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11. NICKEL

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CONTENTS

INTRODUCTION

Even for a year's coverage of the literature, it is difficult to avoid being selective for such a widely investigated transition metal as nickel. However, although most of the kinetic work which has appeared could have been left out, some of the more relevant work has been included, as this is one of the major areas of advance at present.

Two articles not strictly concerned with complexes, but nevertheless of considerable interest, deserve mention. The first concerns Mg_2NiH_4, which has now been shown to undergo allotropic transitions at 228—245 and 280—300°C (with decomposition) [1]; its space group has been re-assigned, as $F\bar{4}3m$ or $Fm3m$. The material is of interest because it is under test as a hydrogen-storage material. The second article is an elegant work on the coordination-chemistry-like behaviour of a series of molecules (e.g. MeCN, MeNC, C_2N_2, C_2H_2, etc.) on the (111) surface of nickel. Bonding modes similar to those in coordination chemistry were established [2].

11.1 NICKEL(0) COMPLEXES

The metal—ligand co-condensation technique provides a convenient means for synthesising complexes of highly π-accepting ligands which stabilise low oxidation states, and has been applied to the preparation of dialkylaminodi-

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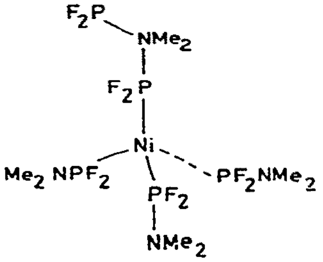
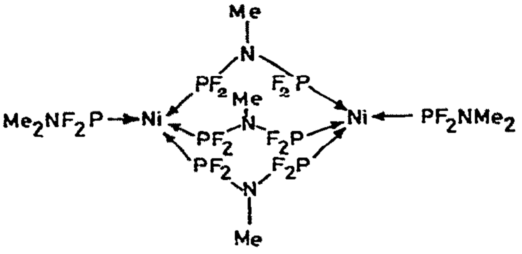
fluorophosphine Ni(0) complexes [3]. Reaction of nickel metal with Me_2NPF_2 leads to $[Ni(Me_2NPF_2)_4]$, and with $MeN(PF_2)_2$ to polymeric $[Ni\{MeN(PF_2)_2\}_2]_n$. Co-condensation of nickel vapour with a 4 : 1 $Me_2NPF_2 : MeN(PF_2)_2$ mixture gives a mixture of volatile white $[Ni\{Me_2NPF_2\}_3\{MeN(PF_2)_2\}]$ (1) with the much less volatile light yellow $[Ni_2\{Me_2NPF_2\}_2\{MeN(PF_2)_2\}_3]$ (2). A UVPES study of gaseous



(1)



(2)

$[Ni\{MeN(PF_2)_2\}_2]_n$ provides evidence that the coordination geometry in the gas phase may not be tetrahedral. The broad sequence of bands in the $3d^{10}$ ionisation region have maxima (at 7.65 and 8.65 eV) in approximate intensity ratio 2 : 3, whereas a tetrahedral arrangement of donor PF_2 groups around each Ni atom (as in $[Ni(PF_3)_4]$) would require a 3 : 2 intensity ratio [4]. However, the nature of the vapour species was not unambiguously established.

Metal—vapour synthesis has also been used to prepare $[Ni(PF_2H)_4]$, not preparable by known bulk methods [5]:

$$Ni + 4\,PF_2H \xrightarrow[-196^\circ C]{\text{metal—atom reactor}} [Ni(PF_2H)_4]$$

$[Ni(PF_2H)_4]$ is a white solid (m.p. $-50 \pm 2^\circ C$); it decomposes only slowly at room temperature, but completely if left for 8 h at 40° C. 80% of the originally coordinated PF_2H was recovered, the rest undergoing decomposition to give $PF_3(g)$, $PF_3H_2(g)$, and yellow solids of empirical formula $(PH)_n$. The compound was characterised unequivocally by NMR and IR. Changes in the P—F stretching frequency on coordination are significantly greater for PF_2H (in both gaseous and liquid state) than those observed for PF_3 (ca. 50 cm^{-1}, compared to 6 cm^{-1}), since the π-bonding is distributed over only two P—F linkages rather than three. PF_2H forms a less stable complex with Ni(0) than does PF_3, but a more stable one than does PH_3. On this basis, it was concluded that the unusual stability of $F_2HP \cdot BH_3$ relative to that of $F_3P \cdot BH_3$ and $H_3P \cdot BH_3$ must be attributed to specific hydride proton interactions involving BH_3, rather than to any unusual base strength of PF_2H.

$[Ni(Me_2NPF_2)_n(CO)_{4-n}]$ ($n = 3$ or 1) complexes have been successfully isolated using high-pressure liquid chromatography [6]. The complexes were previously believed to exist only as equilibrium species in solution during preparation of the $n = 2$ analogue [7]. The reactions of the $n = 4$ and $n = 2$ complexes with BF_3 have also been investigated. BF_3 adds to $[Ni(Me_2NPF_2)_4]$, giving solid adducts $Ni(Me_2NPF_2)_4 \cdot xBF_3$ ($x = 2.6$) and very viscous oils ($x = 1.78$ or 1.24); it adds to $[Ni(Me_2NPF_2)(CO)_2]$ giving solids with $x \simeq 1$. Characteristic IR spectra with ν(B—N) at 610 cm^{-1} indicate that the BF_3 coordinates to the nitrogen atom of the dimethylaminodifluorophosphine [6].

The sign and magnitude of the P—P coupling constant in several tetrahedral trimethylphosphite complexes, including $[Ni\{P(OMe)_3\}_4]$ ($^2J_{PP} = +12$ Hz), have been determined [8].

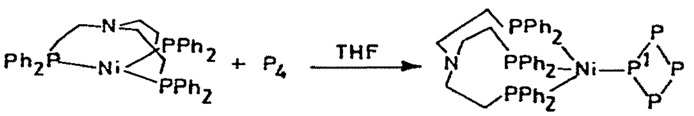
Displacement of ethene from $[(PPh_3)_2Ni(C_2H_4)]$ provides a convenient route to mixed-ligand complexes containing $[EPh_3]^-$ (E = Ge, Sn or Pb) [9].

$$2\,[(PPh_3)_2Ni(C_2H_4)] + 4\,M[EPh_3] \xrightarrow{thf} M[Ni(PPh_3)_3(EPh_3)(thf)_x] +$$

$$+\,M_3[Ni(PPh_3)(EPh_3)_3(thf)_y]$$

The analogous complexes of $[SiPh_3]^-$ could not be prepared, because $SiPh_4$ formed via reaction of the $Li[SiPh_3]$ with coordinated PPh_3. Similarly, the complex with $[SnPh_3]^-$ could not be isolated; only decomposition products, such as $Na_xNi(PPh_3)_{4-x} \cdot (SnPh_4)_x(thf)_y$, were isolated.

There has been a report this year of the tetraphosphorus unit acting as a ligand in a Ni(0) complex (3), prepared according to [10]

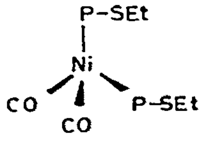


(3)

Crystal structure determination shows that the central nitrogen atom is not bonded to the nickel $\{r(Ni\cdots N) = 3.09$ Å$\}$, and that the Ni—P^1 distance, 1.99(1) Å, is ca. 0.2 Å shorter than the sum of the covalent radii. It was suggested that this indicates the possible presence of some d_π—p_π interaction between these atoms.

