me_2)_2$		856.6
$KNi(\eta\text{-}B_9C_2H_{11})_2$		855.6
$KNi(\eta\text{-}B_9C_2H_9Me_2)_2$		855.6

Significant qualitative conclusions are that in $Ni_2(CN)_6^{4-}$ and NiF_6^{2-}, not only the formal charges but also the effective charges are respectively smaller and greater than those of nickel(II) complexes. On the other hand, in dithiolene complexes the binding energies are quite insensitive to the value of z. The observed magnitude of binding energies suggests that in these complexes the effective charge on the metal remains close to zero while the ligand undergoes electron transfer.

Electrochemical techniques — particularly dynamic voltammetry — are becoming increasingly important in the study of uncommon oxidation states of metal ions, nickel ions being no exception. This technique is extremely useful for the identification of oxidation states, even when such states exist as short-lived intermediates, for thermodynamic and kinetic characterisation of electron-transfer behaviour and for the study of chemical reactions coupled to such electron transfer. A nickel(III) species is likely to exhibit characteristic response for the $Ni^{3+} + e \rightarrow Ni^{2+}$ process and often for the reversal of this process (cyclic voltammetry). For a nickel(IV) system a direct two-electron step or two successive one-electron steps may be observable in electrochemical experiments. On the other hand, nickel(I) species can display oxidation to nickel(II) or reduction to nickel(0). Thus from the characteristics of the electrochemical response it is often possible to pinpoint the oxidation state of the nickel ion. Many examples will be cited in the text.

Since cyclic voltammetry is now a commonly used technique, certain important relations [30] are stated below for ready reference. For the reversible electrode reaction,

$$\text{ox} + n\text{e}^- \rightleftharpoons \text{red} \tag{6}$$

we have

$$E^0_{298} = 0.5(E_{\text{pc}} + E_{\text{pa}}) = \bar{E}_{\text{p}} \tag{7}$$

$$\Delta E_{\text{p}} = E_{\text{pc}} - E_{\text{pa}} \simeq 60/n \text{ mV} \tag{8}$$

where E^0_{298} is the formal electrode potential, E_{pc} and E_{pa} are cathodic and anodic peak potentials respectively. For the proton-coupled electron transfer,

$$\text{ox} + n\text{e}^- + m\text{H}^+ \rightleftharpoons \text{H}_m\text{red}, \tag{9}$$

the formal potential is

$$E^0_{298} = \bar{E}_{\text{p}} + 0.059(m/n)\text{ pH} \tag{10}$$

and

$$m = -(n/0.059)(\Delta\bar{E}_{\text{p}}/\Delta\text{pH}) \tag{11}$$

where $\Delta\bar{E}_{\text{p}}$ is the shift in $\bar{E}_{\text{p}}$ due to a change in pH equal to ΔpH.

(iii) Methods of generation

The preparation of nickel(III) and nickel(IV) compounds usually involves chemical ($S_2O_8^{2-}$, HNO_3, halogens, O_2 etc.) or electrochemical oxidation of nickel(II) species. On the other hand, nickel(I) complexes are prepared either by a reductive step — chemical (H^-, alkali metals etc.) or electrochemical — starting from nickel(II) species, or occasionally by an oxidative step (halogens) starting from a nickel(0) compound. These are also produced by disproportionation reactions between nickel(0) and nickel(II) substrates. Good examples of electrochemical synthesis exist in the nickel chemistry of macrocyclic ligands.

The pulse radiolytic technique is a powerful tool for the generation of species having nickel in an unusual oxidation state in aqueous solution. This is usually not a method for bulk synthesis; the radiolysed solutions are directly investigated by various physicochemical techniques. Pulse radiolysis of water can be grossly represented by eqn. (12) [31].

$$4\,\text{H}_2\text{O} \xrightarrow{100\text{ eV}} 2.6\text{e}^-_{\text{aq}} + 2.6\text{ OH} + 0.6\text{ H} + 2.6\text{ H}^+ + 0.4\text{ H}_2 + 0.7\text{ H}_2\text{O}_2 \tag{12}$$

Thus roughly equal numbers of reducing (e^-_{aq}) and oxidising (OH) equivalents are produced. It is possible to make the system totally reducing or totally oxidising with the help of suitable reactive solutes. For example, presence of

N_2O during radiolysis leads to a completely oxidising (OH radical) solution [32].

$$e^-_{aq} + N_2O + H_2O \rightarrow N_2 + OH^- + OH \qquad (13)$$

$$Ni(en)_3^{2+} + OH \rightarrow Ni(en)_3^{3+} + OH^- \qquad (14)$$

On the other hand, a totally reducing situation can be created by adding alcohols or formate ion and such solutions can reduce $Ni(CN)_4^{2-}$ to $Ni_2(CN)_6^{4-}$ [33].

$$OH + CH_3OH \rightarrow {}^{\cdot}CH_2OH + H_2O \qquad (15)$$

$$OH + HCO_2^- \rightarrow {}^{\cdot}CO_2^- + H_2O \qquad (16)$$

$$2\ Ni(CN)_4^{2-} + 2\ {}^{\cdot}CO_2^- \rightarrow Ni_2(CN)_6^{4-} + 2\ CN^- + 2\ CO_2 \qquad (17)$$

Irradiation of nickel(II) species held in a solid matrix (including frozen solution) with high energy photons (u.v., γ or X-radiations) can bring about electron reorganisation, thus leading to the formation of nickel(III) or nickel(I) species or both in small quantity held in the lattice.

The electrochemical method of synthesis is usually very neat since the potential can be precisely set at the desired value thus avoiding complicating side reactions. Moreover the number of electrons transferred can be monitored accurately. While the electrochemical method is suitable for bulk synthesis it can also be used to generate the required oxidation state in solution that can be immediately and directly used for further studies such as EPR without going through isolation and purification cycles.

C. OXIDES AND RELATED SYSTEMS

(i) Binary oxides

As expected oxides and oxo-compounds of nickel(I) are not known. However, the literature shows the existence of a plethora of higher oxides of nickel and indeed their chemistry has a lengthy and confused history [34—42]. Compounds of nickel containing oxygen, hydrogen and variable quantities of alkali metals have been obtained under different experimental conditions in which there is an excess of oxygen above that required by the formula NiO. Although the product formulated as NiO_2 has found widespread applications in oxidising various organic substrates [43], it is doubtful that stoichiometric Ni_2O_3, Ni_3O_4 and NiO_2 have ever been obtained in a pure state. Among the higher oxides of nickel, the better characterised species are three different forms (α, β and γ) of NiO(OH). Nickel hydroxide and its higher oxidation products play a very important role in the energy conversion of the nickel—cadmium cell [42]. β-$Ni(OH)_2$ (brucite modification) undergoes electrochemical oxidation to the +3 state without any change in the main structural feature [35,41,42,44,45]. γ-NiO(OH) has a $CdCl_2$ structure with an elongated cell

[35,41,42,46]. Several nickel(III, II) hydroxides have also been reported [35,37].

(ii) Ternary oxides

The alkali metal nickelates of composition $MNiO_2$ have been obtained with lithium and sodium [47]. $LiNiO_2$ is rhombohedral and has a β-$NaFeO_2$ structure, whereas $NaNiO_2$ is dimorphic with the transition temperature at 493 K. The high temperature form is isomorphous with $LiNiO_2$, and the low temperature modification is monoclinic. Compounds of composition $Li_xNi_{1-x}O$ $(0 < x < 0.65)$ are obtained [48] by heating the oxides of lithium and nickel in an atmosphere of oxygen. When $x \leqslant 0.28$, the compounds are antiferromagnetic; for $0.28 \leqslant x \leqslant 0.5$ they are ferrimagnetic. Paramagnetic behavior is shown by the compositions with $x > 0.5$. The compounds with $x \leqslant 0.28$ have a NaCl structure and in the interval $0.28 < x < 0.61$ they have a β-$NaFeO_2$ structure. The phase richer $(x > 0.61)$ in oxygen is monoclinic. Analogous to alkali metal nickelates $MNiO_2$, $AgNiO_2$ has been isolated [49]. Various other alkali metal (K, Rb, Cs) nickelates rich in oxygen content have been reported and are discussed elsewhere [10,50].

The ternary oxide $BaNiO_3$ has been the subject of several investigations [51—55]. The original structure proposed by Lander [52] has been confirmed by a recent single crystal X-ray analysis [53] which reveals hexagonal close packing of BaO_3 layers, and trigonally distorted NiO_6 octahedra sharing a pair of opposite faces to form nickel chains parallel to the *c*-axis. The nickel—nickel distance in this compound (2.40 Å) is less than that in nickel metal (2.49 Å). This compound has high resistivity [51,56] which precludes the presence of substantial Ni—Ni interaction. $SrNiO_3$ is isostructural to $BaNiO_3$, although a hexagonal close packed structure with corner sharing was expected for the smaller cation strontium. Hexagonal layer structures also prevail in $Ba_2Ni_2O_5$ and $Sr_2Ni_2O_5$ [51,54,55]. The magnetic properties of these and their oxygen deficient variations have been investigated [54]. X-ray diffraction studies [57] of the $Ba_{1-x}Sr_xNiO_{3-y}$ system reveal that the two-layer structure of $BaNiO_3$ does not persist over the entire composition range. A nine-layer structure and a two-layer compressed phase analogous to $Ba_3Ni_3O_8$ exist [51,54]. Although Perovskite structure has been reported for Sr_2NiSbO_6 [58], powder diffraction data of Ba_2NiSbO_6 are entirely different.

Among the rare earth perovskites $LnNiO_3$, only $LaNiO_3$ and $YNiO_3$ are known [54,59—62]. The former is hexagonal and the latter is orthorhombic. The reaction between Nd_2O_3 and NiO in the presence of Na_2CO_3 leads to the formation of a single phase (monoclinic) whose composition varies between $Nd_{1.67}Ni^{2+}_{0.72}Ni^{3+}_{0.41}O_{3.84}$ and $Nd_{1.75}Ni^{2+}_{0.57}Ni^{3+}_{0.43}O_{3.84}$ [59]. Magnetic properties of $LaNiO_3$ have been the subject matter of several investigations. $LaNiO_3$ is a metallic conductor in the temperature range 77—573 K, and exhibits a low, temperature independent susceptibility between 4 and 300 K [63]. The nickel(III) ion has a spin-paired configuration (μ_{eff} = 1.75 B.M. at 300 K) [54] and neutron diffraction data show no evidence for magnetic ordering down to 10 K [64]. The magnetic behavior of the dilute solid solutions Sr_2NiSbO_6—Sr_2AlSbO_6 and $LaNiO_3$—$LaAlO_3$ were recently reported [65]. While in Sr_2NiSbO_6 nickel(III) is low-spin, in $LaNiO_3$ a spin-free configuration obtains. A concentration dependent study has shown that in $LaNiO_3$ there is a strong super exchange interaction via oxygen atoms. In Sr_2NiSbO_6 this interaction is small.

Cahen et al. [66] have reported the crystal structure and properties of a platinum bronze of composition $Ni_{0.25}Pt_3O_4$. The formal oxidation state of platinum in this compound is 7/3 which implies the presence of nickel(IV). The compound shows metallic conductivity ($3 \cdot 10^3$ ohm^{-1} cm^{-1} at room temperature). Magnetic measurements have shown the presence of weak temperature independent paramagnetism. The gross structural feature of this compound is filled β-tungsten type.

The oxide chemistry of the higher valent states of nickel is in an unsatisfactory state of development. The factors determining composition, magnetism and transport properties are not well understood. Systematic studies both in the area of synthesis and physicochemical characterisation are called for.

(iii) Oxo-compounds

Nickel in the tetrapositive state has been stabilized by a number of heteropoly anions. The earliest nickel(IV) species discovered by Hall [5] was isolated as the barium salt of 9-molybdonickelate. The corresponding ammonium salt $(NH_4)_6NiMo_9O_{32} \cdot 5.5\ H_2O$ is well characterised [67,68]. Another 9-molybdo series of composition $M_5HNiMo_9O_{32}$ (M = NH_4, K) has been isolated recently [69]. Flynn and Pope [70] have characterised $K_7NiV_{13}O_{38} \cdot 16\ H_2O$ whose crystal structure [71] consists of $NiV_{13}O_{38}$ polyanions having one NiO_6 and thirteen VO_6 octahedra sharing edges. The heteropolyniobates of nickel(IV) having the compositions $Na_{12}Nb_{12}O_{38} \cdot (48$—$50)\ H_2O$ and $K_8Na_4NiNb_{12}O_{38} \cdot 21\ H_2O$ are known [72]. The sodium salt of nickel(IV) complex is isomorphous with the corresponding manganese(IV) compound, the crystal structure of which revealed [72] that the manganese atom is octahedrally coordinated by oxygen atoms from two Nb_6O_{19} groups and the Mn—O distances are equal (1.87 Å). The periodates of nickel $MNiIO_6 \cdot x\ H_2O$ (M = K, Na) [73] consist of hexagonal sheets of linked NiO_6 and IO_6 octahedra with alkali metal atoms lying in the octahedral holes between the sheets [74—76]. They are weakly paramagnetic (ca. 1 B.M. at room temperature) and the EPR spectra of $KNiIO_6$ showed [77] the presence of some nickel(III) atoms in the lattice. The spectrum at 77 K is rhombic: $g_1 = 2.130$, $g_2 = 2.206$ and $g_3 = 2.258$, which at room temperature becomes isotropic, $g = 2.21$ possibly due to the dynamic Jahn—Teller effect. The implication of the substitutional occupancy of Ni^{3+} ions in $KNiIO_6 \cdot x\ H_2O$ is the presence of some vacant holes in the lattice, as a result of which the compound shows semiconductor behavior [77].

D. CYANO AND RELATED SPECIES

For monovalent nickel two discrete cyano complexes, viz. dimeric $K_4Ni_2(CN)_6$ and monomeric $K_3Ni(CN)_4$ are known. Other than these, cyano complexes of nickel(I) have been produced as transient species during pulse radiolysis, electrode reduction or γ-irradiation of $Ni(CN)_4^{2-}$. No discrete cyano compounds of nickel(III) and (IV) have been isolated. However, by X- or electron irradiation of $K_2Ni(CN)_4$ doped in NaCl or KCl crystals $Ni(CN)_4Cl_2^{3-}$ has been produced along with $Ni(CN)_4Cl_2^{5-}$.

Bellucci and Corelli [6,78,79] obtained a red compound of empirical composition $K_2Ni(CN)_3$ by reducing $K_2Ni(CN)_4$ with sodium or potassium amalgam. Later this compound was prepared in pure state [80] through the reduction of $K_2Ni(CN)_4$ in liquid ammonia with potassium. A dimeric composition $K_4Ni_2(CN)_6$ was proposed for this compound on the basis of preliminary X-ray studies [81], diamagnetic behaviour [82] and cryoscopic measurement [83]. Several alternative structures involving either metal—metal linkage or cyano bridging were proposed [84—87] from infrared spectral studies. This aspect will not be discussed here since Miller [88] has already covered it elsewhere, and moreover, none of these could depict the exact structure of this compound. Initial X-ray crystallographic studies [81,89] also failed to determine the structure due to the problems associated with twinning and disorder in layers. More recent studies [13,14] have solved the crystal structures of $K_4Ni_2(CN)_6$ and $Rb_4Ni_2(CN)_6$. The main structural features are summarised in Table 2.

In aqueous solution $Ni_2(CN)_6^{4-}$ absorbs carbon monoxide and the reaction is quite sensitive to pH. It was originally suggested [90,91] that the product is a diamagnetic compound, $K_4Ni_2(CN)_6(CO)_2$. A later study [92], however, has expressed doubt about the authenticity of this product, and a disproportionation reaction has been suggested.

$$Ni_2(CN)_6^{4-} + 2\ CO \rightarrow Ni(CN)_2(CO)_2^{2-} + Ni(CN)_4^{2-}$$

The diamagnetic compound $K_2Ni(CN)_3NO$ obtained by reaction of $K_4Ni_2(CN)_6$ with nitric oxide was found [85] to be a zero-valent compound since the infrared spectra showed the presence of NO^+.

The mechanism of the reduction of $Ni(CN)_4^{2-}$ to $Ni_2(CN)_6^{4-}$ has been the subject matter of several investigations [33,93—96]. The ion $Ni(CN)_3^{2-}$ is believed to be the intermediate as in the pulse radiolytic reaction sequence [33]

$$Ni(CN)_4^{2-} + CO_2^- \rightarrow Ni(CN)_4^{3-} + CO_2; \qquad k = 1.2 \times 10^9\ M^{-1}\ s^{-1}$$

$$Ni(CN)_4^{3-} \rightarrow Ni(CN)_3^{2-} + CN^-; \qquad k = 9.1 \times 10^3\ M^{-1}\ s^{-1}$$

$$2\ Ni(CN)_3^{2-} \rightarrow Ni_2(CN)_4^{6-}; \qquad k = 1.5 \times 10^8\ M^{-1}\ s^{-1}$$

Rapid reduction of $Ni(CN)_4^{2-}$ also occurs with hydrogen atoms and aquated electrons [33].

$Ni(CN)_4^{2-} + H \rightarrow HNi(CN)_4^{2-}$; $\quad k = 1.7 \times 10^{10}\ M^{-1}\ s^{-1}$

$Ni(CN)_4^{2-} + e_{aq}^{-} \rightarrow Ni(CN)_4^{3-}$; $\quad k = 5.5 \times 10^{9}\ M^{-1}\ s^{-1}$

On the other hand, $Ni(CN)_4^{2-}$ is oxidised to a nickel(III) species $Ni(CN)_4^{-}$ by OH radical [33] ($k = 9.1 \times 10^9\ M^{-1}\ s^{-1}$).

Polarographic studies [95,96] have revealed that $Ni_2(CN)_6^{4-}$ does not undergo further reduction, instead it is irreversibly oxidised to $Ni(CN)_4^{2-}$. In aqueous solution $Ni_2(CN)_6^{4-}$ undergoes cyanide ion assisted oxidation. It was suggested [96,97] that the rate of oxidation is first order with respect to the concentration of both $Ni(CN)_4^{2-}$ and CN^-. A more recent study has reported [98] that the rate is controlled by the disproportionation of $Ni_2(CN)_6^{4-}$ in the following way.

$$Ni_2(CN)_6^{4-} + CN^- \xrightarrow{k_1} Ni(CN)_3^{3-} + Ni(CN)_4^{2-} \quad (k_1 = 1.18 \times 10^{-3}\ M^{-1}\ s^{-1})$$

$$Ni_2(CN)_6^{4-} + HCN \xrightarrow{k_2} HNi(CN)_3^{2-} + Ni(CN)_4^{2-} \quad (k_2 = 4.8 \times 10^{-1}\ M^{-1}\ s^{-1}).$$

The EPR spectra of $Ni(CN)_4^{3-}$ generated by γ-irradiation of $Ni(CN)_4^{2-}$ either in a solid matrix ($K_2Ni(CN)_4 \cdot H_2O$, $Na_2Ni(CN)_4 \cdot 3\ H_2O$) or in a glassy solvent (ethyleneglycol—water) at 77 K have been investigated [99,100]. The same nickel(I) species was also produced in the glassy solvent by electrons released in photoionization of *N*, *N*, *N'*, *N'*- tetramethyl-*p*-phenylenediamine [101]. The spectrum observed in the glassy solvent has axial symmetry ($g_{\parallel} = 2.131$, $g_{\perp} = 2.030$) and is markedly different from the one observed in solid matrix, which is rhombic. It has been suggested that $Ni(CN)_4^{3-}$ has different structural orientations in the two cases — a reinvestigation is needed. The spin-Hamiltonian parameters in the EPR spectra of X-irradiated $Ni(CN)_4^{2-}$ in a NaCl lattice have characterised the formation of $Ni(CN)_4Cl_2^{3+}2\boxed{+}+$ and $Ni(CN)_4Cl_2^{5-}$ [102,103]. The nickel(III) species ($g_{\parallel} = 2.008$, $g_{\perp} = 2.153$) has been stated to be associated with a two cation vacancy. X-irradiation at low temperature has generated the same nickel(III) complex associated with one cation vacancy ($g_{\parallel} = 2.009$, $g_{\perp} = 2.162$). In both cases hyperfine splitting due to the chlorine atoms has been noted. The *g*-parameters for the nickel(I) species $Ni(CN)_4Cl_2^{5-}$ are $g_{\parallel} = 2.143$ and $g_{\perp} = 2.051$. The lack of hyperfine splitting in this case is consistent with the fact that the unpaired electron ($d_{x^2-y^2}$) resides mainly in the plane of the cyanide ions and the interaction with the chlorine nuclei is less than the observed line width. A similar study has reported [104] the EPR spectra of electron (2 MeV) irradiated $K_2Ni(CN)_4$ doped in single crystals of KCl. Observations with 70% ^{13}C enriched samples have established the existence of four EPR centres and have been assigned to $Ni(CN)_4Cl_2^{3-}$ and $Ni(CN)_4Cl_2^{5-}$ in the isomeric states *cis* and *trans*. The form and magnitudes of *g*- and *A* tensors have indicated that the greater anisotropies observed in the *cis*-species are due to the influence of the vacancy created by charge compensation.

The other discrete mononuclear nickel(I) complex $K_3Ni(CN)_4$ was obtained [105] by the reduction of $K_2Ni(CN)_4$, in a strongly alkaline solution, with hydrazine hydrate. This compound is extremely reactive and has been far less investigated. It has a magnetic moment of 1.73 B.M.. The series [106] of nickel(I) acetylides having the empirical composition $K_3Ni(C_2R)_4$ (R = H, CH_3, C_6H_5) are diamagnetic and therefore should be formulated as dinuclear species $K_6Ni_2(C_2R)_8$.

E. FLUORO COMPLEXES

The only stoichiometric binary compound of nickel and fluorine is yellow [107] NiF_2 which has a rutile structure based on shared NiF_6^{4-} coordination octahedra. Such octahedra are also present in $KNiF_3$. The trifluoride, NiF_3, though estimated to have marginal thermodynamic stability, could not be obtained either by high-temperature reactions or by low-temperature solvolysis of fluoro complexes in anhydrous HF solvent. Instead partially oxidised and rather ill-defined brown solids of composition NiF_{2+x} (x = 0.1—0.5) result [108].

Discrete complex fluoro anions NiF_6^{n-} have been characterised for both nickel(III) [109—112] and nickel(IV) [109,111,113—116]. Fluorination of nickel(II) salts in the presence of alkali metal salts yields M_3NiF_6 (violet) or M_2NiF_6 (red) depending on the conditions. The potassium salts (M = K) are commonly employed in most studies. In a recent report [108], K_3NiF_6 is prepared by direct fluorination of the mixture 3 KCl—$NiSO_4 \cdot 6\ H_2O$ at 470—520 K in a 1 : 1 F_2 : N_2 stream for 3 h while K_2NiF_6 is obtained [116] by direct fluorination of $K_2Ni(CN)_4$ in a 1 : 1 F_2 : N_2 stream at 520 K for 3 h. The ions NiF_6^{4-} (as in NiF_2 or $KNiF_3$), NiF_6^{3-} and NiF_6^{2-} have characteristic vibrational spectra [111,117,118]. The ν_3 stretching band for these ions increases progressively, 445, 580 and 663 cm^{-1}.

A new synthetic technique [107] viz., fluorination utilising high pressure of F_2 or F_2/Ar mixture (300—3000 atm at temperatures up to 770 K) has been developed. Use of this technique affords the nickel(IV) species, M_2NiF_6 in pure form. The otherwise inaccessible alkaline earth metal salts $BaNiF_6$ and $SrNiF_6$ are readily prepared by the high pressure method.

Attention has been drawn by Hoppe to a number of nagging problems in the chemistry of metal fluorides, particularly those having the metal ion in unusual valence states [107]. Methods of producing even small single crystals are virtually absent, making accurate structural characterisation extremely difficult. The assessment of sample purity by analysis of such compounds which can not be purified at all after synthesis, is inherently unsatisfactory. Very often the known analytical methods may not be able to reveal the small differences in composition from sample to sample. Yet such differences may dramatically affect the physical and chemical properties of the samples. Thus well-fluorinated samples of K_2NiF_6 are remarkably stable [107] even when covered with water while less tempered ones decompose [111] immediately: $K_2NiF_6 + H_2O \rightarrow 2\ KF + 2\ HF + NiF_2 + 0.5\ O_2$. Some ozone is formed as a secondary product. K_3NiF_6 is also said [111] to oxidise water in a similar manner.

K_3NiF_6 is stable under vacuum at 720 K while K_2NiF_6 decomposes [109, 111]: $3\ K_2NiF_6 \rightarrow 2\ K_3NiF_6 + NiF_2 + F_2$. This reaction is utilised [109] in the purification of K_3NiF_6. While K_2NiF_6 dissolves in HF without decomposition giving a dark-red solution, K_3NiF_6 undergoes a disproportionation reaction in the same solvent [108,111]. A simplified version of this reaction is: $2\ NiF_6^{3-} \rightarrow NiF_6^{2-} + NiF_2 + 4\ F^-$. A red solution ($NiF_6^{2-}$) and a brown precipitate which contains slightly more fluorine than NiF_2 results. A possible rationalisation [108] of the disproportionation reaction may lie in the solvolysis of NiF_6^{3-} ion to give solvated F^- and fluorine-bridged units containing nickel(III), such as NiF_5^{2-} which may then undergo internal electron transfer and rearrangement to form NiF_6^{2-} and insoluble NiF_2 (or NiF_{2+x}). By a rather obscure reaction between solutions of K_2NiF_6 in HF with AsF_5 or BF_3, the black solids $NiF_3 \cdot 2\ KAsF_6$ or $NiF_{2.8} \cdot 2\ KBF_4$ deposit [108]. These are believed to contain nickel in an oxidation state which is exactly or nearly equal to 3. The electrolysis of KF or NH_4F in HF with nickel electrodes gives a red solution in the anode region from which a solid containing both NiF_6^{2-} and NiF_6^{3-} can be isolated. The possible involvement of higher oxidation states of nickel in fluoride media has been implicated for the Simon process in which fluorocarbons are produced through electrolysis of organic compounds in HF with a nickel anode [111].

The M_2NiF_6 (M = Na, K, Rb, Cs) salts are isomorphous belonging to the space group *Fm*3*m*. A complete series of mixed crystals is found between K_2NiF_6 and Rb_2NiF_6 as well as between Rb_2NiF_6 and Cs_2NiF_6. While $SrNiF_6$ and a high-pressure form of $BaNiF_6$ have the $BaGeF_6$ structure, the normal form of $BaNiF_6$ is monoclinic. Lattice constants for the various M_2NiF_6 and $MNiF_6$ species are known [107]. The Ni—F distance is estimated [115] to be 1.70 Å.

NiF_6^{2-} is diamagnetic [119] and it is generally agreed that it has more or less strict O_h symmetry, the ground state being $^1A_{1g}(t_{2g}^6)$. The expected ligand field bands are observed [116,120,121] and analyses of such bands yield [121] the parameters $Dq \sim 2000\ \text{cm}^{-1}$, $B \sim 500\ \text{cm}^{-1}$ and $\beta \sim 0.4$. A characteristic feature of the spectrum [116,121] is the pronounced vibrational fine structure (having a $\sim 500\ \text{cm}^{-1}$ interval) of the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition at $\sim 19{,}000\ \text{cm}^{-1}$. This is believed to be caused by the superposition of a symmetric α_{1g} progression on the vibronically (τ_{1u}) allowed transition. As seen from the value of β, the nephelauxetic effect in NiF_6^{2-} is large. This implies a high degree of covalency associated with the large formal charge on the metal. In spite of such high covalency, the effective charge on the metal is still quite high. The $^2P_{3/2}$ binding energy of K_2NiF_6 is 5 eV higher than the average value found for typical nickel(II) complexes [28].

Na_3NiF_6 is monoclinic and is isotypic with some other Na_3MF_6 (M = Al, Co, Fe) species; K_3NiF_6 is tetragonal [110,122]. Magnetic, spectroscopic and molecular orbital studies [110,112,122,123] taken collectively reveal that both the salts contain nickel(III) in a low-spin ($S = 1/2$) ground state with a high-spin ($S = 3/2$) state lying close enough to become thermally populated to a measurable extent. In an octahedral ligand field, the low-spin $^2E_g(t_{2g}^6e_g^1)$ state is less stable than the high-spin $^4T_{1g}(t_{2g}^5e_g^2)$ state. Tetragonal Jahn—Teller distortion sharply splits (~6000 cm^{-1}) ^2E_g into $^2B_{1g}$ + $^2A_{1g}$ while $^4T_{1g}$ undergoes a much smaller splitting (~700 cm^{-1}) into ^4E_g and $^4A_{2g}$. In effect, $^2A_{1g}$ becomes the ground state with $^4A_{2g}$ lying only slightly above (~700 cm^{-1}) it. The result is the equilibrium $^2A_{1g} \rightleftharpoons {}^4A_{2g}$. Selected variable temperature μ_{eff} data [122] for K_3NiF_6 are: 200 K, 2.29 BM; 120, 1.99; 41, 1.74; 3—8, 1.36. The ligand field parameters [112] are: Dq, 1620 cm^{-1}; Dt, 423 cm^{-1}; B, 703 cm^{-1} and β, 0.63.

The cubic elapsolite species Cs_2KNiF_6, Rb_2KNiF_6, Rb_2NaNiF_6 and K_2NaNiF_6 were recently reported [122]. In these systems the Jahn—Teller distortion of the NiF_6 octahedra is dynamic at room temperature but gets frozen at low temperature in ferrodistortive order [124,125] with consequent axial EPR spectra ($S = 1/2$): Cs_2KNiF_6; $g_\parallel = 2.12$, $g_\perp = 2.54$; Rb_2KNiF_6, $g_\parallel = 2.12$, $g_\perp = 2.39$. The spectra remain unchanged in the interval 77—4 K. Interestingly Cs_2NaNiF_6 is not an elpasolite but has the Ba_2CuTeO_6 structure. Half of the Ni^{3+} ions (NiF_6 octahedra sharing common faces) are in a nearly perfect octahedral environment (site A) with high spin configuration while the other half (NiF_6 sharing common corners) is elpasolite-like in spin character (site B). At 4.2 K, the EPR spectrum shows three signals: $g \sim 4$ due to site A; $g_\parallel = 2.19$ and $g_\perp = 2.42$ due to site B.

F. COMPLEXES OF NITROGENOUS LIGANDS

This is the largest single group of ligands which has been used to bind nickel(III) and nickel(IV), particularly the former. Proven cases of nickel(I) stabilisation exist but are relatively much less abundant. The fascinating nickel chemistry of macrocycles which are also primarily nitrogen ligands is considered separately in the next section.

(i) Amines and amino acids

The pulse radiolytic technique (Section B(iii)) has been extensively used to study complexes of ammonia [126], ethylenediamine [32], ethylenediaminetetraacetic acid and related species [127—130]. Radiolysis of ~10^{-4} M $NiSO_4$ solution in 0.67 M ammonia (pH = 11.3) saturated with N_2O, leads to transient $Ni(NH_3)_n^{3+}$ which displays a moderately intense band at 295 ± 5 nm ($\epsilon = 1300\ \text{M}^{-1}\ \text{cm}^{-1}$) [126]. The formation reactions are

$$OH + NH_3 \rightarrow NH_2 + H_2O$$

$$H_2O + NH_2 + Ni(NH_3)_6^{2+} \rightarrow Ni(NH_3)_n^{3+} + NH_3 + OH^-$$

The half-life of $Ni(NH_3)_n^{3+}$ is several milliseconds. The nickel—ethylenediamine system [32]

$$Ni(en)_n^{2+} + OH \rightarrow Ni(en)_n^{3+} + OH^-$$

($n = 2, 3$)

behaves in a qualitatively similar fashion (λ_{max} = 295 ± 5 nm, ϵ = 2000 M^{-1} cm^{-1}) but the nickel(III) species are more stable (half-life ~1 s).

The decompositions of all the above nickel(III) species persistently follow a second-order rate law. This has led to the speculation [32,126] that the primary reaction may be the disproportionation 2 Ni(III) → Ni(II) + Ni(IV) which is followed by intramolecular electron transfer in the nickel(IV) complex resulting in oxidation of bound ligand(s) or solvent molecules, Ni(IV) → Ni(II) + oxidation products. In the case of $Ni(NH_3)_n^{3+}$ the oxidation products are presumably H_2O_2 and/or N_2H_4 while for $Ni(en)_n^{3+}$, NH_2CH_2CHO and NH_3 are believed to be the products. The proposal is attractive but unfortunately direct kinetic and spectroscopic evidence for the formation of a transient nickel(IV) intermediate is lacking.

When the radiolytic condition is not exclusively oxidative (e.g., when the solution being irradiated is not saturated with N_2O), aquated electrons can reduce nickel(II) to nickel(I). For example the reaction [126]

$$Ni(NH_3)_n^{2+} + e^-(aq) \rightarrow Ni(NH_3)_n^+$$

occurs when $Ni(NH_3)_n^{2+}$ in 0.67 M ammonia solution saturated with argon is radiolysed. A related phenomenon is the generation of nickel(I) species in a glassy matrix (ethyleneglycol—water or xylene) by irradiating the nickel(II) complex frozen in the matrix at 77 K by γ-rays [99]. A number of systems have been produced in this manner and subjected to characterisation by EPR studies. The EPR spectra are of axial symmetry with $g_\parallel > g_\perp$ suggesting that the nickel(I) configuration is tetragonally elongated with a $(d_{x^2-y^2})^1(d^9)$ ground state. Typical examples are (py = pyridine; bpy = 2,2-bipyridine; en= ethylenediamine): $Ni(H_2O)_n^+$ ($g_\parallel$ = 2.466; $g_\perp$ = 2.076), $Ni(py)_4(H_2O)_2^+$ (2.282; 2.068), $Ni(en)_2(H_2O)_2^+$ (2.282; 2.064), $Ni(bpy)_2(H_2O)_2^+$ (2.259; 2.074) [99]. Similar ions are also produced in the crystalline matrix (77 K) of the corresponding nickel(II) complex by γ-irradiation [100].

Aliphatic diamine complexes of nickel(III) [128] can be obtained by chemical and electrochemical means. Thus crystalline solids of composition $[Nien_2X_2]Y$ (X = Cl, Br; Y = Cl, Br, ClO_4, NO_3) result from chemical oxidation of nickel(II) species by X_2 [130]. Similar propylenediamine complexes are also described [131]. Observed magnetic moments (1.7—1.9 B.M.) correspond to one unpaired electron [132] and infrared data [131] suggest *trans* octahedral geometry for $Nien_2X_2^+$. Electrolysis of aqueous ethylenediamine containing nickel(II) at the platinum electrode produces $Ni(en)_3^{3+}$ which decomposes yielding $Ni(en)_2^{2+}$ and organic oxidation products [133]. Since $Ni(en)_3^{3+}$ can be regenerated from the $Ni(en)_2^{2+}$ thus formed, the process is catalytic to a certain extent.

The ion $Ni(bpy)_3^{2+}$ can be both oxidised and reduced. Anodic oxidation of a suspension of $Ni(bpy)_3(ClO_4)_2$ in 2 M $HClO_4$ at 278 K produces a solution of lime-green $Ni(bpy)_3^{3+}$ which oxidises H_2O_2 to O_2 + 2 H^+ and Br^- to $\frac{1}{2}Br_2$ [134,135]. The reactions are first order in $Ni(bpy)_3^{3+}$ and first order in the reducing agent. The pathway of the reaction with Br$^-$ is proposed to be

$$\mathrm{Ni(bpy)_3^{3+} + Br^- \xrightarrow{k} Ni(bpy)_3^{2+} + Br^\cdot}$$

$$\mathrm{Br^\cdot + Br^\cdot \xrightarrow{fast} Br_2}$$

Electrolysis of Ni(bpy)$_3$(ClO$_4$)$_2$ in acetonitrile at −1.3 to −1.9 V vs. SCE gives a green solution which contains both Ni(bpy)$_3^+$ and Ni(bpy)$_3$. On making the potential more negative (−2.1 V) Ni(bpy)$_3^-$ is produced. Solution EPR data ($\langle g \rangle = 2.136$) of Ni(bpy)$_3^+$ agree with a nickel(I) formulation [136]. On the other hand, Ni(bpy)$_3^-$ has $\langle g \rangle = 2.007$ implying that the unpaired electron is primarily on a ligand orbital and the metal oxidation state is zero. This oxidation state also obtains in Ni(bpy)$_3$. Both Ni(bpy)$_3$ and Ni(bpy)$_3^-$ have tendencies to undergo ligand dissociation. Complexes of type Ni(bpy)(PPh$_3$)X (X = Cl, Br) with magnetic moments of ~2.1 B.M. are described [137].