Not all the Ni(0) complexes reported this year have been with all-phosphorus ligands; several complexes with the hybrid donor ligand 1-(thioethyl)-2-(diphenylphosphino)ethane, $Ph_2PCH_2CH_2SEt$ (P-SEt), have been reported [11]. The reduction of $[Ni(P\text{-}SEt)_2][BF_4]_2$ with sodium amalgam in benzene gave the red complex $[Ni(P\text{-}SEt)_2]$, which could not be further purified. This complex forms a dicarbonyl, $[Ni(P\text{-}SEt)_2(CO)_2]$ (4), for which a tetrahedral structure with monodentate ligands was suggested. It also forms an isolable hydride

$$[Ni(P\text{-}SEt)_2] + H[BF_4] \xrightarrow{Na[BPh_4]} [NiH(P\text{-}SEt)_2][BPh_4]$$



(4)

This hydride reacts with dienes forming cationic π-allyl derivatives

$$[\mathrm{NiHL_4}]^+ + \text{diene} \xrightarrow{-\mathrm{L}} \underset{\text{(red)}}{[(\pi\text{-allyl})\mathrm{NiL_3}]^+} \xrightarrow{-\mathrm{L}} \underset{\text{(yellow)}}{[(\pi\text{-allyl})\mathrm{NiL_2}]^+}$$

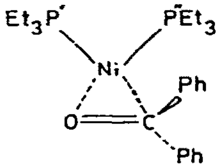
However, neither the red intermediate nor the yellow product could by isolated. The hydride has catalytic properties towards the isomeration of allyl benzene to *trans*-propenylbenzene, of allyl alcohol to propionaldehyde, of allyl cyanide to crotonitrile, and of 1-pentene to *trans*- or *cis*-2-pentenes. As for other nickel-catalysed isomerisations, the last-mentioned reaction involves formation of an olefin—metal hydride adduct which rearranges first to a metal alkyl and then to a metal hydrido complex of the isomeric olefin.

It was previously reported [12] that a zerovalent nickel tert-butyl isocyanide complex gave stable complexes with ketones having electron-withdrawing substituents. A similar study has now been carried out with $[\mathrm{Ni(PEt_3)_4}]$, which readily dissociates in organic solvents (e.g. thf, benzene or hexane) [13].

$$[\mathrm{Ni(PEt_3)_4}] \xrightleftharpoons[-\mathrm{PEt_3}]{K_1} [\mathrm{Ni(PEt_3)_3}] \xrightleftharpoons[-\mathrm{PEt_3}]{K_2} [\mathrm{Ni(PEt_3)_2}]$$

(where $K_1 = 1 \times 10^{-2}$, $K_2 < 10^{-6}$ in thf).

Reaction with benzophenone gave red, crystalline $[\{\mathrm{PhC(O)Ph}\}\mathrm{Ni(PEt_3)_2}]$, a crystal structure determination proving the structure (5). The *trans* influence arises because of important contributions to bonding due to π-back-bonding, i.e. the presence of electron-withdrawing substituents lowers the energy of the antibonding π^* orbital of the unsaturated ligand, favouring formation of the π complex. The coplanarity of the ligand is destroyed on coordination, and the carbon and oxygen atoms are out of the $\mathrm{NiP_2}$ plane (C by 0.024 Å above, and O by 0.51 Å below, the plane) [13]. A detailed kinetic investigation showed that addition of benzophenone to $[\mathrm{Ni(PEt_3)_4}]$ follows second-



(5)

$\widehat{\mathrm{ONiC}} = 40.7°$
$r(\mathrm{C{=}O}) = 1.335$ Å
$r(\mathrm{Ni{-}C}) = 1.974$ Å
$r(\mathrm{Ni{-}O}) = 1.849$ Å
$r(\mathrm{Ni{-}P'}) = 2.190$ Å
$r(\mathrm{Ni{-}P''}) = 2.136$ Å

order kinetics, the mechanism suggested being

$$[NiL_4] \overset{K_1}{\rightleftharpoons} [NiL_3] + L \qquad (K_1 = 4.2 \times 10^{-3}\ M)$$

$$[NiL_3] + Ar_2C{=}O \overset{k_2}{\rightarrow} [(Ar_2C{=}O)NiL_2] + L \qquad (k_2 = 22.2\ M^{-1}\ s^{-1})$$

The π-complex formation is accelerated by electron-deficient benzophenones and retarded by electron-rich ones [13].

A thorough study of the oxidative addition of aromatic halides to $[Ni(PEt_3)_4]$ has also been carried out [14]. *Trans*-arylnickel(II) halides are formed, as well as paramagnetic Ni(I) halides, as by-products.

$$[NiL_4] + ArX \rightarrow [ArNiXL_2] + [XNiL_3]$$

The relative yield of Ni(II)/Ni(I) strongly depends on the halide (I, Br or Cl), the aromatic substituents, and the solvent polarity. There is evidence that both products have a common paramagnetic ion-pair intermediate, the rate-limiting step being the electron-transfer from the Ni(0) donor to the aryl halide acceptor.

$$[NiL_4] \overset{K_1}{\rightleftharpoons} [NiL_3] + L$$

$$[NiL_3] + ArX \overset{k_2}{\rightarrow} [NiL_3ArX]^{\pm}$$

$$[NiL_3ArX]^{\pm} \begin{cases} \longrightarrow [ArNiXL_2] + L \\ \xrightarrow[\text{diffuse}]{} [NiL_3X] + [Ar] \end{cases}$$

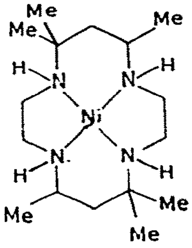
Some time ago, it was suggested, on the basis of Hückel MO calculations, that M—SO_2 bonding should be more sensitive to the basicity of the metal ion centre (i.e. to the nature of the other ligands present) in four-coordinate d^{10} transition metal ion systems than in other configurations and geometries [15]. This suggestion has been further investigated via crystal structure determination of the Ni(0) complexes $[Ni(SO_2)(PPh_3)_3]$ and $[Ni(SO_2)_2(PPh_3)_2]$ [16]. In the former, coordination is almost tetrahedral, with $S{-}\widehat{Ni}{-}P < 109.4°$ and $P{-}\widehat{Ni}{-}P > 109.4°$. The $NiSO_2$ group is almost coplanar, whereas in the isoelectronic complex $[Pt(SO_2)(PPh_3)_3]$, the geometry at the sulphur atom is pyramidal. This near-coplanarity in the nickel complex attests to the importance of the relative basicity of Pt compared to Ni in determining the geometry of the MSO_2 group (in similar environments). Although less than the tetrahedral angle, the S—Ni—P angles are greater than those in the platinum analogue, in agreement with a higher M—S π interaction in the Ni complex. $[Ni(SO_2)_2(PPh_3)_2]$ also has a tetrahedral geometry, the two SO_2 groups being coplanar with the metal, with a dihedral angle between the SO_2 planes of 23.5°: it was suggested that this maximises π—π interaction perpendicular to this plane and stabilises the coplanar M—SO_2 geometry. The structure of this complex is also different from the isoelectronic platinum complex $[Pt(SO_2)_2(PPh_3)_2]$, which contains two pyramidal SO_2 groups, both of which are extremely labile, whereas the nickel complex is substantially inert. Thus:

$$[Pt(SO_2)_2(PPh_3)_2] + O_2 \rightarrow [Pt(SO_4)(PPh_3)_2]$$

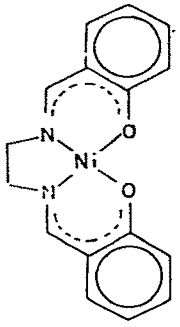
$$[Ni(SO_2)_2(PPh_3)_2] + O_2 \nrightarrow [Ni(SO_4)(PPh_3)_2]$$

11.2 NICKEL(I) COMPLEXES

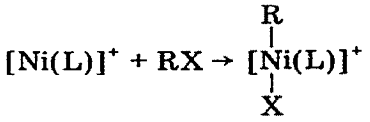
Few Ni(I) complexes have been prepared to date, and over the past year the major report of note appears to be the suggestion that Ni(I) intermediates occur in the cathodic reduction of the square-planar macrocyclic Ni(II) complexes (6) and (7) in MeCN at a platinum electrode, followed by reaction of the resulting compounds with alkyl bromides and iodides [17]. The reaction mechanism put forward involves nucleophilic attack by the Ni(I) complex on the alkyl halide, with the formation of a Ni—C bond, e.g. for (6)



(6; $[Ni(L)]^{2+}$)

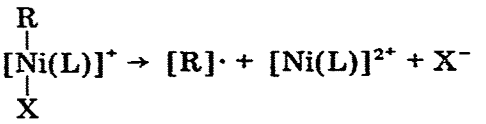


(7)



$$[Ni(L)]^+ + RX \rightarrow [\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{N}}i(L)]^+$$

The lifetime of the intermediate formed determines the products obtained. With secondary and tertiary alkyl bromides, the intermediate is very unstable, and the Ni—C bond cleaves rapidly giving a radical and an electroactive complex (i.e. an electroactive current is observed)