The ligand 1,8-naphthyridine (napy) can act as a chelating or a bridging bidentate ligand. Of particular interest here is [Ni$_2$(napy)$_4$X$_2$]Y (X = halogen, NCS, NO$_3$; Y = PF$_6$, BPh$_4$) in which napy is bridging and the formal oxidation state of nickel is 1.5 [17,138]. These are obtained as black crystals on boiling NiX$_2$ in n-butanol with napy in the presence of NaBPh$_4$. The three-dimensional X-ray structure of the complex [Ni$_2$(napy)$_4$Br$_2$]BPh$_4$ is essentially of the dimeric copper acetate type (Table 2). The effective magnetic moments of the complexes lie in the range 4.19—4.33 B.M. (per dimer) showing that three unpaired electrons are present ($S = 3/2$). The Curie—Weiss behaviour obtains in the temperature range 77—400 K [138]. Evidently a large ferromagnetic coupling is operative between the two nickel atoms, one with $S = 1$ and the other with $S = \frac{1}{2}$. It is estimated that $J > 300$ cm^{-1}. The coupling pathway can be either a direct Ni—Ni interaction or an Ni—ligand—Ni interaction. Assuming approximate axial symmetry, and an $S = \frac{3}{2}$ spin-Hamiltonian, the powder EPR spectrum of [Ni$_2$(napy)$_4$Br$_2$]BPh$_4$ can be rationalised with the parameters $g_\parallel = 2.20$, $g_\perp = 2.14$ and $D \geqslant 30$ cm^{-1} [138].

Lastly the complexes of amino acids are considered. Transient glycine complexes of nickel(III) are produced in radiolytic experiments [32]. A complex of H$_4$edta also prepared by the radiolytic technique is stable in aqueous solution ($t_{1/2}$ ~3 days). This complex, Ni(edta)$^-$, however, rapidly oxidises I$^-$ but not Br$^-$. It also disappears in contact with O$_2$ [127—129]. Solutions of Ni(edta)$^-$ display an EPR signal ($\langle g \rangle = 2.204$) at room temperature. When frozen to 77 K an axial spectrum results $g_\parallel = 2.337$ and $g_\perp = 2.139$. The $g_\parallel > g_\perp$ situation ($(d_{x^2-y^2})^1$ ground state) is very rare in low-spin pseudo-octahedral nickel(III). An axially compressed *cis*-NiN$_2$O$_4$ coordination sphere is claimed to be responsible for this unusual ground state. The nickel(III) complex of nitrilotriacetic acid (H$_3$nta), prepared radiolytically, is more oxidising and much less stable than Ni(edta)$^-$ [128]. A nickel(III)—edta complex is formed as a 'precipitate' on platinum working electrodes on pre-electrolysis of aqueous solutions containing H$_4$edta: Ni^{2+} = 1.2 : 1 at pH 9—12 at a potential of 1.1 V vs. SCE [139]. An electrode so treated displays quasi-reversible ($\Delta E_p \sim 100$ mV; E_{pc}, 0.35—0.53 V; E_{pa}, 0.42—0.63 V) pH-dependent cyclic voltammograms apparently due to the process (charges on complexes not shown)

$$\mathrm{Ni(III)\ edta(OH)}_n + e^- \rightleftharpoons \mathrm{Ni(II)\ edta(OH)}_{n-m} + m\mathrm{OH}^-$$

$$1 \leqslant m \leqslant 2$$

(ii) Amides, peptides and related ligands

The deprotonated amide function has proved to be very effective in stabilising nickel(III). A good example [140] is the biuret (H_2bi) complex KNi(bi)$_2$ synthesised by persulphate oxidation of Ni(bi)$_2$. Nickel(III) complexes of substituted biurets are also reported [141]. Insolubility and/or instability of the complexes have hampered fruitful physicochemical and structural studies. The magnetic moment of KNi(bi)$_2$ is 2.5 B.M. A grossly planar bis-bidentate NiN_4 structure with intermolecular axial interaction is a possibility.

Recently the solution chelate chemistry of nickel(III) bound to a variety of peptides and peptide amides was discovered [142—144]. The stabilisation occurs mainly due to binding of the function $-C(=O)\bar{N}-$ as present in deprotonated peptides and peptide amides. Electrochemical oxidation of an aqueous solution containing nickel(II) perchlorate and excess of the ligand produces [141] the nickel(III) species having characteristic electronic bands, electrochemical redox response and EPR spectra. The complexes which have been studied only in the solution phase, in general decompose over a period of several hours at pH 5 (298 K). At higher pH values (~9) decomposition occurs within several minutes. Molecular oxygen reacts with nickel(II)—peptide complexes in aqueous solution by a facile autocatalytic process in which the nickel(III) intermediate plays a major role [145]. The ready accessibility of the nickel(III)—peptide complexes in aqueous solution and their ability to catalyse peptide degradation may be of interest in biological systems since nickel is emerging as a trace bio-element.

Physicochemical data for a few selected complexes are set out in Table 3. The ligands and abbreviations are set out below. In each abbreviation the protons are amide protons some or all of which dissociate on complex formation.

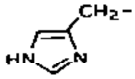
		n	R	abbreviation
 $NH_2(CH_2CONH)_n\underset{\displaystyle R}{\underset{\vert}{C}}HCO_2^-$	I	2	H	$H_2G_3^-$
	II	3	H	$H_3G_4^-$
	III	4	H	$H_4G_5^-$
	IV	2		$H_2G_2his^-$
$NH_2(CH_2CONH)_2CH_2CONH_2$	V	—	—	H_3G_3a

TABLE 3

Spectral [a], electrochemical [a,b] and EPR [c] data of nickel(III) peptide complexes

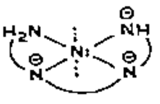
Complex	λ(nm)	ε [d]	E^0_{298} (V)	g_{xx}	g_{yy}	g_{zz}	g_{av}
NiG_3	340 250	4500 [e]	0.60	2.242	2.295	2.015	2.184
NiG_2his	—	—	0.71	2.256	2.278	2.015	2.183
NiG_4^-	327 205	5240 [e]	0.54	2.297	2.278	2.010	2.195
$NiHG_5^-$	325 240	5820 11300	0.58	2.340	2.278	2.011	2.210
NiG_3	325 235	5360 10700	0.58	2.310	2.281	2.006	2.199

[a] Ref. 142.
[b] E^0_{298} (vs. SCE) for the couple Ni(III)L + e ⇌ Ni(II)L measured by cyclic voltammetry: carbon paste electrode, scan rate 100 mV s^{-1}, pH = 9.6 in aqueous 0.1 M $NaClO_4$.
[c] Ref. 143. Best fit g values for aqueous glassy spectra at 123 K.
[d] Molar extinction values.
[e] Not determined due to decomposition of the complex.

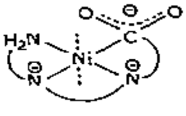
Oxidation causes a change in the visible spectrum. The low-intensity *d*—*d* absorption band of the nickel(II) complex near 420 nm is replaced by intense CT bands, near 330 nm and 250 nm (Table 3) [142]. The circular dichroism of some of the complexes is reported [143].

In cyclic voltammetric experiments [142] with nickel(II) complexes, the anodic oxidation peak due to the process Ni(II) → Ni(III) is observed; on switching the potential a cathodic peak arises from the reversal of this process. The peak separation, ΔE_p is 70—90 mV showing that the electrochemical process (charges not shown) Ni(III) L + e ⇌ Ni(II) L is quasi-reversible. The E^0_{298} values obtained as the mean of the two E_p's are constant over the pH range 6.5—10.5. The results in Table 3 are in line with the following trends established from studies with a large number of systems [142]. The E^0_{298} values (i) decrease with the number of deprotonated peptide groups and with the increase in crystal field stabilisation energy of the nickel(II) species, (ii) increase with bulky C-substituents and (iii) are in general higher for histidine containing peptides. The net observed variations in E^0_{298} are however small for a series of thirty ligands [142]. In contrast the potentials of copper(III)/copper(II) couples in peptide complexes are quite sensitive to the nature of the ligands [146]. This difference is attributed to substantially larger gains in CFSE for the conversion from copper(II)(d^9) to copper(III)-(d^8) compared to the conversion from nickel(II)(d^8) to nickel(III)(d^7).

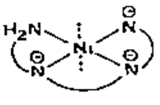
Electron paramagnetic resonance studies [144] of aqueous glasses containing the immediate products of controlled oxidation of nickel(III)—peptide complexes reveal the formation of species with $S = \frac{1}{2}$ and $g_{xx} \sim g_{yy} > g_{zz}$ (Table 3). It is reasonable to assume that the nickel(III) complexes belong to



VI



VII



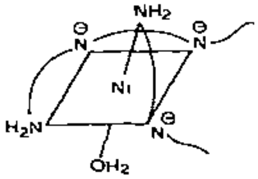
VIII

structural types VI—VIII where VI applies to a tripeptideamide, VII to a tripeptide and VIII to tetra and higher peptides. In these structures the dotted axial positions are believed to be occupied by water molecules. The species can thus be formulated as $NiL(H_2O)_2$. The $g_{xx} \sim g_{yy} > g_{zz}$ relation is strongly indicative of the $(d_{z^2})^1$ ground state for the pseudo-octahedral complexes. The general trend in g values reflects the trend in donor strength $N^- > —NH_2 >$ —imidazole $\sim —CO_2^-$. Conclusive evidence for axial coordination has been obtained by replacing water with ammonia. As the concentration of ammonia in solutions of $Ni(G_3a)(H_2O)_2$ is increased, $Ni(G_3a)(H_2O)(NH_3)$ and $Ni(G_3a)(NH_3)_2$ are successively formed [144]. The EPR spectra of the ammonia adducts are axial i.e., $g_{xx} = g_{yy} > g_{zz}$. The significant point is that the correct number of ^{14}N hyperfine lines in the $g_{zz}(g_\parallel)$ region are observed due to the axially placed NH_3. The EPR parameters (aqueous glass 123 K) are: $Ni(G_3a)(H_2O)(NH_3)$, $g_\perp = 2.217$, $g_\parallel = 2.011$, $a_\parallel = 23.4$ G; $Ni(G_3a)(NH_3)_2$, $g_\perp = 2.178$, $g_\parallel = 2.019$, $a_\parallel = 19.0$ G. The ammonia association reactions when written as

$$Ni(G_3a) + NH_3 \rightleftharpoons Ni(G_3a)(NH_3)$$

$$Ni(G_3a)(NH_3) + NH_3 \rightleftharpoons Ni(G_3a)(NH_3)_2$$

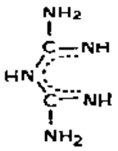
have equilibrium constants $\sim 10^7$ M^{-1} and ~ 60 M^{-1} respectively. The oxidising power of nickel(III) decreases upon adduct (ammine) formation and the kinetic stability is much increased. In solution $NiL(H_2O)_2$ is slowly converted to the bis complex IX for ligands such as $H_2G_3^-$, $H_3G_4^-$, H_3G_3a etc. This again reflects the enhancement of stability due to axial binding of a nitrogen donor.



IX

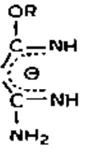
Species of the type IX display EPR spectra closely similar to that of the mono-ammine adduct. In the case of $Ni(HG_3a)(H_2G_3a)(H_2O)$ the spin-Hamiltonian parameters are $g_\perp = 2.196$, $g_\parallel = 2.023$ and $a_\parallel = 21.3$ G. (frozen aqueous glass at 123 K) [142]. The species IX has much lower [145] standard electrode potentials compared to those of VI—VIII.

The ligands biguanide(X) and amidinoisourea(XI) are related to amides and stabilise nickel(III) as in $[Ni(Hbig)_2Cl_2]X$ (X = Cl, F), $[Ni(Hbig)_2Br_2]Br$, $[Ni(aiu)_2]Cl$, $[Ni(maiu)_2]_2SO_4 \cdot 2\ H_2O$ and $[Ni(eaiu)_2]_2SO_4 \cdot 2\ H_2O$ [147]. The complexes are low spin ($S = \frac{1}{2}$) and display polycrystalline EPR spectra that are rhombic. The probable structure is a basic grossly planar NiN_4 coordination sphere with axial ligation by Cl^-, Br^-, SO_4^{2-}, H_2O etc. A $(d_{z^2})^1$ ground state is likely. The species are highly oxidising with $E^0_{298} \sim 0.85$ V in aqueous medium. Nickel(III) complexes of composition $[NiL_2(H_2O)_2]^{3+}$ (L = N',N'-oxydiethylenebiguanide) and $[NiL_3]Cl_3$ (L = N'-chlorophenyl-N^5-isopropylbiguanide) have also been reported [148].



Hbig

X

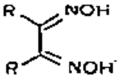


XI

R = H, aiu
R = Me, maiu
R = Et, eaiu

(iii) Oximes

Oxime ligands have been known to stabilise higher oxidation states of nickel for a very long time [7] and Feigl utilised for quantitative estimation the intense red colour that develops when a strongly alkaline solution containing dimethylglyoxime (H_2dmg) and a nickel(II) salt is oxidised [149]. This red colour is also given by other ligands belonging to the general group of α-dioximes, XII



XII

R = Me, H_2 dmg
R = n-Pr, H_2 dprg
R = Ph, H_2 dpg

The stoichiometry, structure and metal oxidation state of the red complex have been the subject of many investigations as summarised or catalogued elsewhere [150—152]. It is now amply clear that depending on experimental conditions, nickel(III) and/or nickel(IV) species are present in the red solution.

On pulse radiolysis of N_2O-saturated solution (0.5 N NaOH or 4 N NH_4OH) containing $NiSO_4$ and H_2dmg a species is produced with a strong absorption peak at ~450 nm. The mechanism of formation is pseudo-first order in nature. Since OH or NH_2 radicals are one-electron oxidants, this observation suggests that a nickel(III) species is formed [151]. The red solution obtained by lead peroxide oxidation of $NiSO_4$ + H_2dmg in 1.5 M NaOH displays a reversible polarogram with $E_{1/2} = -0.297$ (vs. SCE) in which two electrons are transferred meaning that a nickel(IV)—nickel(II) couple is operative. The number of dioxime ligands bound to nickel was estimated to be three or more [153]. Diamagnetic crystals of composition $K_2Ni(dmg)_3 \cdot 6\ H_2O$ can be isolated from complexation and oxidation reactions among nickel(II) salts, H_2dmg, KOH and I_2 [154].

TABLE 4

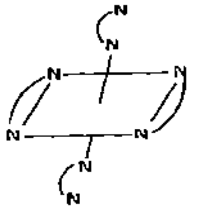
EPR data of nickel(III) dioxime complex in glassy phase [a]

System	Medium	Oxidant	$g_{\parallel}$	$g_{\perp}$	$a_{\parallel}$(G)	$a_{\perp}$(G)
Ni—H_2dmg	H_2O	Cl_2, Br_2, I_2 or H_2O_2	2.027	2.134	23.6	—
	py	I_2	2.034	2.174	21.0	14.5
Ni—H_2dprg	H_2O	I_2	2.027	2.136	23.5	—
	py	I_2	2.031	2.172	21.5	13.8
	quinoline	I_2	2.028	2.172	21.8	—
Ni—H_2dpg	py	I_2	2.033	2.172	20.5	—
	py [b]	I_2	2.034	2.162	20.1	—
	py + $CHCl_3$ + toluene	I_2	2.034	2.171	22.0	14.0
	py + CH_2Cl_2 [b]	I_2	2.034	2.162	20.1	15.5
	piperidine	I_2	2.031	2.172	20.0	—

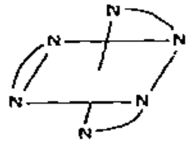
[a] All data unless otherwise noted refer to glassy spectra at 123 K (ref. 155).

[b] Glassy spectra at 133 K (ref. 157).

On the other hand, an oxidised (I_2, Br_2, Cl_2, H_2O_2) solution of $NiSO_4$ in 3 M NaOH when frozen to glass (123 K) exhibits an axial EPR spectrum with a 5-line (intensity 1 : 2 : 3 : 2 : 1) nitrogen hyperfine structure in the parallel region (Table 4). A nickel(III) species with $(d_{z^2})^1$ ground state having axial nitrogen coordination is implicated. Concentration of this species is maximised (20—30%) at the ratio Ni : H_2dmg : I_2 = 1 : 6 : 1.8 when I_2 is the oxidising agent. Structure (XIII) is proposed where the axial ligands bind in a monodentate fashion [155]. However, a structure such as (XIV) is also tenable. When $(NH_4)_2S_2O_8$ is used as the oxidising agent, no EPR spectrum is observed apparently due to formation of nickel(IV) rather than nickel(III) [155,156].



XIII



XIV

Oxidation of bis-dioximato complexes of nickel(II) with iodine in the presence of a strongly coordinating base such as pyridine yields the dark brown *trans*-pseudo-octahedral nickel(III) ion Ni(dioxime-H)$_2$(base)$_2^+$ which can be isolated in the solid state in combination with a suitable counter anion [152, 155,157]. The complex ion has one unpaired electron [157] and displays axial EPR spectra $(d_{z^2})^1$ (Table 4) with ^{14}N hyperfine structure in parallel and perpendicular regions [155,157]. The EPR spectra of isoelectronic Co(Hdpg)$_2$-

(py)$_2$ and Ni(Hdpg)$_2$(py)$_2^+$ are alike. The total spin density on each pyridine is 27% larger in the nickel(III) complex reflecting the expected larger pyridine—metal interaction [157].

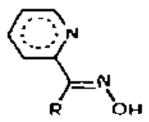
In the absence of strongly coordinating base, the reaction between α-dioximato complexes of nickel(II) with X_2 (X = I, Br) produces an entirely different material. In the case of Ni(Hdpg)$_2$, the product of such a reaction normally carried out in an inert chlorinated hydrocarbon solvent, is usually formulated as Ni(Hdpg)$_2$X. This product, particularly Ni(Hdpg)$_2$I, has been the subject of many investigations [157—168] because of the recognition that it may be an example of a one-dimensional solid state chain compound with partially filled bond structure [166]. It has a highly reflecting lustrous appearance. When pure, Ni(Hdpg)$_2$I is essentially diamagnetic and carefully prepared samples display no EPR signals [157,159—161]. More often an axial EPR spectrum due to an unidentified radical ($g_\parallel$ = 2.009; $g_\perp$ = 2.022) present in small amount is observed [157]. When heated, tetragonal crystals of Ni(Hdpg)$_2$X lose halogen and are reconverted to orthorhombic Ni(Hdpg)$_2$. This phenomenon has been studied using differential scanning calorimetry and thermogravimetric techniques [165]. The dc electrical conductivity of Ni(Hdpg)$_2$X is several orders of magnitude higher than that of Ni(Hdpg)$_2$. Even then the absolute conductivities (10^{-7}—10^{-5} ohm^{-1} cm^{-1}) are small and Ni(Hdpg)$_2$X is only a relatively poor semiconductor [161,164]. When Ni(Hdpg)$_2$X is dissolved in pyridine, the discrete complex [Ni(Hdpg)$_2$(py)$_2$]$^+$X$^-$, described earlier, is formed [157].

Three dimensional X-ray work [161,167] has shown that planar Ni(Hdpg)$_2$ units stack at intervals of 3.271 Å in Ni(Hdpg)$_2$I. Such stacking also occurs in Ni(Hdpg)$_2$ crystals but here the Ni···Ni distance is ~0.3 Å longer. In Ni(Hdpg)$_2$I, the iodine atoms which are not bonded to the metal atoms, form chains filling 'tunnels' defined by phenyl rings of Hdpg. The Ni and I chains are parallel. Because of the presence of a large (0.756 Å) root mean square vibration of the iodine atoms and the associated disorder it has not been possible to identify the molecular groups (I^-, I_2, I_3^-) which may possibly build up the chain. However, Raman [167] and ^{129}I Mössbauer [168] spectra are in agreement with the I_3^- model. It is speculated that a dynamic process such as $I_2 + I^- \rightleftharpoons I_3^-$ may account for the observed electrical conductivity [164,165]. The I_3^- model means that one electron is removed per three Ni(Hdpg)$_2$ units. In Ni(Hdpg)$_2$X the formal nickel oxidation state is then 2.33. If a d_{z^2} band structure (nickel chain along z axis) is formed due to the ···Ni···Ni··· interaction, the band should only be partially occupied. However, in practice no dramatic transport property is seen to result.

The composition Ni(Hdpg)$_2$X is not unique: a whole series of isomorphous complexes of composition Ni(Hdpg)$_2$X$_p$ (X = Br, $p \leqslant 1.14$; X = I, $p \leqslant 1.02$) exist. The interhalogen species Ni(Hdpg)$_2$(IBr)$_{0.54}$ and Ni(hdpg)$_2$I$_{0.45}$Br$_{0.67}$ also exist and are in turn isomorphous with Ni(Hdpg)$_2$X$_p$ [165]. The halogen containing channels in the solid structure can thus be filled in different ways and to different extents without straining the basic tetragonal crystal geometry.

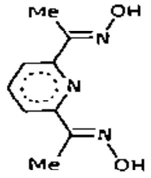
Interestingly iodine oxidation transforms bis(benzoquinonedioximato)nickel-(II), Ni(Hbqd)$_2$, into golden yellow lustrous crystals of composition Ni(Hdqd)$_2$I$_{0.5}$. Here again planar Ni(Hbqd)$_2$ units form columnar stacks (Ni···Ni distance 3.153 Å) with iodine chains running parallel to the stacks. This species has higher electrical conductivity than that of Ni(Hdpg)$_2$X [169, 170].

The pyridine oxime ligands XV and XVI stabilise nickel(III) and nickel(IV), respectively [12,171]. The synthetic method involves persulphate oxidation of



R = Ph, Hppk
R = CH$_2$Ph, Hbpk

XV

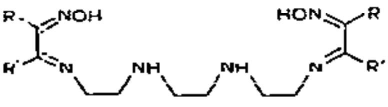


H$_2$dapd

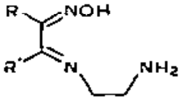
XVI

nickel(II) species in alkaline solution. Black paramagnetic (1.75 B.M.) Ni(ppk)$_3$ exhibits a polycrystalline rhombic EPR spectrum: $g_1 = 2.08$, $g_2 = 2.10$ and $g_3 = 2.14$ characteristic of pseudo-octahedral nickel(III). The complex Ni(dapd)$_2$ forms deep violet needles and is indefinitely stable as a solid and in solution. The three-dimensional X-ray work [25] on the tetragonal crystals has revealed the presence of discrete Ni(dapd)$_2$ molecules with a pseudo-octahedral NiN$_6$ coordination sphere (Table 2). The average Ni—N distance (1.93 Å) in this complex is much shorter than the Ni—N distance in octahedral nickel(II) chelates. A nickel(IV) description of Ni(dapd)$_2$ is appropriate. Attempts to detect the formation of nickel(III) intermediate either during the reduction of Ni(dapd)$_2$ or during oxidation of the nickel(II) species Ni(dapd)$_2^{2-}$ were not successful and cyclic voltammetry on Ni(dapd)$_2$ did not yield curves which could be interpreted [12].

Nickel(IV) is stabilised exceedingly well by the N$_6$ core of the hexadentate ligand system H$_2$RR′L (XVII). The dark-violet diamagnetic crystals of the 1 : 2 electrolytic Ni(RR′L)(ClO$_4$)$_2$ result from conc. HNO$_3$ oxidation of the brown nickel(II) complex, Ni(H$_2$RR′L)(ClO$_4$)$_2$ [172].



XVII



XVIII

While crystalline Ni(RR′L)(ClO$_4$)$_2$ is indefinitely stable in vacuo, in solution it acts as a two-electron oxidant towards many reducing agents as typified in the reaction

$$2\ Fe^{2+} + Ni(RR'L)^{2+} + 2\ H^{+} \rightarrow 2\ Fe^{3+} + Ni(H_2RR'L)^{2+}$$

The electronic and ir spectra of $Ni(RR'L)^{2+}$ are reported in some detail [172].

The pH-dependent redox equilibria of several $Ni(RR'L)(ClO_4)_2$ complexes were revealed by cyclic voltammetric studies [173]. Below pH 5, the reversible nickel(IV)—nickel(II) couple A_1 alone is present. Above pH 5 this is replaced by two discrete one-electron couples — nickel(IV)—nickel(III), nickel(III)—nickel(II) — B_1 and C_1. Finally above pH ~8.5 C_1 becomes pH-independent C_1'. The E^0_{298} values of the various couples as computed from peak potential data, are shown in Table 5. The ΔE_p and $\Delta \bar{E}_p/\Delta pH$ values (mV) for the various couples are as follows, A_1: ΔE_p, 30—40, $\Delta \bar{E}_p/\Delta pH$, 60; B_1: 60—70, 0; C_1: 70—75, 60; C_1': 70—75, 0.

A_1 $Ni(RR'L)^{2+} + 2\,e^- + 2\,H^+ \rightleftharpoons Ni(H_2RR'L)^{2+}$

B_1 $Ni(RR'L)^{2+} + e^- \rightleftharpoons Ni(RR'L)^+$

C_1 $Ni(RR'L)^+ + e^- + H^+ \rightleftharpoons Ni(HRR'L)^+$

C_1' $Ni(RR'L)^+ + e^- \rightleftharpoons Ni(RR'L)$

Nernstian character of the electrode reactions is a good indication that only minor stereochemical readjustments are needed during the redox process: an octahedral NiN_6 coordination sphere is implicated for all the oxida-

TABLE 5

E^0_{298} values (V)[a] vs. SCE of various couples

Complex			Couple[b]			
Ligand	R	R'	A_1	B_1	C_1	C_1'
$H_2RR'L$	Me	Me	0.71	0.42	0.64	0.15
	Me	Et	0.68	0.40	—	0.10
	Et	Me	0.69	0.39	—	0.09
	Me	Ph	0.70	0.45	—	0.16
	Ph	Me	0.69	0.47	—	0.14
			A_2	B_2	C_2	C_2'
HRR'T	Me	Me	0.71	0.40	0.66	0.07[c]
	Et	Me	0.69	0.37	0.63	—
	Me	Et	0.69	0.37	0.62	—
					C_3	
HRR'Y	Me	Me			0.64	
	Et	Me			0.65	
	Ph	Me			0.68	
	Me	Ph			0.68	

[a] Determined from cyclic voltammetric peak potentials: $v = 0.012$ Vs^{-1}, $C \sim 10^{-3}$ M, buffered 0.1 N NaCl.

[b] The meaning of symbols is given in the text.

[c] Estimated value.

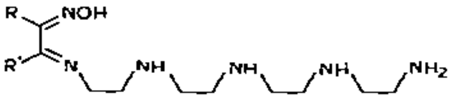
tion states. The two one-electron couples B_1 and C_1 become a single two-electron couple A_1 at low pH because of the greater proton affinity of the reduced complex. As pH is lowered Ni(RR′L) goes to $Ni(HRR'L)^+$ and finally to $Ni(H_2RR'L)^{2+}$ while the nickel(III) and nickel(IV) species continue to remain unprotonated. The $\bar{E}_p$ of the couple C_1 shifts progressively closer to the invariant $\bar{E}_p$ of couple B_1 as pH decreases. Superposition occurs at pH ~5 and beyond this only a single two-electron step is possible. It is demonstrated that the total free energy change in couples such as A_1 and C_1 is a sum of separable electron transfer and proton transfer contribution [174].

The ligand HRR′T (XVIII) gives bis-complexes of nickel(IV), $Ni(RR'T)_2(ClO_4)_2$ which are closely similar to $Ni(RR'L)(ClO_4)_2$ [175]. Couples entirely analogous to A_1, B_1 and C_1 are observed. In Table 5 these are designated A_2, B_2 and C_2. However, there is one major difference between the two systems, viz. that in acidic aqueous solution the voltammograms show relatively small anodic currents due to decomposition of the nickel(II) complex after it is generated from $Ni(RR'T)_2^{2+}$.

$$Ni(RR'T)_2^{2+} + 2e^- + 2\,H^+ \rightleftharpoons Ni(HRR'T)_2^{2+} \xrightarrow{k_f} Ni(H_2O)_6^{2+} + \text{other products}$$

The pseudo-first order rate constant k_f is calculated to be 0.16 s^{-1} (283 K) from voltammetric data [30,175].

There is unequivocal electrochemical evidence (couples B_1, B_2, C_1 and C_2) for the formation of nickel(III) species of ligands (XVII) and (XVIII). Partial chemical oxidation of nickel(II) complexes of (XVII) and (XVIII) does give solids which display strong axial EPR spectra suggestive of the presence of nickel(III). However, no pure species could be isolated in the crystalline state.



XIX

On the other hand, the nickel(II) complex of the hexadentate ligand XIX, HRR′Y is oxidised by persulphate to the paramagnetic (2.1 B.M.) nickel(III) complex $Ni(RR'Y)(ClO_4)_2$ isolated as dark red crystals [176]. No nickel(IV) species could be prepared. Polycrystalline $Ni(RR'Y)(ClO_4)_2$ display axial EPR spectra ($(d_{z^2})^1$ ground state) even at room temperature. The $g_\parallel$ and $g_\perp$ values respectively are $Ni(Me_2Y)(ClO_4)_2$, 2.030, 2.134; $Ni(EtMeY)(ClO_4)_2$, 2.054, 2.142; $Ni(PhMeY)(ClO_4)_2$, 2.040, 2.145; $Ni(MePhY)(ClO_4)_2$, 2.040, 2.143. In cyclic voltammetric experiments only a single quasi-reversible electrode reaction (couple C_3) is observed (Table 5)

$$C_3 \quad Ni(RR'Y)^{2+} + e^- + H^+ \rightleftharpoons Ni(HRR'Y)^{2+}$$

No electrochemical evidence for the formation of the nickel(IV) state could be obtained. The data of Table 5 show that there is no vast difference in the nickel(III)—nickel(II) electron-transfer thermodynamics of ligands (XVII),

(XVIII) and (XIX) (c.f. couples C_1, C_2 and C_3). The difference seems to lie with regard to the stability of nickel(IV). It may be significant that in systems where nickel(IV) is stabilised there are two oximato groups per nickel atom as in $Ni(RR'L)^{2+}$ and $Ni(RR'T)_2^{2+}$. The ligand HRR'Y with only one oxime function appears to be unable to support a two-electron oxidation of nickel(II) although nickel(III) species are readily formed. It seems that in amine—imine—oxime type ligands under consideration, for each unit increase in oxidation state of the metal (beyond +2) the presence of at least one oxime function is needed. This generalisation falls in line with the conjecture that negative charge on the oximato oxygen plays an important role in stabilising the high oxidation states of nickel through σ donation and inductive transmission [172,173].

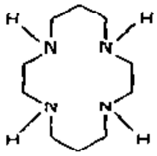
G. MACROCYCLES

The last few years have witnessed significant progress in the understanding of the chemistry of nickel(I) and nickel(III) complexes derived from macrocyclic ligands. The macrocycles used so far are all of the tetraaza type. No information is available concerning the formation of nickel(IV) species with these ligands, although many nickel(III) complexes of dianionic tetraaza systems undergo one-electron oxidation. The nature of these oxidized products is not properly understood.

Nickel(I) and nickel(III) complexes have been generated mostly in solution either by electrochemical or by pulse radiolytic redox reactions and are generally characterised from their EPR spectra. Among these two oxidation states, the complexes of nickel(III) are more prevalent. A remarkable aspect of the tetraaza macrocycles is that many of them exert an unusually high ligand field on the nickel(II) ion thus raising the anti-bonding orbital energies sufficiently so that the removal of an electron is a ready process. Moreover, nickel(II) complexes being quite inert with regard to ligand dissociation, their reduction or oxidation generally causes direct transfer of electron to or from the metal without jeopardizing the ligand frame.

In several cases under suitable experimental conditions nickel(I) and nickel(III) complexes of some macrocycles have been isolated in the solid state. So far as nickel(I) is concerned, the isolated species are confined to those reported by Olson and Vasilevskis [177] who obtained stable $NiLClO_4$ (L = *cis* and *trans* Me_6 [14] 4,11-diene N_4) complexes either by constant potential electrolysis or by sodium amalgam reduction of the corresponding nickel(II) complexes. These authors also isolated the nickel(III) complexes $NiL(ClO_4)_3$ by the electrolytic oxidation (+1.7 V) of the above nickel(II) complexes. Chemical oxidising agents like ammonium persulfate or nitric acid have been used by Gore and Busch [178] in preparing $[Ni(Me_2$ [14] $aneN_4)X_2]$ ClO_4 (X = Cl, Br, NCO, NO_3, $\frac{1}{2}$ SO_4). Similarly by persulfate oxidation compounds like $[Ni([14]aneN_4)X_2]ClO_4$ (X = Cl, Br) [179] and $[Ni(Me_6$ [14] 4,11-diene $N_4)]$-$(ClO_4)_3$ [180] have been isolated. Barefield and Mocella [181] have prepared bisacetonitrile adducts of the nickel(III) complexes of [14]aneN$_4$ and Me$_6$-[14]aneN$_4$ by the oxidation of the corresponding nickel(II) species with nitrosonium perchlorate. It may be pointed out that although several nickel(III) complexes have been isolated, no crystal structures have been so far reported.

Following the pioneering electrochemical work of Olson and Vasilevskis [177] which established that macrocycle ligands facilitate the generation of unusual oxidation states of nickel, Rillema et al. [182] investigated the redox behaviour of a few more nickel(II) macrocyclic complexes. Their study indicated that the potential for reduction of the metal centre shifts to very negative values when the ligand contains an unsaturated conjugated system. Most extensive and highly informative studies, however, have been carried out by Busch and co-workers [183—185] on a large number of macrocyclic complexes of nickel. In most cases the formation of nickel(I) and nickel(III) species have been delineated by EPR studies [183]. Some of the macrocyclic systems investigated by these workers are shown below, XX—XLVI. The systems vary in the nature and degree of ligand unsaturation, charge type, and ring size. Table 6 summarises the half-wave potentials for some of these Ni$^+$/Ni^{2+} and Ni^{2+}/Ni^{3+} couples. Electrochemical studies have been carried out mostly in acetonitrile and in a few cases in dimethylformamide solutions using 0.1 M Bu$_4$NBF$_4$ as the supporting electrolyte and Ag/AgNO$_3$ (0.1 M) as the reference electrode.