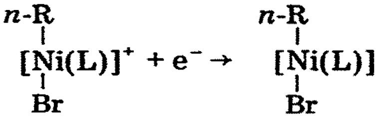


$$[\overset{\overset{R}{|}}{\underset{\underset{X}{|}}{N}}i(L)]^+ \rightarrow [R]\cdot + [Ni(L)]^{2+} + X^-$$

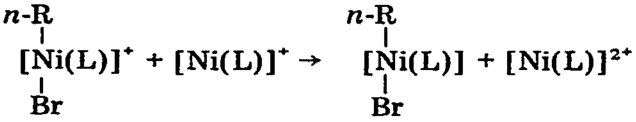
In high concentration of halide ion, the reaction

$$[\mathrm{Ni(L)}]^{2+} + 2\,\mathrm{X}^- \rightarrow [\mathrm{Ni(L)X_2}]$$

must also be considered, although electrolyses in the presence of high RBr : $[\mathrm{Ni(L)}]^{2+}$ ratios indicate this is of little importance on the time scale involved (ca. 30 min). With n-$\mathrm{C_8H_{17}Br}$, the Ni—C bonded intermediate is sufficiently long-lived to undergo reduction at the electrode or in solution.

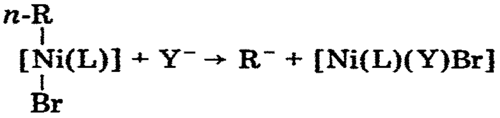


$$[\underset{\mathrm{Br}}{\overset{n\text{-}\mathrm{R}}{\mathrm{Ni}}}(\mathrm{L})]^+ + e^- \rightarrow [\underset{\mathrm{Br}}{\overset{n\text{-}\mathrm{R}}{\mathrm{Ni}}}(\mathrm{L})]$$



$$[\underset{\mathrm{Br}}{\overset{n\text{-}\mathrm{R}}{\mathrm{Ni}}}(\mathrm{L})]^+ + [\mathrm{Ni(L)}]^+ \rightarrow [\underset{\mathrm{Br}}{\overset{n\text{-}\mathrm{R}}{\mathrm{Ni}}}(\mathrm{L})] + [\mathrm{Ni(L)}]^{2+}$$

Decomposition of this reduced organo species must then lead to an electroinactive species (probably octahedral Ni(II))



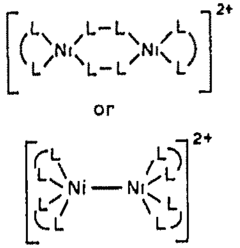
$$[\underset{\mathrm{Br}}{\overset{n\text{-}\mathrm{R}}{\mathrm{Ni}}}(\mathrm{L})] + \mathrm{Y}^- \rightarrow \mathrm{R}^- + [\mathrm{Ni(L)(Y)Br}]$$

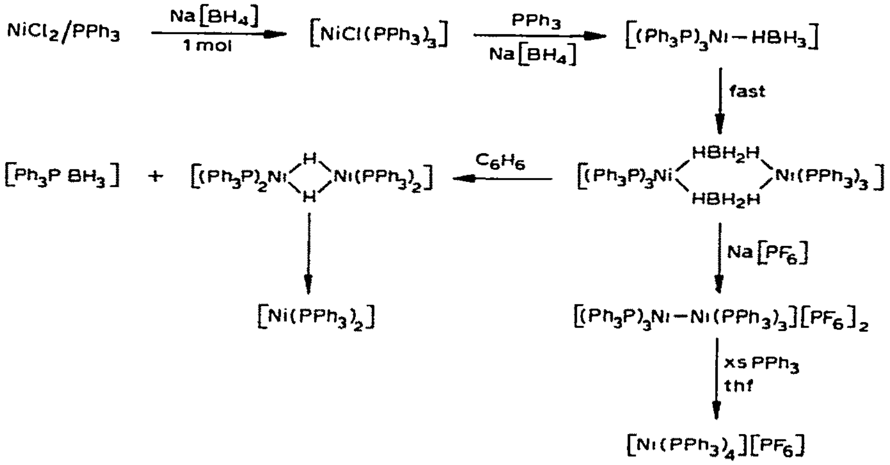
The mechanisms for (7) are similar, but results with n-octyl halides show that (7) is a weaker nucleophile (i.e. the Ni—C bond is weaker with this complex than with (6)). The differences between the Ni complexes and comparison with their Co analogues show that systems which are both catalytic, and lead selectively to radicals or carbanions, can be designed by suitable choice of metal centre and ligand.

Reduction of Ni(II) species with $\mathrm{Na[BH_4]}$ still appears to be one of the best methods for preparing Ni(I) complexes, and the reactions of $\mathrm{NiCl_2/PPh_3/Na[BH_4]}$ have now been investigated over a wider range of conditions than before [18]. All reactions between $\mathrm{NiCl_2}$ and $\mathrm{PPh_3}$ (in minimum mole ratio of 1 : 6) and excess $\mathrm{Na[BH_4]}$ in EtOH in strict absence of $\mathrm{O_2}$ lead to $[\mathrm{Ni(BH_4)(PPh_3)_3}]_2$. Even traces of $\mathrm{O_2}$ give phosphine oxide, the borane adduct $\mathrm{Ph_3P \cdot BH_3}$, and Ni(0) triphenyl phosphine complexes. Conversely, when less $\mathrm{PPh_3}$ is used (e.g. Ni : P = 1 : 2), reduction to Ni(0) is rapid and complete. Several other complexes, with $[\mathrm{ClO_4}]^-$ and mono- and bidentate phosphines have also been prepared (Table 1). The possible mechanism accounting for the occurrence of the dimeric, diamagnetic $[\mathrm{Ni_2(PPh_3)_6}][\mathrm{PF_6}]_2$ is illustrated in Scheme I.

TABLE 1

Some new Ni(I) complexes [18]

Complex	μ_{eff}/μ_B	Preparation	Assigned structure	Comments
$[Ni_2(PPh_3)_6][PF_6]_2$	Diamagnetic	See Scheme I	Binuclear with Ni—Ni bond	
$[Ni(PPh_3)_4][PF_6]$	2.27	See Scheme I	Tetrahedral	Shoulder at 6000—7000 cm^{-1} assigned to $^2E \rightarrow {}^2T_2$ transition
$[Ni(PPh_3)_4][ClO_4]$	2.31	Analogous to Scheme I	Tetrahedral	—
$[Ni(PPh_3)_3][ClO_4]$	2.17	$Ni[ClO_4]_2$/ 1 mol $Na[BH_4]$/PPh_3	—	
$[Ni(dppee)_2][ClO_4]$	1.94	$[Ni(dppee)_2][ClO_4]_2$/ $Na[BH_4]$	Distorted square planar	
$[HNi(dppe)_2][ClO_4]$	Diamagnetic	As above	Five-coordinate Ni(II)	
$[Ni_2(dppm)_4][ClO_4]_2$	Diamagnetic	As above		
$[Ni(BH_4)(PPh_3)_{1.5}]$	Diamagnetic	$[NiX_2(PPh_3)_2]$/ $Na[BH_4]$ (X = Cl, Br or I)	At least dimeric, probably with chelating $[BH_4]^-$ groups	Pyrophoric, minor product from reaction; major product is $[Ni(PPh_3)_2]$



Scheme I. The preparation and reactions of some nickel(I) phosphine complexes [18].

11.3 NICKEL(II) COMPLEXES

11.3.1 Electronic structural aspects

Among other transition metal halides, $NiCl_2$ and $NiBr_2$ have been the object of a detailed UVPES study [19]. The spectra (Fig. 1 shows that for the bromide) were correlated with energy levels for linear symmetry, calculated using spin-restricted and spin-polarised transition state calculations for all valence orbitals. Satisfactory correlations were obtained using spin-polarised orbitals and it was found that the $2\delta_{g\downarrow}$ (the uppermost occupied orbital in $FeBr_2$ and $CoBr_2$) is buried under the ligand *p*-like orbitals in $NiBr_2$. The highest valence ionisation energies (14—15 eV) were more visible in the bromides than in the chlorides, and were assigned to the $11\sigma_{g\uparrow}$ components (which would correspond to $8\sigma_{g\uparrow}$ in the chlorides). Finally, spin splittings were found to be quite large for gerade levels (up to 3.5 eV for $2\delta_g$) and quite small for ungerade ones (<0.04 eV), as expected since gerade levels involve admixture of metal *s* and *d* orbitals, whereas ungerade ones do not.