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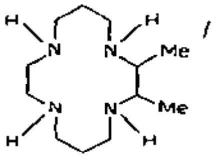

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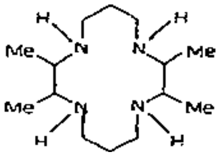

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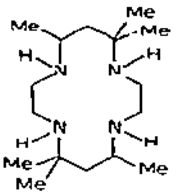

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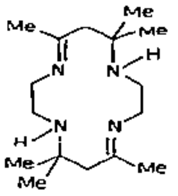

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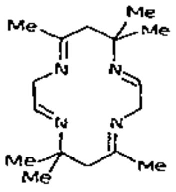

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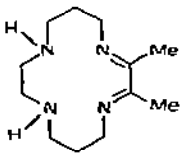

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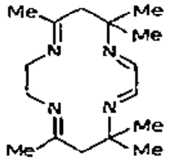

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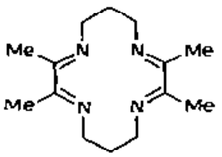

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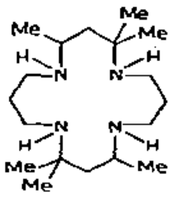

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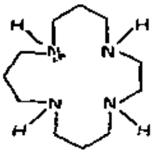

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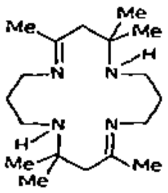

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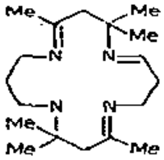

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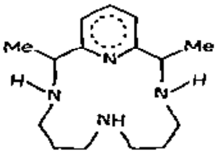

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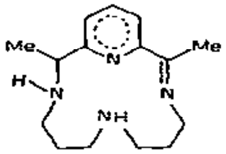

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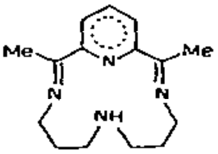

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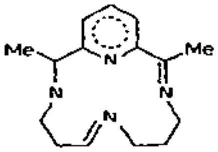

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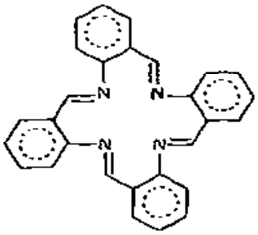

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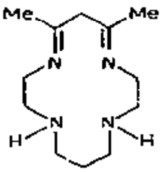

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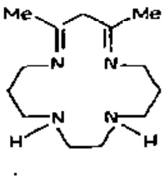

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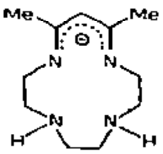
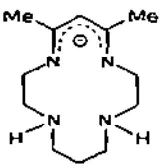
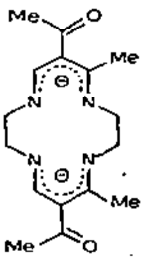


XL



XLI



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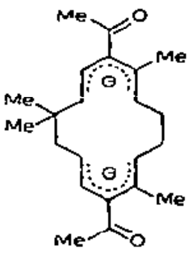

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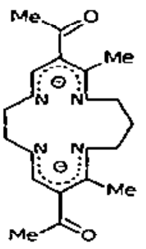
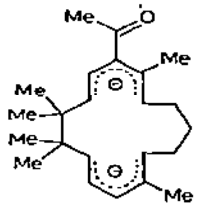
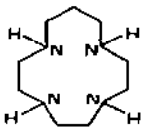
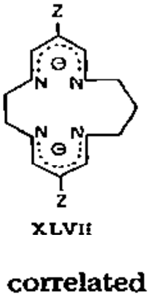

XLIV


XLV


XLVI

In general, it has been observed that the lower the oxidation potential for nickel(II) → nickel(III), the more negative would be the reduction potential for nickel(II) → nickel(I). The ring size is important in influencing the variation in redox potential. While increase of ring size causes easier reduction of nickel(II) to nickel(I), the reverse trend is observed in the oxidation behavior. This has been attributed to the "hole size" effect, since it is easier to accommodate the larger Ni^+ ion in the "hole" of the macrocycle. From EPR studies it has been shown [183] that oxidation of nickel(II) complexes containing neutral ligands produces six coordinate nickel(III) species in which two solvent molecules (acetonitrile) are axially and equivalently coordinated. The redox patterns of systems containing anionic ligands have convincingly demonstrated the influence of negative charge in determining the course of an electron transfer reaction. Whereas delocalized monoanionic ligands promote the formation of nickel(III) compounds, reduction to nickel(I) occurs at a large negative potential. In the case of dianionic ligands, oxidation to the nickel(III) state occurs at quite low positive potential or even at negative potential. The effect of varying substituents in the dianionic ligands of the type XLVII has also been investigated by Busch and co-workers [184—186].

Table 7 shows that the half-wave potential of the Ni^{2+}/Ni^{3+} couple in the planar complexes may be caused to vary by about 0.8 V. These data may be correlated with Hammet σ values, showing that the electron density change on the ligand is transmitted directly to the metal ion.


XLVII

The one-electron reduction products of the parent nickel(II) macrocycles are not necessarily nickel(I) species; depending upon the nature of ligand unsaturation, nickel(II) stabilized anion radicals may also result (Table 8). In contrast to nickel(I) complexes whose EPR spectra have axial symmetry with

TABLE 6

Electrochemical characteristics of macrocyclic nickel complexes [183]

Macrocycle	Half-wave potentials [a] (V)		Remark
	Oxidation	Reduction	
Neutral Ligand(L)	$NiL^{2+} \rightarrow NiL^{3+}$	$NiL^{2+} \rightarrow NiL^{+}$	
[14]aneN$_4$ (XX)	+0.67	−1.70	
Me$_2$[14]aneN$_4$ (XXI)	+0.78	−1.73	
Me$_4$[14]aneN$_4$ (XXII)	+0.71	−1.66	
Me$_6$[14]aneN$_4$ (XXIII)	+0.87	−1.57	
Me$_6$[14]4,11-dieneN$_4$ (XXIV)	+0.98	−1.57	
Me$_6$[14]1,4,8,11-tetraeneN$_4$ (XXV)	+1.05	−1.35	
[15]aneN$_4$ (XXX)	+0.90	−1.5	Irreversible reduction
Me$_6$[16]aneN$_4$ (XXIX)	+1.3	−1.4	Oxidation wave distorted
Me$_6$[16]4,12-dieneN$_4$ (XXXI)	+1.3	−1.37	
Me$_6$[16]1,4,12-trieneN$_4$ (XXXII)	+1.3	−1.30	
Me$_2$[14]1,3-dieneN$_4$ (XXVI)	+0.86	−1.16	The reduction product is nickel(II) stabilized ligand radical
CR + 4 H (XXXIII)	+0.89	−1.53	Additional oxidation wave appears
CR + 2 H (XXXIV)	+0.93	−1.25	The reduction product is nickel(II) stabilized ligand radical
CR (XXXV)	+1.03	−0.96	
CR − 2 H (XXXVI)	+1.05	−0.84	
Me$_6$[14]1,3,7,11-tetraeneN$_4$ (XXVII)	+1.05	−0.76	The reduction product is nickel(II) stabilized ligand radical
Me$_6$[14]1,3,8,10-tetraeneN$_4$ (XXVIII)	+1.00	−0.82	
Me$_2$[14]4,7-dieneN$_4$ (XXXVIII)	+0.72	−1.5	Irreversible reduction
Monoanionic ligand (L^-)	$NiL^{+} \rightarrow NiL^{2+}$	$NiL^{+} \rightarrow NiL^{0}$	
(Me$_2$[13]dienoN$_4$)$^-$ (XL)	+0.27	−2.30	
(Me$_2$[14]dienoN$_4$)$^-$ (XLI)	+0.23	−2.34	
Dianionic ligand (L^{2-})	$NiL^{+} \rightarrow NiL^{2+}$	$NiL^{+} \rightarrow NiL^{0}$	
(Me$_2$(CH$_3$CO)$_2$[14]tetraenoN$_4$)$^{2-}$ (XLII)	+0.97	+0.25	The oxidation waves are irreversible and the oxidation state of nickel ion in the oxidised form is not known
(Me$_4$(CH$_3$CO)$_2$[14]tetraenoN$_4$)$^{2-}$ (XLIII)	+0.98	+0.26	
(Me$_2$(CH$_3$CO)$_2$[15]tetraenoN$_4$)$^{2-}$ (XLIV)	+0.92	+0.27	
(Me$_6$(CH$_3$CO)$_2$[15]tetraenoN$_4$)$^{2-}$ (XLV)	+0.96	+0.28	

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[a] Electrochemical data have been obtained in acetonitrile solutions; Ag/AgNO$_3$ (0.1 M) reference electrode; 0.1 M n-Bu$_4$NBF$_4$ supporting electrolyte.

TABLE 7

Half-wave potentials for Ni^{2+}/Ni^{3+} in complexes of dianionic ligands of structure (XLVII) having different substituents (Z) [186]

Substituent (Z)	Oxidation potential [a] ($E_{1/2}$) (V)
$-CH_2CH_2COOC_2H_5$	−0.39
−H	−0.36(i)
$-COCH_3$, −H	−0.14(i)
$-CONH-\alpha-C_{10}H_7$	+0.03
$-COC_6H_5$	+0.21
$-COCH_3$	+0.22
$-NO_2$	+0.42

[a] Data have been obtained in dimethylformamide solutions; $Ag/AgNO_3$ (0.1 *M*) reference electrode; 0.1 *M* n-Bu_4NBF_4 supporting electrolyte; (i) irreversible wave.

$g_{\perp} < g_{\parallel}$, the metal ion stabilised ligand radicals show isotropic spectra with $g \sim 2$. The EPR parameters of some of the nickel(III) species are also listed in Table 8 for comparison.

It has been reported [187] that the nickel(I) complex of $Me_6[14]aneN_4$ reacts with alkyl bromides and iodides leading to the formation of alkyl radicals and regeneration of the nickel(II) complex. Thus electrolysis of these alkyl halides in the presence of catalytic amounts of the nickel(II) complex virtually leads to their complete reduction.

Although electrochemical behaviour of the macrocyclic complexes of nickel have been investigated almost exclusively in acetonitrile solution, it has been recently demonstrated [188] that stable solutions of nickel(III) complexes of the 14-membered macrocycles, viz., $[14]aneN_4$(A), cyclam (B) and [14] 4,11-dieneN_4(C) are obtained by electrochemical oxidation of the corresponding nickel(II) complexes in mild acidic aqueous solutions in the presence of SO_4^{2-} ion. The half lives of these $NiLSO_4^+$ species have been determined to be greater than a year, ca. 5 days and ca. 1 day when the ligands (L) are A, B and C respectively.

In general nickel(III) macrocyclic complexes are indefinitely stable in the solid state when they are preserved in a dry atmosphere. Their solutions in purified acetonitrile have also extended periods of stability. However, the solid in a wet environment and particularly the aqueous solution decomposes rapidly. The rate of decomposition depends upon the ligand type as well as upon the nature of the axial donors present. It has been observed that axial donors which are more basic than acetonitrile will induce decomposition. Barefield and Mocella [181] investigated the mechanism of base promoted reduction of nickel(III) macrocycles. When bis(acetonitrile)-$[14]aneN_4$ nickel(III) is treated with basic solvents like pyridine, triethylamine or water, a nickel(II) ligand radical species is formed according to the reaction: $Ni^{III}N\leqq + B \rightarrow Ni^{II}N\dot{<} + BH^+$. The formation of a nickel(II) ligand

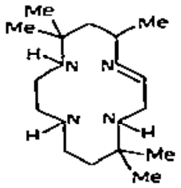
TABLE 8

EPR data of some nickel macrocyclic compounds in frozen acetonitrile (77 K) [183]

Macrocycle	1e⁻ reduction product		Oxidation state	1e⁻ Oxidation product				Oxidation state
	$g_\parallel$	$g_\perp$		$g_\parallel$	$g_\perp$	$a_\parallel$(G)	$a_\perp$(G)	
$Me_2[14]aneN_4$ (XXI)	2.261	2.060	nickel(I)	2.020	2.205	21.3	16.5	nickel(III)
$Me_6[14]aneN_4$ (XXIII)	2.266	2.055	nickel(I)	2.029	2.215	21.3	—	nickel(III)
$Me_6[14]4,11$-dieneN$_4$ (XXIV)	2.226	2.055	nickel(I)	2.024	2.199	22.5	—	nickel(III)
$Me_6[14]1,4,8,11$-tetraeneN$_4$ (XXV)	2.195	2.053	nickel(I)	2.018	2.186	24.2	17	nickel(III)
$Me_2[14]1,3$-dieneN$_4$ (XXVI)	2.004	(isotropic)	ligand radical	2.023	2.197	23.1	16	nickel(III)
$Me_6[14]1,3,7,11$-tetraeneN$_4$ (XXVII)	2.003		ligand radical	2.016	2.180	24	21	nickel(III)
$Me_4[14]1,3,8,10$-tetraeneN$_4$ (XXVIII)	1.999		ligand radical	2.023	2.172	25.4	19	nickel(III)
CR + 4 H (XXXIII)	2.250	2.066	nickel(I)	2.023	2.198	22.2	—	nickel(III)
CR + 2 H (XXXIV)	2.005		ligand radical					
CR (XXXV)	2.003		ligand radical	2.023	2.175	23.9	19	nickel(III)
$(Me_2(CH_3CO)_2[14]$-tetraenoN$_4)^{2-}$ (XLII)				2.138	2.016			?

radical has been substantiated by chemical and spectroscopic evidence. A similar species is formed in the decomposition of bis(acetonitrile)Me$_6$[14]-aneN$_4$ nickel(III) by pyridine but not by water. In the case of aqueous decomposition, product analysis has suggested the formation of a different type of radical species. Careful investigation has revealed that depending upon the nature of the solvent, 1—25% of the radical species decomposes with the rupture of the macrocyclic ring; the remainder is converted either to a nickel(II) tetramine by hydrogen abstraction from ligand fragments or forms a secondary radical species. In the latter process formation of a monoimine nickel(II) complex results. Under certain conditions the monoimine species (XLVIII) may also generate through the oxidation of nickel(II) ligand radical by nickel(III) complex.

Since macrocyclic complexes of nickel(II) possess sufficient stereochemical rigidity, quite a few nickel complexes in less familiar oxidation states have been generated through pulse radiolytic redox reactions. For example, nickel(I) complexes of Me$_6$[14] 4,11-dieneN$_4$ and Me$_6$[14]aneN$_4$ have been obtained by radiolysis of the corresponding nickel(II) complexes [189]. The reduction has been accomplished by aquated electrons, hydrogen atoms and the CO_2^- radical ($k \sim 10^6$—10^{10} M^{-1} s^{-1}). The reactivities of the nickel(I) complexes as bases and reducing agents have been investigated with a number of acids, organic electron acceptors, metal complexes and some neutral molecules. On the other hand, nickel(II) complexes of Me$_6$[14] 4,11-dieneN$_4$ and Me$_6$[14] 1,4,8,11-tetraneN$_4$ have been oxidised by $OH^·$ radical to generate the corresponding nickel(III) complexes [190]. The half-lives of the diene and tetraene N$_4$ species have been determined to be 20 and 0.5 s respectively. Nickel(III) complexes of the above two ligands as well as of Me$_6$[14]aneN$_4$ have been radiolytically produced by Cl_2^-, Br_2^- and $(NCS)_2^-$ [180]. In each case transient electronic spectra of the complexes resemble spectra of the analogous nickel(III) complexes produced in non-polar solvents.



XLVIII

H. COMPLEXES OF PHOSPHINES AND ARSINES

Recent work has unfolded a rich chemistry of nickel in the +1 oxidation state with phosphine ligands. Arsenic bonded complexes are similar but have been less investigated. In combination with halide donors, particularly bromine, quite a few phosphorus (and arsenic) bonded nickel(III) complexes are known. The known stable nickel(IV) complexes are those of *o*-phenylenebisdimethylarsine (diars) and *o*-phenylenebisdimethylphosphine (diphos). In what follows, a brief account has been presented for nickel(III) and nickel(IV) complexes as some coverage has already been given elsewhere [10]. A more detailed survey has been made for nickel(I) species.

Of the $NiX_3(PR_3)_2$ (X = Cl, Br; R = Me, Et, n-Pr, n-Bu) series, $NiBr_3(PEt_3)_2$ is the most stable member [191,192]. With bulkier phosphines (R = cyclohexyl, phenyl, benzyl) the nickel(III) complexes could not be isolated [192]. The trigonal bipyramidal $NiX_3(PR_3)_2$ complexes are non-electrolytes, and have zero dipole moment in pentane [192]. As a general synthetic procedure bromine oxidation of the precursor nickel(II) complexes has found wide application. For example, $NiBr_3(PMe_2Ph)_2$ was generated in this way [193]. This compound is a non-electrolyte having a magnetic moment of 2.12 B.M. When recrystallised from benzene—hexane solution, partial reduction takes place and well developed crystals of $NiBr_3(PMe_2Ph)_2 \cdot 0.5\ NiBr_2(PMe_2Ph)_2 \cdot C_6H_6$ are obtained. A crystal structure analysis (Table 2) of this compound has revealed the presence of well separated nickel(III) (trigonal bipyramidal) and nickel(II) units (*trans*-planar) [21,193]. The magnetic moment calculated for nickel(III) in this compound is 2.09 B.M. Neither $NiBr_3(PMe_2Ph)_2$ nor $NiBr_3(PMe_2Ph)_2 \cdot 0.5\ NiBr_2(PMe_2Ph)_2 \cdot C_6H_6$ show EPR signals even at low temperatures due to ill-understood relaxation effects.

Several bidentate phosphines have been shown to stabilise nickel in the +3 state. By oxidising $NiBr_2(Et_2P(CH_2)_2PEt_2)$ with bromine, $NiBr_3(Et_2P(CH_2)_2PEt_2)$ is obtained. The magnetic moment of this compound is 2.00 B.M. A polymeric octahedral structure has been proposed [194]. Similarly, $NiBr_3(Me_2P(CH_2)_2PMe_2)$, a non-electrolytic compound with magnetic moment of 2.12 B.M. is obtained [195]. On the other hand, $NiX_2(Me_2P(CH_2)_2PMe_2)$ (X = Br, I) undergoes aerial oxidation in the presence of HX to form $[NiX_2(Me_2P(CH_2)_2PMe_2)]X$. These are 1 : 1 electrolytes and magnetic moments are 2.05 B.M. Further reaction of bromine with $[NiBr_2(Me_2P(CH_2)_2PMe_2)]Br$ leads to the formation of another nickel(III) complex $[NiBr_2(Me_2P(CH_2)_2PMe_2)]Br_3$ [195]. By bromine oxidation, complexes of the type $NiLBr_3$ have been obtained with phenyl substituted diphosphines ($L = Ph_2P(CH_2)_nPPh_2$, $n = 2$ and 3; $Ph_2PCH = CHPPh_2$) [196,197]. Their magnetic moments are 2.02 ($n = 2$) and 1.93 B.M. ($n = 3$). $NiBr_3(Ph_2P(CH_2)_3PPh_2)$ exhibits a broad symmetrical EPR signal centred at $g = 2.218$ [196]. $NiBr_3(Ph_2PCH = CHPPh_2)$ slowly reverts back to $NiBr_2(Ph_2PCH{=}CHPPh_2)$ on exposure to air [197]. Some cursory information is available on two nickel(III) complexes derived from two tridentate arsines [198,199]. These are of the type $NiLBr_3$ ($L = MeAs(C_3H_6AsMe_2)_2$; $MeAs(C_6H_4AsMe_2)_2$).

The chemistry of nickel in higher oxidation states with diars and diphos is considerably different. Nyholm's pioneering work [200] provided the first example of nickel(III) complexes $[NiX_2(diars)_2]^+$ (X = Cl, Br, NCS) with octahedral geometry. The nickel(IV) complexes $[NiX_2(diars)_2](ClO_4)_2$ (X = Cl, Br) were also readily obtained [9].

Nickel(III) complexes are stable in the solid state and in aqueous solution.

Magnetic moments of $[NiCl_2(diars)_2]Cl$ obey the Curie—Weiss law in the range 15—190 K with $\theta = 10$ K. Initially on the basis of incomplete EPR data the existence of nickel(III) in $[NiCl_2(diars)_2]Cl$ was questioned [201]. It was suggested that the cation contains nickel(II)-stabilised ligand σ-radical, diars$^+$. More complete studies [202,203] do not support such an extreme view. The unpaired electron spends very considerable time in the metal d_{z^2} orbital and probably is extensively delocalised over the As_4Cl_2 frame. The EPR spectra (dilute crystals and solution) are rich with ligand superhyperfine structures. In powder form the spectrum is rhombic [202]: $g_1 = 2.054$, $g_2 = 2.091$ and $g_3 = 2.142$. However, in the diamagnetic host lattice of isostructural $[CoCl_2(diars)_2]Cl$ the spectrum is axial [203]: $g_\parallel = 2.008$, $g_\perp = 2.142$. An X-ray structure determination (Table 2) of $[NiCl_2(diars)_2]Cl$ has established a *trans*-octahedral geometry with considerably elongated Ni—Cl bond [22]. An ill-understood, presumably polymeric nickel(III) diars complex $NiBr_3(diars)$ is reported [204].

The nickel(II) chemistry of *cis*-1,2-bis(dimethylarsino)ethylene (edas) is closely analogous to that of diars. However, nickel(III) and particularly nickel(IV) complexes are considerably less stable in the case of edas [205]. In fact $[NiCl_2(edas)_2]^+$ could not be isolated as a pure salt due to ready decomposition. The Ni—Cl stretching frequencies in $[NiCl_2(diars)_2]Cl$ and $[NiCl_2(edas)_2]Cl$ being closely comparable indicate similarity in structure.

Of more recent origin are the nickel(III) and nickel(IV) complexes of diphos [206,207]. They are very similar to the diars species. The magnetic moments of these nickel(III) complexes are ~1.9 B.M. Ni—Cl stretching frequencies in diphos- and diars-nickel(III) complexes are almost the same (ca. 260 cm^{-1}). In acetonitrile solution both $[NiCl_2(diphos)_2]^+$ and $[NiCl_2(diars)_2]^+$ undergo irreversible reduction to nickel(II), the $E_{1/2}$ values are -0.11 and -0.26 V, respectively. The reduction becomes reversible in the presence of chloride ion. On the other hand, both diphos and diars complexes of nickel(III) undergo reversible one-electron oxidation to the corresponding nickel(IV) species. The redox potentials for the Ni(IV)/Ni(III) complexes are +0.80 V (diphos) and +0.84 V (diars). It may be noted that nickel(III) → nickel(II) electron transfer occurs at a lower negative potential (~150 mV) with diphos than with diars, showing greater tendency of diphos to achieve the d^8 configuration. Variation of the axial donors (Br for Cl) also displays pronounced effect on reduction; $[NiBr_2(diphos)_2]^+$ undergoes more facile reduction than the chloro complex. Detailed EPR studies of $[Ni(diphos)_2X_2]Y$ ($X = Cl, Br$; $Y = ClO_4, PF_6$) with single crystals doped in the corresponding cobalt(III) lattices and of powdered materials in pure form have yielded [208] the following g-tensors: $g_1 = 2.1123$, $g_2 = 2.1157$, $g_3 = 2.0089$ (when $X = Cl$, $Y = ClO_4$); $g_1 = 2.0961$, $g_2 = 2.1413$, $g_3 = 1.9936$ (when $X = Br$; $Y = PF_6$). A comparison of the ligand hyperfine tensors has indicated that the order of increasing covalency in the complexes is $[NiCl_2(diphos)_2]^+ < [NiCl_2(diars)_2]^+ < [NiBr_2(diphos)_2]^+$. It has been reasoned [207] that the two important factors which contribute to the ability of diphos and diars to

TABLE 9

Synthetic routes and characteristics of nickel(I) complexes of phosphines and arsines

Nickel(I) complex	Synthetic route	Comments	Ref.
$Ni(PPh_3)_3X$ X = Cl, Br, I	$Ni(PPh_3)_4 + 0.5\ X_2$; $Ni(PPh_3)_4 + Ni(PPh_3)_2X_2$; ($\pi$-allyl)$Ni^{II}X$ + 3 PPh_3; $Ni(PPh_3)_2X_2 + PPh_3$-(excess) + $NaBH_4$(Ni : $NaBH_4$ ~1 : 1); $(PPh_3)_2\ NiC_2H_4 + BBr_3$; controlled potential electrolysis of $Ni(PPh_3)_2Cl_2$	Magnetic moments, 1.9—2.0 B.M; order of stabilities $Cl < Br < I$; in solution $Ni(PPh_3)_3X$ dissociates to $Ni(PPh_3)_2 + PPh_3$; $Ni(PPh_3)_3Cl$ reacts with $NaBH_3CN$ to form paramagnetic (1.88 B.M.) $Ni(BH_3)CN(PPh_3)_3$ of structure XLIX	209—213
$[Ni(PMe_3)_4]BPh_4$	Recrystallisation of $MeNi(PMe_3)_4BPh_4$ from tetrahydrofuran causes dissociative reduction to yield pure $[Ni(PMe_3)_4]BPh_4$	Magnetic moment is rather high (2.43 B.M.) isotropic EPR signal, $\langle g \rangle = 2.12$ in dichloromethane; crystal structure analysis (Table 2) shows tetrahedral geometry	15
NiL_3Cl L = 5-phenyl-5-H-dibenzophosphole	Nickel(II) complex + $NaBH_4$	Magnetic moment, 1.95 B.M.	211
$[(PPh_3)_2NiBPh_2 \cdot \frac{1}{2}Et_2O]_2$	$(PPh_3)_2NiC_2H_4 + Ph_2BBr$	Due to the diamagnetic behaviour a nickel-boryl bridged structure (L) has been proposed	212
$(PPh_2Me)_3NiX$ X = Br, I	Electrochemical reduction of $(PPh_2Me)_2NiX_2$	NMR spectral shift occurs primarily from π-spin densities in the phenyl ring and spin-transfer takes place probably through d_π—d_π and σ-bondings	214
$[NiL_2X]_2$ L = tricyclohexylphosphine; X = Cl, Br	Reduction of NiL_2X_2 with sodium in toluene	In solid state tetracoordinated planar structure with halide bridge has been proposed (from IR and electronic spectra). In benzene monomeric tricoordinated NiL_2X species results (molecular weight determination)	215
$HNi(N_2)(Et_3P)_2$	Nickel(II) acetylacetonate + Et_3P + triisobutylaluminium at 200 K in nitrogen atmosphere	Analogous compound has been obtained with Bu_3P, but no reaction takes place with Ph_3P and $EtPh_2P$	216
$Ni(PPh_3)_2X$ X = Cl, Br	$(PPh_3)_2NiC_2H_4 + Ni(PPh_3)_2X_2$	Cryoscopic measurement supports tricoordinated formulation. EPR spectra of $Ni(PPh_3)_2X$ in the host lattices of $CuX(PPh_3)_2 \cdot 0.5\ C_6H_6$ have been investigated (text)	209, 212 218

$Ni[N(SiMe_3)_2](PPh_3)_2$	$NiCl_2(PPh_3)_2$ + $Li[N(SiMe_3)_2]$	Obeys Curie—Weiss law from 98 to 298 K (μ_{eff} = 1.85 B.M.). EPR studies have been made (text). X-ray structure determination (Table 2) has confirmed triangular geometry. Related compounds of the type $Ni[N(SiMe_3)_2]L_2$ (L = PMe_2Ph, $PMePh_2$, $PEtPh_2$, PEt_2Ph, PEt_3, $\frac{1}{2}PPh_2(CH_2)_2PPh_2$) have been reported	20, 217
$NiL(PPh_3)_2$ L = 2,5-dimethylpyrolinium ion	$Ni(PPh_3)_3Cl$ + lithium 2,5-dimethyl pyrole	The EPR spectra of the paramagnetic compound (1.77 B.M.) is anisotropic ($g_{\parallel}$ = 2.316; $g_{\perp}$ = 2.059)	217
$Ni_2L_3(CN)_2$ L = $Ph_3P(CH_2)_nPPh_3$; n = 2,3	$NaBH_4$ reduction of $NiL_{1.5}(CN)_2$	Magnetic moments, 2.0—2.3 B.M. A binuclear planar structure has been proposed (electronic spectra)	220
$[NiH(R_2P(CH_2)_nPR_2)]_2$ n = 2,4; R = cyclohexyl	$Ni(R_2P(CH_2)_nPR_2)Cl_2$ + $NaBMe_3$	Compounds are diamagnetic and dimeric (molecular weight and mass spectral data); the structure (LI) has been proposed (text)	221
NiLX L = $MeC(CH_2PPh_2)_3$ X = Cl, Br, I	$NaBH_4$ reduction of the nickel(II) complexes	Non-electrolytes; magnetic moments, 1.93—1.98 B.M.; NiLBr obeys Curie—Weiss law from 4 to 295 K with θ = 0. Distorted tetrahedral structure of NiLI (Table 2)	16, 222
NiLX L = $MeC(CH_2AsPh_2)_3$ X = Br, I	$NaBH_4$ reduction of the nickel(II) complexes	Have similar features as the phosphine analogue	223
NiLX L = $N(CH_2CH_2PPh_2)_3$; X = Cl, Br, I, NCS, CN	NiX_2 + L + $NaBH_4$	Magnetic moments, 1.72—1.99 B.M.; EPR spectra (polycrystalline) show axial symmetry; $g_{\parallel} \simeq 2$, $g_{\perp}$ decreases from 2.21 to 2.15 in the order Cl > Br > I. Electronic spectra indicate trigonal bipyramidal geometry which is also supported by preliminary X-ray analysis of NiLI. [Ni(CO)L]X (X = BF_4, BPh_4) are also known	224, 225
$[NiH_nL]X$ L = $N(CH_2CH_2PPh_2)_3$ X = BF_4; n = 0.04—0.83 X = ClO_4; n = 0.04—0.92; X = NO_3; n = 0—0.53	NiX_2 + L + varying quantities of $NaBH_4$	In these non-stoichiometric compounds the formal oxidation state of nickel varies from +1 to +2. Their magnetic moments vary as a function of n, e.g. in $[NiH_nL]ClO_4$ the moment varies from 2.08 to 0.64 B.M. as n increases from 0.04 to 0.92. Crystal structure of $[NiH_{0.5}L]BF_4$ has been determined (Table 2)	18

TABLE 9 (Continued)

Nickel(I) complex	Synthetic route	Comments	Ref.
NiLX L = $N(CH_2CH_2AsPh_2)_3$; X = Cl, Br, I.	$NiX_2 + L + NaBH_4$	Have similar characteristics as the phosphine analogue	19
$[Ni_2L_2X]BPh_4$ L = $N(CH_2CH_2AsPh_2)$; X = Br, I.	$[NiLX]BPh_4 + NaBH_4$ (in less than stoichiometric amount).	Antiferromagnetic interaction between the nickel atoms occurs through the halide bridge. Crystal structure analysis of $[Ni_2L_2I]BPh_4 \cdot 3THF$ (Table 2) has established trigonal bipyramidal geometry of each nickel atom with a sharing iodine vertex	19

TABLE 10

EPR parameters [a] of $Ni(PPh_3)_2X$ doped in $Cu(PPh_3)_2X \cdot 0.5\ C_6H_6$ at 77 K

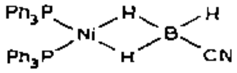
$Ni(PPh_3)_2Cl$				$Ni(PPh_3)_2Br$		
Axis	g	$A^{(P_1)}$	$A^{(P_2)}$	g	$A^{(P_1)}$	$A^{(P_2)}$
1	2.111	67	41	2.112	72	35
2	2.167	55	39	2.209	53	35
3(Z)	2.446	55	35	2.435	53	34
Av.	2.241	59	38	2.252	59	35

[a] All superhyperfine constants are in units of 10^{-4} cm^{-1}.

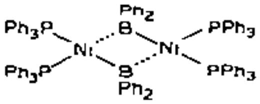
stabilise higher oxidation states are: (i) the small size (cone angle) and strong σ-donor power of the $P(CH_3)_2$ and $As(CH_3)_2$; (ii) the rigidity of the *o*-phenylene backbone, which stabilises the complexes toward ligand dissociation relative to monodentate P and As donors and more flexible bidentate counterparts.

Stabilisation of nickel in +1 oxidation state by a phosphine ligand was initiated by Heimbach in 1964 [209] who obtained $Ni(PPh_3)_3X$ and $Ni(PPh_3)_2X$ (X = Cl, Br). Table 9 summaries syntheses and characteristics of nickel(I) complexes of phosphine and arsine derivatives [201—225]. Some additional comments are given below for a few nickel(I) complexes.

In the tricoordinated species $Ni[N(SiMe_3)_2](PPh_3)_2$ axial EPR spectra has been observed both in polycrystalline form ($g_\parallel = 2.251$, $g_\perp = 2.078$) and in frozen toluene solution ($g_\parallel = 2.257$, $g_\perp = 2.090$). At room temperature the spectrum becomes isotropic ($\langle g \rangle = 2.148$). In solution, triplet fine structure due to superhyperfine coupling of the two equivalent phosphorus atoms has been noted [20]. On the other hand, in an EPR study of $NiX(PPh_3)_2$ (X = Cl, Br) doped in single crystals of $CuX(PPh_3)_2 \cdot 0.5\ C_6H_6$ (X = Cl, Br) marked inequivalency of the two phosphorus superhyperfine tensors was reported [218]. The EPR parameters of these compounds set out in Table 10 indicate that this inequivalency is more pronounced for the bromide complex than for the chloride complex. A possible explanation for the inequivalency of the two phosphorus atoms may lie with the steric factors present in the crystal. In fact an X-ray crystal structure determination of the copper host [219] has indicated slight differences in the two Cu—P bond lengths and moderate differences in the X—Cu—P bond angles. However, it is uncertain whether this small difference imposed by the host upon the guest is responsible for such a pronounced effect on the superhyperfine tensors. A real explanation should wait till crystal structures of $NiX(PPh_3)_2$ are available.



XLIX



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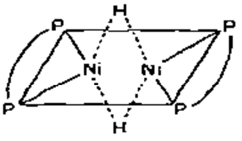


LI

The hydrido nickel complex $[NiH(R_2P(CH_2)_nPR_2]_2$ ($n = 2,4$; $R = C_6H_{11}$) reacts with the corresponding nickel(II) complex $NiCl_2(R_2P(CH_2)_nPR_2)$ to yield $NiCl(R_2P(CH_2)_nPR_2)$. $NiI(R_2P(CH_2)_nPR_2)$ is obtained by reacting the hydrido species with iodine. NMR spectra of the diamagnetic hydrido complex $[NiH(R_2P(CH_2)_nPR_2)]_2$ (LI) show the presence of two equivalent hydrogen atoms and four equivalent phosphorus atoms [221]. The structure (LI) has been confirmed by a crystal structure determination of $[NiH(Ph_2PCH_2CH_2PPh_2)]_2$ [217]. Each nickel atom has pentacoordinated geometry, the hydrogen atoms occupy bridge positions and the distance between nickel atoms (2.444 Å) indicates metal—metal bonding.

Before concluding this section, mention may be made of the reported [226] catalytic activity of $Ni(PPh_3)_3X$ (X = Cl, Br, I) for selective *cis—trans* isomerisation of but-1-ene. The stereoselectivity (*cis—trans* ratio) of the product decreases in the order I > Br > Cl. Augmentation of catalytic activity takes place with the addition of stannous chloride. More recent reports [227,228] have indicated that a low concentration of nickel(II) hydride is actually responsible for isomerisation of the olefin. The hydride presumably results from the reaction: 2 Ni(I) + olefin $\rightleftharpoons$ Ni(II) hydride + Ni(II) allyl.

I. COMPLEXES OF SULFUR AND SELENIUM LIGANDS

The chemistry of sulfur-bonded nickel complexes in unfamiliar oxidation states is mainly that of dithiocarbamate and 1,2-dithiolene systems. Much less extensive studies have been made with selenium analogues. Prior to some very recent reports on nickel(I) complexes, these investigations were confined to nickel(III) and nickel(IV) species.

(i) Dithiolenes and related ligands

1,2-Dithiolenes being unorthodox ligands have engendered various nickel complexes of the type $[NiS_4]^z$ with $z = 0, -1, -2$. While the species with $z = 0$ and -2 are regarded as nickel(II) complexes, there still remains controversy in assigning the formal oxidation state of nickel in the monoanionic species. Extensive EPR studies have been made with the $[NiS_4]^{-1}$ system in order to decide whether the unpaired electron resides on the metal or the ligand. The two alternative versions, viz. nickel(III) species and nickel(II)-stabilized ligand radicals have originated from two different ways of interpreting EPR data [229]. For further details consult refs. [10,230—233].