The paramagnetic susceptibilities of single crystals of $[Ni(PPh_3)_2X_2]$ ($X =$ Cl or Br) have been measured down to liquid helium temperature and the results treated within the angular overlap model scheme developed by Gerloch and co-workers [20]. No fit was found to be possible unless the $e_\pi(P)$ parameter was assigned a large negative value (see Table 2), and it was suggested that this was associated with a π-accepting role for the triphenylphosphine, in agreement with conclusions arrived at from an earlier study of the polarised spectra of the Co(II) analogues [21]. In addition, it was also sug-

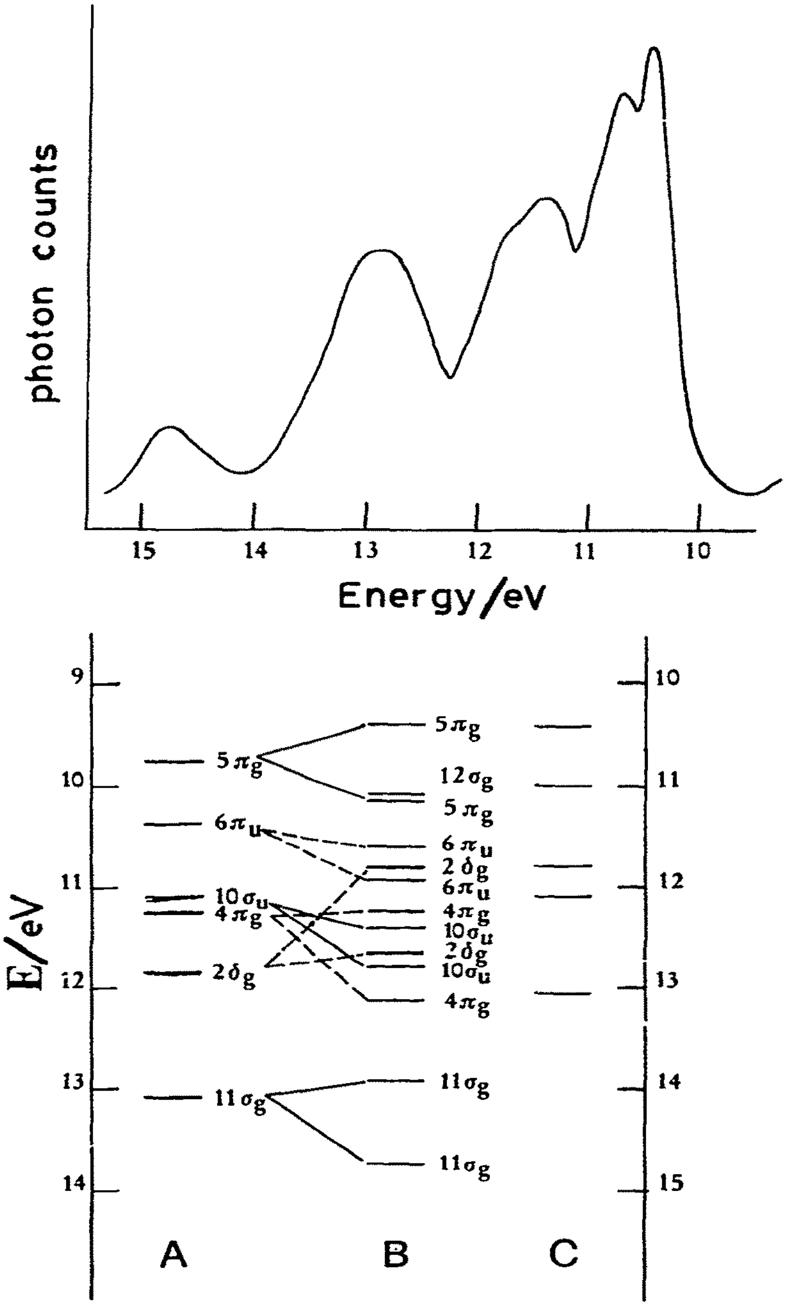


Fig. 1. He—I photoelectron spectrum of $NiBr_2$ (upper) and the assignment of its energy levels (lower) by (A) a spin-restricted calculation and (B) a spin-polarised calculation, compared with (C) the experimental ionisation energies.

TABLE 2

"Best-fit" parameter sets for [Ni(PPh$_3$)$_2$X$_2$], reproducing crystal magnetism and electronic spectra [20]

Parameter	[Ni(PPh$_3$)$_2$Cl$_2$]	[Ni(PPh$_3$)$_2$Br$_2$]
B/cm^{-1}	550	550
	350	300
e_σ(P)/cm^{-1}	4500	4000
e_π(P)/cm^{-1}	−2500	−1500
e_σ(X)/cm^{-1}	4500	4000
e_π(X)/cm^{-1}	2000	1500
k	0.6	0.6

gested that donation by the halogens is encouraged by π acceptance by the phosphine, in line with the electroneutrality principle. The π-acceptor rôle of the triphenylphosphine was estimated to contribute ca. 2999 cm^{-1} to the Δ_{tet} value. The π-acceptor strength of the triphenylphosphine was lower in the Co(II) analogue, and this was interpreted as reflecting an enhanced metal-donor property for the Ni(II) atoms as one more electron is added into the d-orbital manifold. The orbital splitting diagram derived is shown in Fig. 2. This result is interesting, because both magnetic and electronic spectral results are now in agreement in suggesting that phosphines do indeed have a π-acceptor rôle, whereas recent arguments based on the interpretation of bond-length results from accurate X-ray analyses, and bond hybridisation

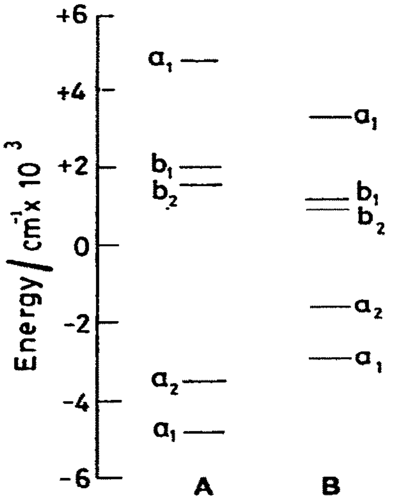


Fig. 2. One-electron-orbital splitting diagram for [Ni(PPh$_3$)$_2$Cl$_2$] (A) calculated with best-fit parameters and (B) calculated neglecting π-interaction with PPh$_3$ [20].

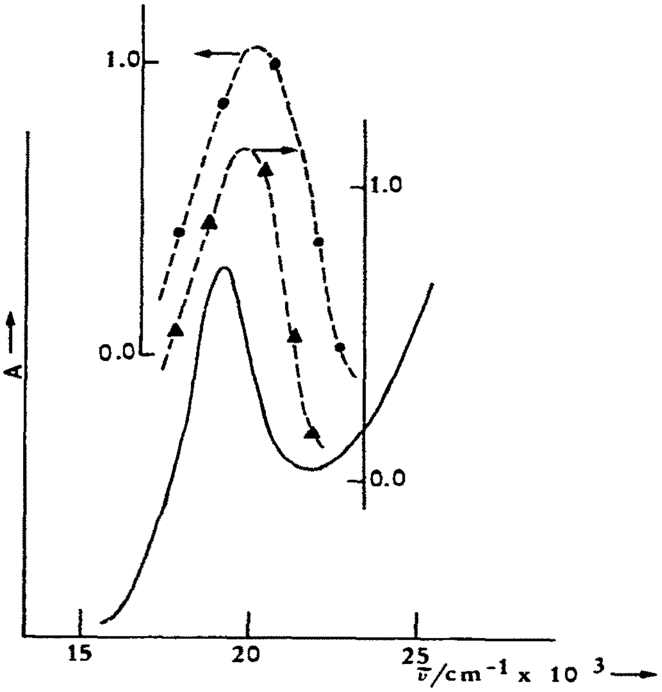


Fig. 3. Resonance Raman spectrum of [Ni(dmg)$_2$] [23].

and addivity, have led Mason and Meek to argue that there is no evidence for such a rôle (in a series of Pt(II) and Pd(II) complexes, at least) [22]. Some further single-crystal electronic spectroscopy on square-planar Ni(II) complexes with phosphine donors appears to be called for.