The electrical transport properties of monoanionic nickel 1,2-dithiolenes

TABLE 11

Electrical conductivity of monoanionic complexes of nickel 1,2-dithiolene [a]

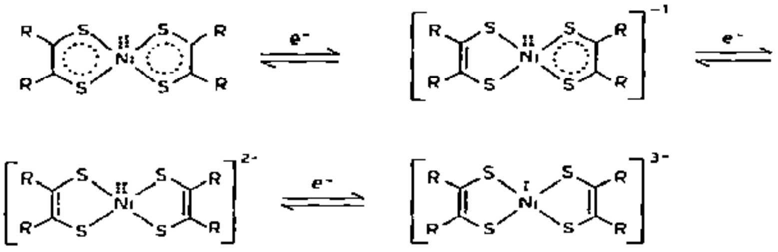
Complexes	(ohm^{-1} cm^{-1})	Ref.
$Q^+[Ni(S_2C_2H_2)_2]^-$	1.3×10^{-7}	234
$Cs^+[Ni(S_2C_2H_2)_2]^-$	1.4×10^{-7}	234
$Mepy^+[Ni(S_2C_2H_2)_2]^-$	3.3×10^{-10}	234
$MeQ^+[Ni(S_2C_2H_2)_2]^-$	5.0×10^{-10}	284
$Mor^+[Ni(S_2C_2H_2)_2]^-$	1.9×10^{-8}	234
$Pr_4N^+[Ni(S_2C_2H_2)_2]^-$	$<10^{-10}$	234
$MePPh_3{}^+[Ni(S_2C_2H_2)_2]^-$	4.2×10^{-9}	234
$PPh_4{}^+[Ni(S_2C_2H_2)_2]^-$	$<10^{-10}$	234
$(TTF)_2{}^+[Ni(S_2C_2H_2)_2]^-$	7.4×10^{-3}	235, 236
$NMP^+[Ni(S_2C_2H_2)_2]^-$	5.0×10^{-4}	237
$CV^+[Ni(S_2C_2(CN)_2)_2]^-$	3.2×10^{-9}	237
$An_3C^+[Ni(S_2C_2(CN)_2)_2]^-$	3.2×10^{-9}	237
$MG^+[Ni(S_2C_2(CN)_2)_2]^-$	3.2×10^{-9}	237
$NMP^+[Ni(S_2C_2(CN)_2)_2]^-$	2.0×10^{-8}	237
	$<10^{-10}$	166
$Thian^+[Ni(S_2C_2(CN)_2)_2]^-$	3.3×10^{-5}	237
$WB^+[Ni(S_2C_2(CN)_2)_2]^-$	2.1×10^{-6}	237
$MePPh_3{}^+[Ni(S_2C_2(CN)_2)_2]^-$	2.0×10^{-11}	237
	$<10^{-10}$	166
$Et_4N^+[Ni(S_2C_2(CN)_2)_2]^-$	1.0×10^{-8}	238
$Me_4N^+[Ni(S_2C_2(CN)_2)_3]^-$	2.3×10^{-11}	239
$Q^+[Ni(S_2C_2(CN)_2)_2]^-$	$<10^{-10}$	166
$TTF^+[Ni(S_2C_2(CN)_2)_2]^-$	5.0×10^{-2}	240
	1.6×10^{-3}	237
$TCTF^+[Ni(S_2C_2(CN)_2)_2]^-$	3.0×10^{-8}	241
$TTT^+[Ni(S_2C_2(CN)_2)_2]^-$	$\sim 10^{-10}$	242
$(Perylene)_2{}^+[Ni(S_2C_2(CN)_2)_2]^-$	50	243
$Na^+[Ni(S_2C_2(CN)_2)_2]^-$	2.5×10^{-7}	240
	4.0×10^{-4}	238
$Na^+[Ni(S_2C_2(CN)_2)_2]^- \cdot H_2O$	2.5×10^{-1}	238
$NH_4{}^+[Ni(S_2C_2(CN)_2)_2]^-$	4.0×10^{-4}	238
$NH_4{}^+[Ni(S_2C_2(CN)_2)_2]^-$ 1.15 H_2O	1.0	238
$NMP^+[Ni(S_2C_2C_6H_4CH_3)_2]^-$	$<10^{-7}$	237
$[Ni(Opd)_2]^+[Ni(S_2C_2H_2)_2]^-$	2.7×10^{-3}	237
$[Pd(Opd)_2]^+[Ni(S_2C_2H_2)_2]^-$	5.0×10^{-4}	237
$[Ni(dmopd)_2]^+[Ni(S_2C_2H_2)_2]^-$	6.2×10^{-7}	237
$[Ni(Opd)_2]^+[Ni(S_2C_2Ph_2)_2]^-$	4.0×10^{-4}	237
$[Ni(Opd)_2]^+[Ni(S_2C_2C_6H_4CH_3)_2]^-$	2.6×10^{-3}	237
$[Ni(dmopd)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$	3.8×10^{-4}	237
$[Ni(Opd)_2]^+[Ni(S_2C_2(CN)_2)_2]^-$	1.2×10^{-6}	237

[a] Measured at room temperature. Q = Quinoline; Mepy = methyl pyridine; MeQ = methyl quinoline; Mor = morpholine; TTF = tetrathiafulvalene; NMP = *N*-methylphenazine; CV = crystal violet; An_3C = tris(*p*-methoxyphenyl)carbene; MG = malachite green; thian = thianthrene; WB = *N,N,N',N'*-tetramethyl-*p*-phenylenediamine; TCTF = tetracyanotetrathiofulvalene; TTT = tetrathiotetracene; opd = *o*-phenylenediamine; dmopd = 4,5-dimethyl-*o*-phenylenediamine.

have recently been measured [166,234—243]. A crystal structure determination of $PPh_3Me^+[Ni(S_2C_2(CN)_2)_2]^-$ has revealed [233] that the nearly planar anions form staggered stacks in which each nickel atom has as nearest out-of-plane neighbours two sulfur atoms at distances of 3.59 and 3.75 Å.

Data collected in Table 11 show that depending upon the cation chosen $[NiS_4]^-$ complexes exhibit variation in electrical conductivity of several orders of magnitude. It may also be noted that in several cases some variation in conductivity has been reported for the same compound by different observers. In general these compounds behave as poor semiconductors. Only in a few systems have higher electrical conductivities been reported, in which the cations are either expected or known to be primarily responsible for the conductivity. For example, a conductivity of ~50 ohm^{-1} cm^{-1} in $(perylene)_2^+$-$[Ni(S_2C_2(CN)_2)_2]^-$ has been related [243] to the wide energy bands in positively charged linear chains of perylene molecules. It is interesting to note that a recent study has reported [238] high levels of conductivity in sodium and ammonium salts of $[Ni(S_2C_2(CN)_2)_2]^-$ showing that electronic conduction should be attributed to the complex anions. Of particular interest is the fact that in both the cases of ammonium and sodium cations, higher conductivities have been observed with the hydrated varieties in comparison to the anhydrous compounds.

While electron-transfer properties of nickel 1,2-dithiolene complexes $[NiS_4]^z$ have been extensively studied [229,230,244] an indication that dithiolenes are capable of stabilising nickel in the +1 oxidation state has been reported relatively recently. It has been demonstrated that $[Ni(S_2C_2R_2)_2]^{2-}$ (R = CN, CF_3) can be electrochemically reduced to a trianion [245,246]. The special significance of the reduction is that since the available π-orbitals of the ligand are already filled in the dianion, the extra electron is forced to go into a largely metal-based (d_{xy}) orbital. The electron-transfer properties of dithiolene complexes have been described as (LII).



LII

Evidence regarding the +1 oxidation state in the trianionic species has been obtained from the EPR spectrum of $[Ni(S_2C_2(CN)_2)_2]^{3-}$ which in frozen 1,2-dimethoxy ethane shows a rhombic g-tensor with $g_1 = 2.205$, $g_2 = 2.081$ and $g_3 = 2.062$ [245]. The 90% ^{61}Ni enriched sample has the characteristic of an axial spectrum. The low-field ($g_\parallel$) region shows a well resolved quartet due to interaction with a single ^{61}Ni nucleus ($I = 3/2$). Analysis of the metal hyper-

TABLE 12

Voltammetric data of the reduction of dianionic nickel dithiolenes to the trianionic species

Compound	Solvent	$E_{1/2}$(V)[a] $2- \rightleftharpoons 3-$	Ref.
$Ni(S_2C_2(CN)_2)_2^{2-}$	Glyme	−1.74	245
$Ni(S_2C_2(CN)_2)_2^{2-}$	Acetonitrile	−1.68	245
$Ni(S_2C_2(CF_3)_2)_2^{2-}$	Glyme	−2.30	246
$Ni(S_2C_2(CF_3)_2)_2^{2-}$	Acetonitrile	−2.44	246

[a] Versus SCE.

fine splittings has been found to be consistent with the expectation that the unpaired electron is residing in an orbital ($^3b_{1g}$) consisting of contributions from the d_{xy} metal orbital and in-plane sulfur orbitals [247]. In Table 12 relevant voltammetric data of nickel dithiolenes are shown.

Similar to the dithiolene compounds, nickel(II) complexes of the type $[Ni(MS_4)_2]^{2-}$ (M = Mo, W) undergo two consecutive reversible one-electron reductions [248].

$$[Ni^{II}(MS_4)_2]^{2-} \overset{e^-}{\rightleftharpoons} [Ni^{I}(MS_4)_2]^{3-} \overset{e^-}{\rightleftharpoons} [Ni^{0}(MS_4)_2]^{4-}$$

The data shown in Table 13 indicate that formation of the monovalent nickel complexes occurs at fairly low negative potentials.

Although a nickel(IV) complex of isomalenonitriledithiolate (imnt), $[Ni(imnt)_3]^{2-}$ has not yet been reported, the corresponding selenium containing complex $(Ph_4As)_2[Ni(imns)_3]$ has been isolated quite recently [249]. This compound has been obtained by iodine oxidation of $(Bu_4N)_2[Ni(imns)_2]$ at room temperature (where imns is $Se_2C{=}C(CN)_2$). By comparing electronic and IR spectra of $[Ni(imns)_3]^{2-}$ with related nickel(IV) complexes of dithiocarbamates it has been inferred that the diselenolate complex has lower metal—ligand covalency and the electron density is less extensively delocalized on the ligands. Voltammetric measurements have shown a one-electron oxidation step for the nickel(II) complex with $E_{1/2}$ = 0.14 V (acetonitrile solution; supporting electrolyte 0.1 M $NaClO_4$; rotating Pt vs. SCE). Careful oxida-

TABLE 13

Voltammetric data of nickel thiomolybdate and thiotungstate complexes

Complex	Solvent	$E_{1/2}$(V)[a]	
		$2- \rightleftharpoons 3-$	$3- \rightleftharpoons 4-$
$[Ni(MoS_4)_2]^{2-}$	Dimethylformamide	−0.61	−1.40
$[Ni(WS_4)_2]^{2-}$	Dimethylformamide	−0.61	−1.57

[a] Versus SCE.

tion of $[Ni(imns)_2]^{2-}$ with iodine in acetonitrile has resulted in the formation of an olive-green solution whose EPR spectrum at low temperature is rhombic. The same spectrum is obtained for an equimolar mixture of $[Ni(imns)_2]^{2-}$ and $[Ni(imns)_3]^{2-}$ thus indicating the formation of intermediate nickel(III) species.

(ii) Dithiocarbamates and related ligands

Contrary to 1,2-dithiolenes, dithiocarbamates (R_2dtc) form discrete nickel(III) and nickel(IV) compounds. Since these compounds have been covered in a recent review [250] we present here only a brief survey. As far as nickel(III) complexes are concerned, only two compounds are known, viz. $Ni(Et_2dtc)_3$ and $Ni(Bu_2dtc)_2I$. $Ni(Et_2dtc)_3$ has been generated in solution by oxidising $Ni(Et_2dtc)_2$ with excess of Et_4tds (thiuram disulfide) and characterised from its EPR spectrum [251]. $Ni(Bu_2dtc)_2I$ is obtained by oxidising $Ni(Bu_2dtc)_2$ with iodine at 243 K [252]. The low magnetic moment (1.33 B.M.) of this compound casts some doubt about its purity.

Nickel(IV) complexes of dithiocarbamates are more numerous. Compound of the type $[Ni(R_2dtc)_3]X$ ($X = Br, I$; $R = Et, Bu$) have been obtained by halogen oxidation of $Ni(R_2dtc)_2$ at room temperature [23,253]. Under suitable experimental conditions compounds of the type $[Ni(R_2dtc)_3]X$ ($X = ClO_4, NO_3, BF_4, FeCl_4$) have also been obtained [254]. The crystal structures of $[Ni(Bu_2dtc)_3]Br$ [23] and the selenium analogue $[Ni(Bu_2dsc)_3]Br$ [24] are known (Table 2). Claims for the preparation of tetracoordinated $[Ni(Et_2dtc)_2]Br_2$ [255] and $[Ni(Et_2dsc)_2]Br_2$ [256] have been doubted [250] on the basis of their IR, NMR and electronic spectral data. Interestingly, a chloroform solution of $Ni(Bu_2dsc)_2$ on standing, is converted to $[Ni(Bu_2dsc)_3]Cl$ [257], and a reaction between $Ni(Bu_2dtc)_2$ and ZnX_2 ($X = Cl, Br$) in ether in the absence of air produces $[Ni(Bu_2dtc)_3]X$ [250]. On the other hand, $[Ni(Bu_2dtc)_3]^+$ has been found to undergo photochemical and thermal bleaching in acetonitrile and related solvents in a reversible manner [23]. The kinetics of the forward (light induced) and backward (dark) reaction

$$Ni(R_2dtc)_3Br \underset{\text{dark}}{\overset{h\nu}{\rightleftharpoons}} \tfrac{1}{2}\,Ni(R_2dtc)_2 + \tfrac{1}{2}\,NiBr_2 + R_4tds$$

have been investigated by electronic and NMR spectral measurements [23,258].

In a comprehensive study [259] the electron transfer properties of sixteen nickel(II) dithiocarbamates in acetone at a platinum electrode have been reported. It has been observed that oxidation of the complexes occurs irreversibly (+0.8 to 1.0 V) with the overall process conforming to the stoichiometry: $3\,Ni(R_2dtc)_2 \rightarrow 2\,Ni(R_2dtc)_3^+ + Ni^{2+} + 4e^-$. In a different study $[Ni(Et_2dtc)_3]BF_4$ was isolated through electrochemical oxidation of $Ni(Et_2dtc)_2$ [260]. The nickel(IV) cation exhibits two successive relatively facile, one-electron reversible reduction steps [259].

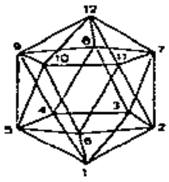
$$\mathrm{Ni(R_2dtc)_3^+} \overset{e^-}{\rightleftharpoons} \mathrm{Ni(R_2dtc)_3} \overset{e^-}{\rightleftharpoons} \mathrm{Ni(R_2dtc)_3^-}$$

Formally nickel(III) species could not be isolated, although they are readily formed from $\mathrm{Ni(R_2dtc)_2}$ and the electrochemically generated radical $\mathrm{R_2NCS_2^{\cdot}}$. The $\mathrm{Ni(R_2dtc)_2}$ complexes undergo a one-electron reduction at quite negative potentials (—1.2 to 1.5 V). The formal oxidation state of nickel in the reduced species, has not been established.

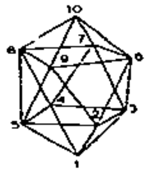
J. η-COMPLEXES

In virtually all systems described so far the metal ligand bonding is primarily of the two-centre σ type. During the last few years, the chemistry of nickel in the +3 and +4 oxidation states bound to cyclopentadienyl anion $\mathrm{C_5H_5^-}$ (abbreviated $\mathrm{cp^-}$) and/or an open face of a borane or carborane anion in a η-fashion has developed. Initial interest in this area arose from the achievable electrochemical conversion of $\mathrm{Ni(\eta\text{-}cp)_2}$ to $\mathrm{Ni(\eta\text{-}cp)_2^{2+}}$ [261,262]. The first η-complexes of nickel(III) and nickel(IV) based on the carborane anions $\mathrm{B_{10}CH_{11}^{3-}}$ and $\mathrm{B_9C_2H_{11}^{2-}}$ were reported in 1967 [263—268]. Mixed species containing both $\mathrm{cp^-}$ and a carborane anion were subsequently synthesised [262,269]. The power to stabilise the highest oxidation state, viz., nickel(IV) was found to increase with increasing negative charge on the ligand e.g., $\mathrm{B_{10}CH_{11}^{3-} > B_9C_2H_{11}^{2-} > cp^-}$.