Another long-standing question, the origin of the well-resolved band in the visible spectrum of [Ni(dmg)$_2$], has also been re-examined recently, using Resonance Raman spectroscopy [23]. As shown in Fig. 3, the excitation profiles of the resonance-enhanced bands at 1510 and 1355 cm^{-1} (assigned to ν(CN), ν(CC), or their coupled vibrations) peak near the electronic absorption at 18 600 cm^{-1}. There was no resonance enhancement in the low-frequency region, where Ni—Ni bands would be expected. These observations provide strong support for the single-molecule origin of this band, rather than as an intermolecular Ni—Ni transition. However, the nature of the transition is not yet clear.

The magnetic susceptibilities for two well-known Ni(II) complexes have been re-measured down to temperatures below 4.2 K. The first is [Ni$_3$(acac)$_6$] (see Fig. 4), again measured as a powder, but for which magnetisation curves were also obtained [24]. An isotropic exchange model for a linear Ni(II) trimer in the HDVV exchange Hamiltonian, $\mathcal{H}_{\text{exchange}}$, was used, where S_a,

$$\mathcal{H}_{\text{exchange}} = J[S_a \cdot S_c + S_b \cdot S_c] + J_{ab}S_a \cdot S_b$$

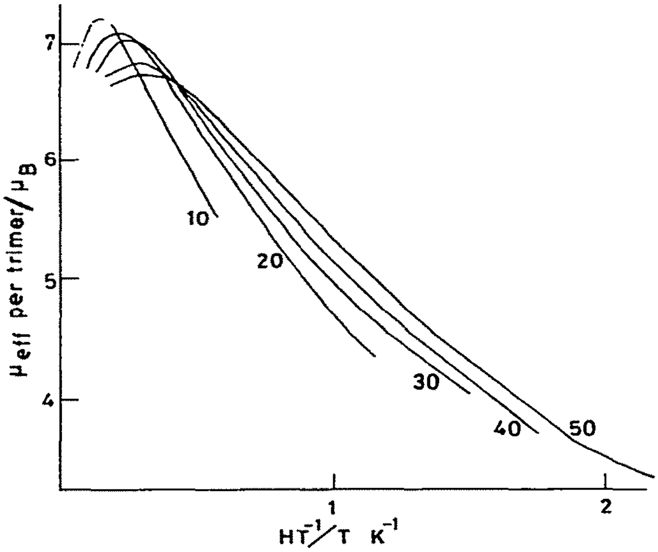


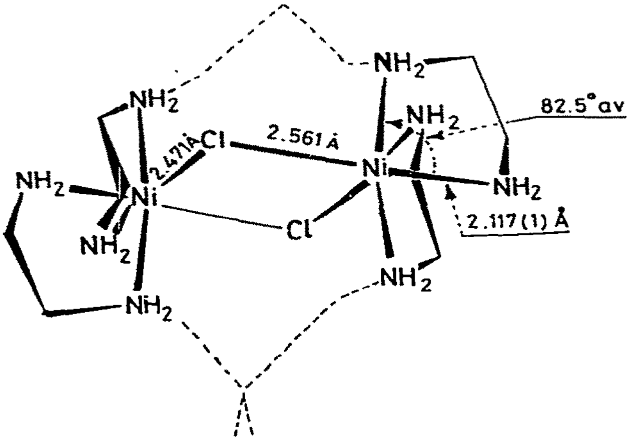
Fig. 4. μ_{eff} per trimer unit of $[Ni_3(acac)_6]$ as a function of H/T for five values of H/kG, illustrating the field dependence of the magnetic moment. The illustrated curves are calculated from the parameters $g = 2.175$, $J = -25\ cm^{-1}$ and $D = -1.3\ cm^{-1}$, and are in good agreement with the experimental data points (omitted for clarity) [24].

S_b are terminal ion spins and S_c that of the central ion. However, at lower temperatures and higher magnetic fields, the effect of single-ion zero-field splitting contributions within the various spin states, mixing of spin states via Zeeman matrix elements and breakdown of the Van Vleck approximation means that additional terms must be included in the Hamiltonian

$$\mathcal{H} = \mathcal{H}_{exchange} + \mathcal{H}_{ZFS} + \mathcal{H}_{ZEE}$$

The magnetic moment per trimer is shown in Fig. 4, together with fits obtained using the above Hamiltonian and a three-state model. The presence of an intra-dimer ferromagnetic interaction (of $-25\ cm^{-1}$) and an antiferromagnetic interaction between terminal Ni(II) ions (of $9\ cm^{-1}$) was confirmed. The magnitudes of these parameters are, however, about half those reported previously [25], underlining the importance of including zero-field splitting effects in analysing low-temperature susceptibility and magnetisation properties. Nevertheless, the general conclusions from the previous work [25] remain the same, i.e. antiferromagnetic interactions between adjacent Ni(II) ions are small for paths of the type $e_g \| 2s \| e_g$, whilst ferromagnetic terms may arise for orthogonalities of the type $e_g \| p_x \| (t_{2g} \perp e_g)$ or $e_g \| p_x \perp p_y \| e_g$.

More refined magnetic measurements have also been carried out on the dimer $[Ni_2(en)_4Cl_2]Cl_2$, (8), as single crystals [26]. Although it has recently been reported that the compound undergoes a phase transition at low temperature (monoclinic → triclinic) between 10 and 20 K [27], it was assumed that no drastic reorientation of such a large dimeric molecule would occur at such low temperatures. From fits of the results, it was found that a relatively large single-ion zero-field splitting was also present in this dimer, the doublet lying lower than the singlet, and D being positive in sign. Again, the inclusion of a ZFS term gave an intradimer exchange constant (J/k = 5.0 ± 0.5 K) smaller than that found previously [28], but the sign remains ferromagnetic ($D/k = 14 \pm 1$ K). The authors note that these parameters have magnitudes similar to those for $[Ni(Cl)_2Ni]_\infty$ linear chains (as occur in $NiCl_2 \cdot py$), and conclude the magnetic properties for this structural unit appear to be more or less independent of the number of units joined together. For the purposes of this magnetic study, the crystal structure of (8) was determined accurately ($R = 2.8$). The octahedral nickel atom environment has some trigonal and slight tetragonal distortion. In addition, the Ni—Cl bridge is unsymmetrical (one of the Ni—Cl bonds being 0.09 Å longer than the other) and there is a trigonal twist (of 51.18°) between opposite octahedral faces (vs. the 60° expected for a perfect octahedron). The crystal structure of this complex has also been reported by another group, the R-factor being higher (7.3) [29].



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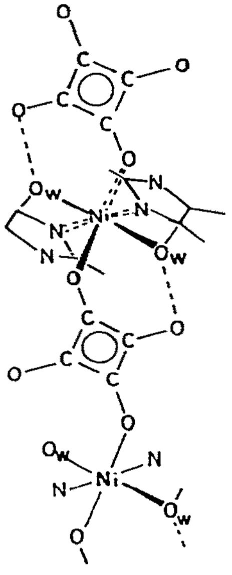
11.3.2 Complexes with O-donor ligands

11.3.2.1 Monodentate ligands

The use of large counter-ions is a well-established method for preparing complexes of very weak donor ligands. The technique has been used successfully to separate hexakis(tetrahydrofuran) complexes of several transition metal ions, including Ni(II) [30]. As expected, the complex obtained, $[Ni(thf)_6][SbCl_6]_2$, is rapidly decomposed by water; the nickel is octahedrally coordinated, and Dq is 840 cm^{-1}.