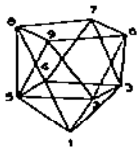
Some of the better known η-complexes [262—286] are set out in Table 14. The complexes are usually yellow to red in colour. The nickel(III) complexes are paramagnetic with $S = \frac{1}{2}$ and the nickel(IV) complexes are spin paired. While biscarborane species are known, in a majority of systems characterised so far, the metal atom is sandwiched between η-cp and an open face (defined by $\mathrm{C_2B_3}$, $\mathrm{CB_4}$, $\mathrm{B_5}$ or $\mathrm{B_4}$) of a polyhedron. It is often more convenient to consider such species as polyhedral heteroboranes having one or more metal vertices. The polyhedra appearing in Table 14 are just three: icosahedron, bicapped square antiprism and monocapped square antiprism



(LIII)



LIV



LV

as depicted in LIII--LV, respectively. In isoelectronic *closo* species of type $\mathrm{B}_n\mathrm{H}_n^{2-}$, $\mathrm{B}_{n-1}\mathrm{CH}_n^-$, $\mathrm{B}_{n-2}\mathrm{C_2H}_n$ a total of $2n + 2$ electrons are used for bonding within the polyhedral framework. When the number of such electrons is increased to $2n + 4$, an open-faced *nido* structure results. Considering the requirement of an 18 electron 'inert gas configuration' of a transition element, a $2n + 14$ electron rule is readily derived for *closo* n-vertex polyhedral

TABLE 14

Carborane and borane complexes of nickel(III) and nickel(IV)

Compound	Polyhedron	Atom positions in polyhedron [a]		Comments	Ref.
		Ni	C		
$[Me_4N][Ni(B_9C_2H_{11})_2]$ (Three isomers)	NiB_9C_2 (LIII)	1 1	2,3 2,3 [b]	Ni(III) sandwiched between two B_3C_2 faces in a symmetrical manner; isomorphous with corresponding cobalt(III) complex of known structure; in the other two isomers the bonding faces are B_3C_2—B_4C or B_4C—B_4C; C-substituted derivatives known	262, 266, 267
		1 1	2,3 2,7 [b]		
		1 1	2,7 2,7 [b]		
$Ni(B_9C_2H_{11})_2$ (Three isomers)	NiB_9C_2 (LIII)	1 1	2,3 2,3 [b, c]	Ni(IV) between two B_3C_2 faces disposed in a staggard 'cisoid' configuration; highly dipolar and forms adduct with Lewis bases; the other two isomers have B_3C_2—B_4C and B_4C—B_4C bonding faces; C-substituted derivatives known; in $Ni(B_9C_2H_9Me_2)_2$ the normal 'cisoid' B_3C_2—B_3C_2 structure not known due to steric reasons but B_3C_2—B_4C and B_4C—B_4C (*dl* and meso varieties) sandwiches exist	262, 266, 267, 282, 283
		1 1	2,3 2,7 [b, d]		
		1 1	2,7 2,7 [b]		
$Cs_2[Ni(B_{10}CH_{11})_2]$	$NiB_{10}C$ (LIII)	1 1	2 2 [b]	Ni(IV) in B_4C—B_4C sandwich; many C-substituted derivatives known	263, 265
$Ni(cp)(B_9C_2H_{11})^{n+}$	NiB_9C_2 (LIII)	1	2,3	Ni(III)(cp) bonded to B_3C_2 face; $n = 1$ exist only in solution produced from stable $n = 0$ electrochemically	262

$Ni(cp)(B_{10}CH_{11})$	$NiB_{10}C$ (LIII)	1	2	Ni(IV)(cp) bonded to CB_4 face; polyhedral rearrangement at 723 K; two isomers both having B_5 as the bonding face produced	269
(Three isomers)		1	7		
		1	12		
$Ni(cp)(B_8CH_9)$	NiB_8C (LIV)	1	10	Ni(IV)(cp) bonded to B_4 face	276
$(cp)Co(B_7CH_8)Ni(cp)$	$NiCoB_7C$ (LIV)	2,3 [e]	10 [c]	Co(III)(cp) and Ni(IV)(cp) vertices; in the isomer of definitely known structure (X-ray) the two metal atoms are indistinguishable and occupy adjacent sites in the same equatorial belt.	275, 284
(Four isomers)		1,2 [e]	10		
		2,4 [e]	10		
		1,6 [e]	10		
$\{Ni(cp)\}_2(B_5C_2H_7)$	$Ni_2B_5C_2$ (LV)	8,9	6,7	Diamagnetic due to bonding between two adjacent Ni(III)(cp) vertices	277, 285
$\{Ni(cp)\}_3(B_5C_2H_7)$	Ni_3B_5C (LV)	6, 7, 8	1 [c]	Ni(III)(cp)—Ni(III)cp—Ni(IV)(cp) system; green diamagnetic with intervalence band at 800—1500 nm; in the isomer of definitely known structure (X-ray) Ni_3B constitutes the open face	277
(Three isomers)		7, 8, 9	6		
		1, 7, 8	6		
$[Me_4N][Ni(cp)(B_{11}H_{11})]$	NiB_{11} (LIII)	1	—	Ni(IV)(cp) vertex	280
$\{Ni(cp)\}_2(B_{10}H_{10})$	Ni_2B_{10} (LIII)	1, 2	—	Ni(IV)(cp) vertices in adjacent positions	280
$[Me_4N][Ni(cp)(B_9H_9)]$	NiB_9 (LIV)	1	—	Ni(IV)(cp) vertex; isomer with Ni in cap position more stable suggesting greater electron density at cap (as in $B_{10}H_{10}^{2-}$)	281
(Two isomers)		2	—		

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[a] Polyhedron stated in the previous column; only metal and carbon positions shown, remaining positions are those of boron atoms; the positions correspond to the numbering scheme in LIII—LV.

[b] Two polyhedra sharing a common metal vertex.

[c] Three-dimensional X-ray data available.

[d] Three-dimensional X-ray data on the dimethyl derivative (all isomers) available.

[e] The two positions correspond to those of cobalt and nickel.

heteroboranes containing one transition metal vertex. *nido*-Polyhedra of this type require $2n + 16$ electrons while *closo*-polyhedra with two transition metal vertices require $2n + 26$ electrons [270]. Certain vertex isoelectronic relationships are particularly useful. An {Nicp} vertex can be considered as 'isoelectronic' with a {CH} vertex with regard to the number of electrons (three) and orbitals (three) contributed towards polyhedral bonding. Thus {Nicp} may be expected to 'replace' {CH} in a polyhedral environment. Similarly {Cocp} is isoelectronic with {BH}. Such isoelectronic relationships [270—274] provide powerful aids for rationalising known information and for predicting the existence of new polyhedral metalloboranes or metallo-carboranes and in understanding their skeletal rearrangements [267, 268—275]. For example, Ni(η-cp)(η-B_8CH_9) is isoelectronic with $B_8C_2H_{10}$ and the predicted square anti-prismatic stereochemistry for the NiB_8C polyhedron obtains in practice [276]. On the other hand, {Ni(η-cp)}$_3$(B_5CH_6) has two more cage electrons than $B_9H_9^{2-}$ and a *nido* structure for the Ni_3B_5C polyhedron is observed [277].

Structural information about the complexes has been routinely derived from ^{11}B and ^1H nmr data; in a few cases three-dimensional X-ray work has provided precise information (Table 14). The nickel $^2P_{3/2}$ binding energies [29] in carborane sandwiches of nickel reflect a small (~1 eV) increase in going from formal oxidation state +3 to +4. However, the absolute magni-

TABLE 15

Cyclic voltammetric peak potential data [a] (V vs. SCE)

System	Couple		Ref.
	Ni(IV)—Ni(III)	Ni(III)—Ni(II)	
Ni(cp)$_2$	0.77	—0.09	262
Ni(cp)($B_9C_2H_{11}$)	0.46	—0.52	262
Ni($B_9C_2H_{11}$)$_2$	0.18	—0.66	262, 267
	(0.00) [b]	(—0.95) [b]	267
	(—0.19) [c]	(—1.22) [c]	267
Ni(cp)($B_{10}CH_{11}$)	—0.27	—1.57	269
	(—1.52) [d,e]	(—2.65) [d,e,f]	269
	(—0.92) [d,g]	(—2.05) [d,f,g]	
Ni(cp)(B_8CH_9)	—0.93	—	276
Co(cp)(B_7CH_8)Ni(cp)	(—0.8 to —0.98) [h]	—	275
Ni(cp)($B_{11}H_{11}$)	—1.5	—	280
(Ni(cp))$_2$($B_{10}H_{10}$)	—0.27	—1.35	280

[a] Unless otherwise noted the solvent is acetonitrile and the couple is reversible.
[b] B_3C_2 + B_4C isomer (see Table 14).
[c] B_4C + B_4C isomer (see Table 14).
[d] Dichloromethane solvent.
[e] B_5 isomer (see Table 14).
[f] Irreversible.
[g] Second B_5 isomer (see Table 14).
[h] Shows the range which covers all four isomer (Table 14).

tudes of the binding energies are close to those of simple nickel(II) complexes. The low binding energies suggest strong electron donation from the polyhedral frame to the metal. The formal nickel(IV)—nickel(III) and nickel(III)—nickel(II) couples have been identified by cyclic voltammetric studies in many cases as documented in Table 15.

The synthesis of the complexes is achieved by insertion of a metal vertex on the top of a *nido* face of the ligand followed by oxidation with air, $FeCl_3$ etc. The simplest situation arises when a *nido* face is already present in the ligand. Examples are the syntheses of $Ni(B_9C_2H_{11})_2^{n-}$ ($n = 0, 1$), $Ni(B_{10}CH_{11})_2^{2-}$ and related species [263—269]. More interesting is the situation where an open face is created by electron addition (e.g. sodium metal) to the ligand cage prior to metal insertion. This type of reaction, called polyhedral expansion [268,273] depends on the fact that the reduced polyhedral structure is subject to Jahn—Teller or other type of distortion resulting in open face(s) required for establishment of a metal vertex. Polyhedral expansion is exemplified in the synthesis of $Co(\eta\text{-cp})(\eta\text{-}B_7CH_8)Ni(\eta\text{-cp})$ [275], $\{Ni(\eta\text{-cp})_2\}_2$-$(\eta\text{-}B_5CH_6)$ [279], and nickelaboranes [280,281].

A limited η-chemistry of nickel(I) as in $[cpNi(CO)]_2$, $cp_3Ni_3(CO)_2$ and codNiX (cod = 1,5-cyclooctadiene, X = Cl, Br) has been known for some time. The dimeric nature of diamagnetic $[cpNi(CO)]_2$ was confirmed from molecular weight data. Dipole moment and infrared data are in accord with a carbonyl bridged metal—metal bonded centrosymmetric structure [287]. Paramagnetic (1.79 B.M.) $cp_3Ni_3(CO)_2$ of rather indefinite structure is produced by the thermolysis of $[cpNi(CO)]_2$ [288]. Air sensitive unstable (cod)NiX is generated by reductive displacement of allyl fragments from π-allyl nickel(II) halides by cod in presence of norbornene [289].

K. MISCELLANEOUS COMPOUNDS

(i) Hydride

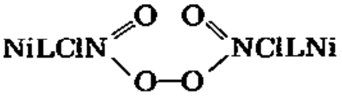
The simplest compound of nickel(I) is the binary hydride NiH obtained by matrix isolation techniques. The infrared active vibrations of NiH and NiD in an argon matrix at 14 K are 1906 and 1374 cm^{-1} respectively [290]. Interestingly, the corresponding bands of chemisorped hydrogen and deuterium on nickel surface are observed at 1880 and 1360 cm^{-1} [291]. The close similarity between the matrix isolation products and surface reaction products indicates the formation of monovalent nickel hydride and deuteride.

(ii) Nitrosyl

There are few claims in literature regarding the formation of nitrosyl compounds of nickel(I) but confirmatory evidence regarding the oxidation state of the metal ion is lacking. One such series is Ni(NO)X (X = Cl, Br, I) whose order of stability and ease of formation was found to be I > Br > Cl [292].

Complexes of composition $Ni(NO)L_2$ (L = diethyl dithiocarbamate and xanthate) were obtained [293] by reacting NiL_2 species with nitric oxide. The EPR spectrum of the dithiocarbamate complex in toluene at room temperature is isotropic ($\langle g \rangle = 2.103$), while at 77 K it is rhombic, $g_1 = 2.034$, $g_2 = 2.129$ and $g_3 = 2.146$. This is suggestive of a + 1 oxidation level [293].

$Ni(NO)LCl$ ($L = Ph_2PCH_2CH_2PPh_2$) on irradiation reacts with molecular oxygen to give $Ni(NO_2)(L)Cl$ [294]. The reaction goes through an intermediate nickel(I) species



which has not been isolated but characterised from its EPR spectrum.

(iii) Nitrate and fluorosulfonate

A formally nickel(III) compound of peculiar composition $[Ni(NO_3)_4]^-(NO_2)^+$ was stated to be obtained by reacting anhydrous nickel(II) chloride with excess of N_2O_5 [295]. The magnetic moment of this compound, 4.54 B.M. indicates it to be a high-spin species. Under vacuum the composition approaches to $Ni(NO_3)_3$.

A nickel(III) compound of composition $NiO(SO_3F)$ was obtained through an ill-understood reaction between $NiCO_3$ and $S_2O_6F_2$ [296].

(iv) Doped Ni^+ and Ni^{3+}

Both Ni^+ and Ni^{3+} ions have been introduced as doped impurities in various host lattices via X-, γ- and u.v.-irradiations of Ni^{2+}-doped crystals. Alternatively Ni^{2+}-doped lattices have been reduced by alkali metal vapours, nitric oxide, selenium etc. In many cases irradiative techniques have generated Ni^+ and Ni^{3+} centres simultaneously. In order to investigate these systems the EPR technique has been used almost exclusively. Some of the early observations on EPR spectra in MgO [297], CaO [298] and NaF [299,300] lattices originally attributed to Ni^+ were subsequently [301] shown to be due to Ni^{3+}. Above a certain critical temperature (T_c), Ni^{3+} in some oxide matrices shows isotropic spectral features. The critical temperatures reported for MgO [297], CaO [298] and Al_2O_3 [302] are 1.2, ~65 and 4.2 K respectively. The occurrence of an isotropic spectrum has been interpreted to be due to averaging of several equally energetic distorted configurations (dynamic Jahn—Teller effect). Relaxation times have been determined for Ni^{3+} in MgO [303], CaO [303], Al_2O_3 [304] and $SrTiO_3$ [304] by line broadening measurements as a function of temperature. The relaxation time $T_1 = A^* \exp(\Delta/RT)$ (where A^* and Δ stand for resonance relaxation life time and splitting) in all cases follows the Orbach mechanism [305]. Table 16 summarises pertinent information for Ni^+ and Ni^{3+} implanted in some representative lattices [306—316].

TABLE 16

Characteristics of Ni^+ and Ni^{3+} ions in some host lattices [a]

Ionic species	Lattice	Comments	Ref.
Ni^+	Zeolites	Ni^{2+}-doped zeolites on heating in sodium vapour produce Ni^+ centre both on intercrystalline surface (S_{II}) and at fully coordinated position (S_I) S_{II}: $g_\parallel \sim 2.10$—2.13; $g_\perp = 2.065$ S_I: $g_\parallel \sim 2.30$—2.40; $g_\perp = 2.096$	306
		Nitric oxide also reduces Ni^{2+}-doped zeolites at two different sites (S_A and S_B). S_A: $g_\parallel = 2.430$, $g_\perp = 2.171$; S_B: $g_\parallel = 2.346$, $g_\perp = 2.171$	307
	$Ni(CH_3COO)_2$	In X-irradiated $Ni(CH_3COO)_2$ seven different Ni^+ centres have been reported	308
	$NaPO_3$	NiO-doped $NaPO_3$ glass on exposure to u.v.- and X-radiations has been reported to produce produce Ni^+	309
	ZnS	$\langle g \rangle = 1.400$ (at 1—3 K); $A = 80 \pm 5 \times 10^{-4}$ cm^{-1}	310
	ZnSe	Broad isotropic photosensitive EPR spectrum has been observed whose intensity increased in light of wave length 0.45—0.6 nm but decreased at 0.8—2 nm $\langle g \rangle = 1.437$; $A = 81 \times 10^{-4}$ cm^{-1}	311
	$CuAlS_2$	$g_\parallel = 2.051$, $g_\perp = 2.330$; $A_\parallel = 13 \times 10^{-4}$ cm^{-1}, $A_\perp = 61 \times 10^{-4}$ cm^{-1}	312
	$AgGaS_2$	$g_\parallel = 2.645$, $g_\perp = 2.220$; $A_\parallel = 17 \times 10^{-4}$ cm^{-1}, $A_\perp = 36 \times 10^{-4}$ cm^{-1}	312
Ni^{3+} (in octahedral crystal field)	MgO	From 4.2 to 300 K isotropic spectrum is observed, $\langle g \rangle = 2.169$; $A^* = 7 \pm 2 \times 10^{-11}$ s; $\Delta = 1300 \pm 100$ cm^{-1}. At 1.2 K the spectrum becomes anisotropic	297, 301, 303
	CaO	From 77 to 300 K, $\langle g \rangle = 2.281$; $A^* = 0.2 \pm 0.05 \times 10^{-11}$ s; $\Delta = 2500$ cm^{-1}. Axial spectrum is observed between 62 and 68 K; $g_\parallel = 2.067$; $g_\perp = 2.383$	298, 301, 303
	Al_2O_3	$\langle g \rangle = 2.146$ at 50—300 K; $A^* = 0.6 \pm 0.3 \times 10^{-11}$ s; $\Delta = 1530 \pm 150$ cm^{-1}. At 4.2 K the spectrum splits	302, 304
	TiO_2	For interstitially occupied Ni^{3+} the spectrum is almost axial in the temperature range 4.2—300 K, $g_1 = 2.085$, $g_2 = 2.084$, $g_3 = 2.254$. Another rhombic spectrum has been observed by illuminating the crystal at room temperature followed by immediate cooling. This has been proposed as due to substitutionally occupied Ni^{3+}, $g_1 = 2.272$; $g_2 = 2.237$; $g_3 = 2.050$	313
	$SrTiO_3$	$\langle g \rangle = 2.190$; $A^* = 20 \pm 5 \times 10^{-11}$ s; $\Delta = 655 \pm 50$ cm^{-1}	304
	NaF	At 20 K, $g_\parallel = 2.766$; $g_\perp = 2.114$	301

TABLE 16 (continued)

Ionic species	Lattice	Comments	Ref.
Ni^{3+} (in tetrahedral crystal field	ZnO	At 1.3 K, $g_{\parallel} = 2.143$; $g_{\perp} = 4.318$	314
	ZnS	$\langle g \rangle = 2.148$	310, 314
	ZnSe	$\langle g \rangle = 2.180$	311
	GaAs	$\langle g \rangle = 2.106$ at 1.3 K	315
CuGaS	$CuGaS_2$	$g_{\parallel} = 2.116$, $g_{\perp} = 2.131$; $\lvert 2D \rvert = 2.55\ cm^{-1}$	316
	$AgGaS_2$	$g_{\parallel} = 2.142$, $g_{\perp} = 2.272$; $\lvert 2D \rvert \sim 30\ cm^{-1}$	316
	$CuAlS_2$	$g_{\parallel} = 2.138$, $g_{\perp} = 2.030$; $\lvert 2D \rvert \sim 19\ cm^{-1}$	316

[a] A^* and Δ stand for resonance relaxation life time and splitting respectively; $\lvert 2D \rvert$ is the zero field splitting.

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