A squarato-bridged chain structure has been found in $Ni(squ)(imid)_2$

$(OH_2)_2$ (squ = $[C_4O_4]^{2-}$) [31]. The structure, (9), is different than that found in Ni(squ)$(OH_2)_2$ (containing a sheet structure in which all squarato ions are bonded to the metal ion [32]), in that only two of the oxygen atoms are coordinated to the Ni(II) to form a chain. The other two squarato ions bind to the water molecules via hydrogen bonding, giving rise to two-dimensional intra-chains; the Ni—O_{squ} bond is long (2.12 Å). The magnetic susceptibility of (9) has been measured down to 1.2 K. At 1.2 K, μ_{eff} is 1.71 μ_B, rises to 3.21



$(O_W \equiv OH_2)$

(9)

μ_B at ca. 16 K, and then remains constant at higher temperatures. Although fits to the susceptibility equation for linear-chain Heisenberg behaviour gave poor results, it was concluded that super-exchange is very much smaller than in oxalate analogues [33], with $(D/J) > 4$. To explain this result, it was suggested that the symmetry of the bridge orbitals greatly affects the interaction, the plane of the squarato molecule being tipped away from the basal plane of the octahedron about the Ni(II), thus giving rise to much smaller overlap between the orbitals of the squarato molecule and the *d* orbitals of the nickel. The presence of a π system in the bridging unit does not therefore mean, a priori, that superexchange is favoured.

N-Oxide complexes continue to occasion interest and several complexes with Ni(II) have been reported over the year (see Table 3). Of particular interest are the 5-coordinate [36] and tetrahedral [44] complexes; the crystal structures of these complexes would be of interest because of the general lack of well-characterised oxygen-donor ligand complexes with these stereochemistries.

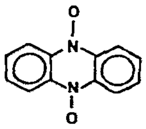
Although sulphoxide complexes have been known for over twenty years, systematic investigation of the electronic and steric factors governing their formation has been lacking. This lacuna has now been filled via a study of

TABLE 3

N-oxide complexes and related species

Ligand	Complex	Stereochemistry assigned	Comments	Ref.
Phenazine-5,10-dioxide (10)	$NiL_2(ClO_4)_2 \cdot 6\ H_2O$	$[NiL_2(OH_2)_4]^{2+}$		34
(10)	$NiL_3(ClO_4)_2 \cdot 6\ H_2O$	$[NiL_3(OH_2)_2(OClO_3)]^{+}$	Obtained when solutions are predried before reaction	34
Iso-nicotinate-*N*-oxide (11)	$NiL_2 \cdot 6\ H_2O$	(17)	$\mu_{eff} = 2.98\ \mu_B$	35
(11)	$NiL_2 \cdot 5\ H_2O$		$\mu_{eff} = 2.93\ \mu_B$	35
2-benzylpyridine-*N*-oxide (12)	$[NiL_5][ClO_4]_2$	5-coordinate (unspecified)	Same complex formed, regardless of M : L ratio	36
2-methylsulphinyl-pyridine-*N*-oxide	$[NiL_3][ClO_4]_2 \cdot 4\ H_2O$	Pseudo-O_h	Ligand bidentate	37
2-ethylsulphinyl-pyridine-*N*-oxide	$[NiL_3][ClO_4]_2 \cdot 4\ H_2O$	Pseudo-O_h	Ligand bidentate	38
Conjugate base of 3,4,5-trimethyl-1-hydroxypyrazole-2-oxide (13)	$[NiL_2(H_2O)]$	5-coordinate		39

N-oxide (14)			not sufficient to stop formation of hexacoordinate complex	
Quinoxaline-1,4-dioxide (15)	$NiL_3(ClO_4)_2 \cdot 6\ H_2O$	(18) or (19)	Significant spin—spin interactions; unidentate $[OClO_3]^-$	41
3-methylisoquinoline-*N*-oxide	$[NiL_5(OClO_3)][ClO_4]$	Pseudo-O_h	Coordinated perchlorate	42
2-picolylchloride-. *N*-oxide	$[NiL_6][ClO_4]_2$	Pseudo-O_h	$Dq = 870\ cm^{-1}$, $B = 756\ cm^{-1}$; bonding less covalent than py-*N*-oxide because of steric hindrance	43
Triethylamine-*N*-oxide, $Et_3N \rightarrow 0$	$[NiL_2X_2]$ (X = Cl, Br or I)	Pseudo-T_d		44
	$[NiL_4][ClO_4]_2$	Distorted T_d		44
Methyldiphenylphosphate	—	—	Yellow-brown liquid	45
Diethylacetylphosphonate (16)	$[NiL_3][ClO_4]_2 \cdot H_2O$	Distorted O_h	$\mu_{eff} = 3.23\ \mu_B$; ligand bidentate	46
Tri-4-tolyl phosphate, $(4\text{-}MeC_6H_4O)_3P{=}O$	NiL_2Cl_2	Ligand-bridged, five-coordinate (probably square pyramidal)	$\mu_{eff} = 3.24\ \mu_B$	47



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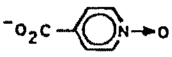

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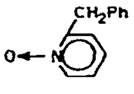

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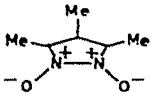

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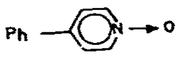

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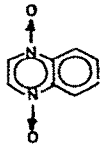

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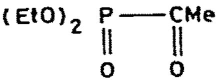

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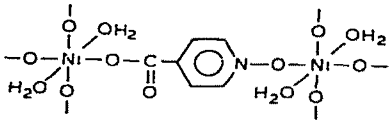

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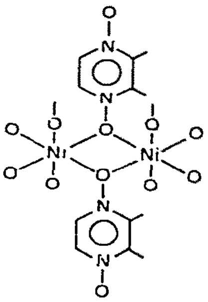

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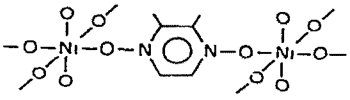

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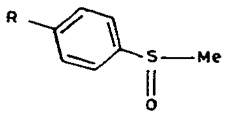
complexes having a 4-substituted phenyl group in phenylmethylsulphoxide **(20)** [48]. All the complexes, prepared as their perchlorate salts, are formu-



(**20**; R = 4-Ph, 4-MeO, 4-MeOC_6H_4 or 4-ClC_6H_4)

lated as $[NiL_6][ClO_4]_2$ and are all *O*-bonding, the ν(SO) band moving to lower frequency on coordination. As expected, all the ligands produce weak fields, *Dq* lying between 829 and 833 cm^{-1}. However, there appears to be no relationship between *Dq* and the electronic properties of the ligands, which is surprising because the pK_a's of these sulphoxides are governed by the nature of the *para* substituents. *Dq* is also greater than for either the dimethyl (*Dq* = 800 cm^{-1}) [49] or the diphenyl (*Dq* = 796 cm^{-1}) [50] analogues, and this was ascribed to an optimisation of size and electronic nature of the substituents in the alkylaryl complexes.

A detailed assignment of the IR spectra of dmso complexes utilising ^{18}O isotope shifts has been carried out [51]. The ^{18}O-induced shift in dmso itself is 11 cm^{-1}, compared to a theoretical value of 38 cm^{-1} for an isolated S=O unit, confirming that vibrational coupling occurs between $\nu(S{=}O)$ and the Me rocking mode. As expected for the approximately O_h symmetry of $[Ni(dmso)_6][ClO_4]_2$, only a single $\nu(M{-}O)$ band is observed (at 443 cm^{-1}). Several mixed complexes of dmso have also been reported [52]. They were prepared by addition of dmso and aqueous 1,2-diaminoethane (en) in a 2 : 1 molar ratio to $Ni(NCS)_2$, which gave $Ni(dmso)(en)(NCS)_2$. Conversely, addition of aqueous en to an alkaline solution of dmso, followed by addition of this mixture to $Ni(NCS)_2$, leads to the complex $[Ni(dmso)_2(en)(NCS)_2]$. Using similar methods, the complexes $[Ni(dmf)_2L(NCS)_2]$ (L = en or pn), $Ni(dmso)(pn)(NCS)_2$, $Ni(en)SO_4 \cdot 6\ H_2O$ and $Ni(en)(NO_2)_2 \cdot 2\ H_2O$ could be prepared; no structures were assigned.

Trifluoromethanesulphonate, $[CF_3SO_3]^-$, can act as an anion (as in $[Ni(OH_2)_6][CF_3SO_3]_2$), but also as a ligand (as in $Ni(CF_3SO_3)_2$, the structure of which is octahedral with bridging ligands [53]). The latter forms a very unstable 2 : 1 adduct with triethylamine (which could not be isolated) and a more stable six-coordinate adduct with the less sterically hindered base quinuclidine [53].

A thorough study of the solvent-exchange kinetics in Ni(II) solutions of aqueous $OP(NMe_2)_3$ has been carried out [54]. During titrations of small amounts of water with solutions of $Ni(ClO_4)_2$ in anhydrous $OP(NMe_2)_3$, the six-coordinate mixed complexes $[Ni\{OP(NMe_2)_3\}_2(OH_2)_4]^{2+}$ are given at a $H_2O : Ni^{2+}$ ratio of 8 : 1 (estimated from electronic and NMR spectra). The ligand substitution process is dissociative and the rate parameters were found to be about three orders of magnitude higher than for similarly substituted Ni(II) complexes. Electronic spectral measurements suggest that the equilibrium present in this system is

$$[Ni\{OP(NMe_2)_3\}_4]^{2+} + 4\ H_2O \rightleftharpoons [Ni\{OP(NMe_2)_3\}_2(OH_2)_4]^{2+} + 2\ OP(NMe_2)_3$$

the correlation time for ligand substitution being identified with the rate constant of the unimolecular reaction

$$[Ni\{OP(NMe_2)_3\}_2(OH_2)_4]^{2+} \xrightarrow{k_M} [Ni\{OP(NMe_2)_3\}(OH_2)_4]^{2+} + OP(NMe_2)_3$$

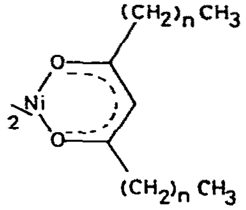
A five-coordinate transition state was suggested. The relatively high k_M ($2.8 \times 10^6\ s^{-1}$ at 25°C) compared with other octahedral Ni(II) complexes (ca. 10^3—$10^4\ s^{-1}$ for common ligands such as H_2O, dmso, and dmf [55]) was ascribed to differences in mobility arising from differences in crystal field stabilisation energy, being weaker for a tetragonal geometry than for an octahedral one [54]. The authors concluded that the order of activation enthalpies

$$T_d\ (ca.\ 4) < D_{4h}\ (ca.\ 26) < O_h\ (ca.\ 50\ kJ\ mol^{-1})$$

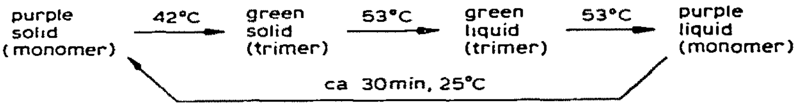
reflects the order of increasing stability due to crystal field effects.

11.3.2.2 Bidentate ligands

Most work, recently, has been concerned with variations on the β-diketonato theme. Of particular interest is the fact that substitution of long-chain alkyl groups in [Ni(β-diketonato)$_2$] complexes (21—23) leads to materials with unusual solubility characteristics [56]. A very small crystal stabilisation energy suffices to produce insolubility in squalane; (23) (solid) is not immediately soluble, whereas the liquid trimeric form of (23) is. However, the smaller size of the pentane molecule confers better stability in pentane, since (23) (solid form) immediately dissolves in pentane to form the solvated trimer. (23) exists in an unusual balance among several physical states (Scheme II). The green liquid (23) dissolves a squalane to give a green solution, which is converted to a red-brown solution at 250° C; the reaction is reversible with change in temperature and is indicative of a monomer—trimer equilibrium as found for [Ni(acac)$_2$]. It is unusual to find complexes in which both a solid state monomer—trimer equilibrium and melting of one of the forms (the trimer) occur so close to room temperature.



(21; n = 5)
(22; n = 6)
(23; n = 8)



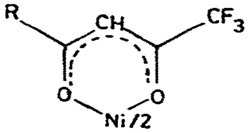
Scheme II. Physical states of (23) [56].

More traditional studies of equilibria of [Ni(β-diketonato)$_2$] with base still appear [57,58]. The formation constants for base adducts of NiL$_2$B and NiL$_2$B$_2$ (HL = 2,2,6,6-tetramethyl-3,5-heptanedione) complexes have been determined [58]. The kinetics of the Ni(II)/acacH system in H$_2$O and MeOH has been re-investigated [59], in both forward and reverse directions

$$\begin{tikzcd}
\text{acacH(keto tautomer)} \arrow[r, shift left, "k_e"] & \text{acacH(enol tautomer)} \arrow[l, shift left, "k_f"] \arrow[d, shift right, "k'_{\mathrm{HE}}"'] \\
& {[\mathrm{Ni(acac)}]^+ + \mathrm{H}^+} \arrow[u, shift right, "k'_{-\mathrm{HE}}"']
\end{tikzcd}$$

The metal was in ten-fold excess so that only the mono-complex was formed. The keto tautomer does not react directly with Ni(II), and the results suggest that a mechanism in which complex formation rates are closely related to solvent exchange is not in operation in reactions of metal ions and oxo-metal ions with simple β-diketones.

It is now rare to find dipole moment measurements being used to investigate stereochemistry in transition metal complexes. Nevertheless, they can still throw light on particular aspects of electronic structure which are of interest. In all cases, the dipole moments of members of the series of complexes, (24), are large (4.32 to 6.95 D), and they were all assigned a *trans*-planar configuration [60]. The lower dipole moment of the trimethoxy substituted complex was ascribed to the presence of steric hindrance caused by the non-linearity of the 4-methoxy groups. This steric effect (i) orients the lone-pair orbitals in a direction such that delocalisation of lone-pair electrons onto the orbitals of the aromatic nucleus is restricted, and (ii) orients the methoxy groups into an orientation which is favourable for producing an additional component of electric moment, which reduces the group moment. Since this interference is absent in the 3,5-dimethoxy analogue, the dipole moment is higher.

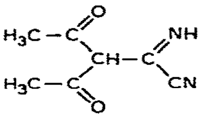


(24; R = 4-EtC$_6$H$_4$, 4-EtOC$_6$H$_4$, 3,5-(MeO)$_2$C$_6$H$_3$ or 3,4,5-(MeO)$_3$C$_6$H$_2$)

As long ago as 1898, Traube [61] attributed the formula 3-(cyanoiminomethyl)pentane-2,4-dione (25) to the product of the insertion of cyanogen into one of the C—H bonds of pentane-2,4-dione:

$$(COCH_3)_2CH_2 + C_2N_2 \rightarrow (COCH_3)_2C(H)C(CN){=}NH\ .$$

Doubt was later cast on this assignment [62], and it has now been proved that the product exists mainly as an amide (26). When cyanogen is reacted with [Ni(acac)$_2$] in CH$_2$Cl$_2$, the crude product obtained has different properties than that obtained from the reaction of NiCl$_2$ with (26) in water [63]. Crystallisation of both species from 1,2-dichloroethane or dichloromethane gave the same product, shown by X-ray analysis to be (27), a surprising reac-



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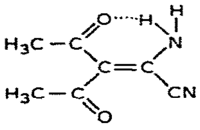

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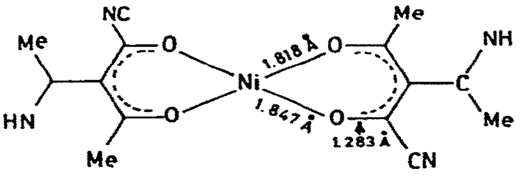

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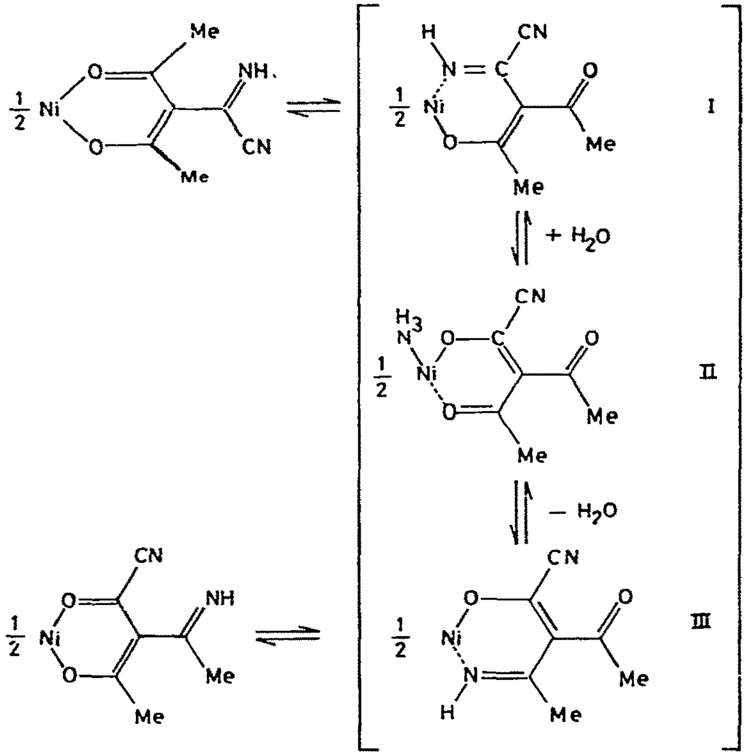


Scheme III. Mechanism for the formation of (27) [63].

tion product (electrophilic substitution on acac would be expected to give a complex of (25) rather than a derivative of 1-(2-iminoethyl)acetoacetyl cyanide). Assuming that the primary reaction product is indeed a derivative of (25), a mechanism of ligand rearrangement to (27) was suggested (Scheme III), in which it isomerises to I, which undergoes water attack, hydrolysis of C=NH, and ammonia extraction to give II. This complex then undergoes ammonolysis of the metal-coordinated CO to give either I or III, which isomerises to the more stable (27) [63].

The nickel complexes $Ni\{PhC(O)N(H)O\}_2 \cdot H_2O$, $Ni\{PhC(O)N(Ph)O\}_2$ and $Ni\{MeC(O)N(Me)O\}_2$ are all octahedral in geometry, with magnetic moments in the range $\mu_{eff} = 3.1$—$3.4\ \mu_B$. Molecular weight measurements show that $Ni\{MeC(O)N(Me)O\}_2$ is tetrameric in $CHCl_3$, and dimeric in propanone or ethanol [64].

A new inclusion system involving Ni(II) and an oxygen donor has been found [65]. Addition of diiodotetrafluorobenzene (ditfb) to nickel(II) iodide dissolved in 1,2-dimethoxyethane gave, under anhydrous conditions, the complex $NiI_2(C_4H_{10}O_2)_2 \cdot 2ditfb$, which could also be obtained from $[Ni(CO)_4]$. Chemical and spectroscopic evidence for the formulation of this complex as a clathrate (rather than as a charge-transfer complex) was presented and a structure for the host system (ditfb) proposed.

The thermal stabilities of some 1 : 1 complexes formed between Ni(II) and benzenedicarboxylic acids (phthalic, isophthalic, and terephthalic) have been investigated [66] using TGA and DSC methods. For the anhydrous phthalates, the order of thermal stability was found to be Co > Ni > Cu, an order the reverse of that found for the stability constants in aqueous solution [67].

11.3.3 Complexes with N-donor ligands

11.3.3.1 Monodentate ligands

Although it may appear that there is little yet to be done in this area, the chemistry of simple pyridine complexes can still reserve surprises. Previously, it was believed that steric hindrance would not permit the complexes of doubly hindered pyridines (e.g. 2,6-disubstituted derivatives) to be obtained. It has now been found that, operating under strictly anhydrous conditions, a series of complexes of nickel(II) halides with 2,6-dimethylpyridine, 2,3,6-trimethylpyridine, and 2,4,6-trimethylpyridine can be prepared [68]. The complexes have formulation [NiL_2X_2] (X = Cl, Br, I or NCS) and were assigned a *trans*-planar geometry on the basis of their electronic spectra (single strong *d*—*d* band at 550—663 nm, followed by a very weak band at 1000—1250 nm). The surprising property of these complexes is that they are inert to exchange by other ligands (including water), and are not attacked even by strong acids (cf. complexes of 2,5-Me_2py decompose instantaneously on contact with water, acids, or bases, and dissolve readily in CH_2Cl_2 to give

TABLE 4

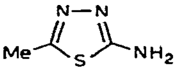
Complexes obtained by controlled decomposition of $Ni(L)_n(NCS)_2$ complexes (n = 4, 3, 2, 1 or 0) [69]

L	n			
	4	3	2	1
2,4-Me_2py	—	p	s	o
2,5-Me_2py	p	—	s	—
2-Me,5-Etpy	p	—	s	—
2,6-Me_2py	p	—	s	—
3-Mepy	o	—	o	o
4-Etpy	o	—	o	o
4-Mepy	o	o	o	o
3,4-Me_2py	o	o	o	o
3,5-Me_2py	o	—	—	p? [a]

p = pentacoordinate, s= square-planar, o = pseudo-octahedral. [a] n = 1.5 for this complex.
— signifies that no $NiL_n(NCS)_2$ complex is formed.

tetrahedral species via partial dissociation). This inertness is due to kinetic causes rather than thermodynamic ones, prolonged contact with hot acids eventually leading to decomposition. The "blocking" action of the hydrophobic Me groups in the 2,6 positions on both the Ni centres and the N atoms makes the complex "impenetrable"; this suggests a lower limit to the effective size of the hydrated proton, which cannot pass through the gaps available in the coordination sphere of the Ni(II). Both five-coordinate and square planar complexes, as well as the more usual pseudo-octahedral ones, are given when dialkylpyridine isothiocyanatonickel(II) complexes are thermally decomposed under controlled conditions [69]. The complexes given are listed in Table 4.

The only other significant work appears to be on the crystal structure and magnetic susceptibility of the clathrate $Mn(NH_3)Ni(CN)_4 \cdot 2C_{12}H_{10}$ (guest = biphenyl), which shows that this complex obeys Curie—Weiss behaviour with $\theta = 0.50 \pm 0.05$ K between 1.2 and 4.2 K [70]. Large disorder, significant guest—guest interaction, guest—host coupling and rapid phosphoresence were found in a study (Raman phonon, vibrational, and singlet—triplet spectroscopy) of aromatic clathrates of $[M(4\text{-}Mepy)_4(NCS)_2]$ (M = Mn or Ni), so that it does not appear that significant results can be obtained from such materials [71].



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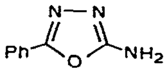

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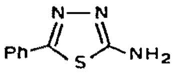
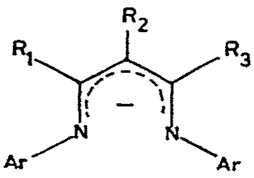


(30)

Although not all have monodentate *N*-bonding, complexes with five-membered heterocyclic rings are collected together for convenience in Table 5; some miscellaneous six-membered heterocyclic ring complexes are also included. One of these studies involves a thorough investigation of the Ni(II)-imidazole-OH^--Cl^- system by potentiometric methods [72]; ternary complexes $Ni(L)Cl^+$, $Ni(L)_2Cl^+$, $Ni(L)_2Cl_2$ and $Ni(L)_4Cl_2$ (L = imidazole) were detected.

11.3.3.2 Bidentate ligands

Substitution of bulky groups at the nitrogen atoms of β-iminoaminoamines can enforce tetrahedral coordination at the metal ion, and some further examples have been reported [85] with the ligands (31). All the complexes



(31; R_1 = H, R_2 = Ph, R_3 = H; Ar = Ph, 2-tolyl or 4-chlorophenyl)

TABLE 5

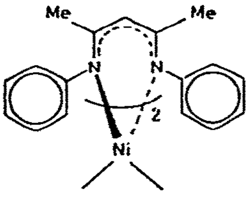
Complexes with five- and six-membered *N*-heterocycles

Ligand	Complex	Stereochemistry assigned	Comments	Ref.
Imidazole	NiL^{2+}, NiL_2^{2+}, NiL_3^{2+}, NiL_4^{2+}	—	Potentiometric study in aqueous solutions containing Cl^-	72
4-Methylimidazole	$[NiL_6]X_2$ (X = Cl, Br, I, $[NO_3]^-$ or $1/2[SO_4]^{2-}$)	Pseudo-O_h	Thermal decomposition study	73
	$[NiL_4(NCS)_2]$	Pseudo-O_h		73
1*H*-3,5-diethyl-4-methylpyrazole-N2	$[NiL_2(NO_3)_2]$	*cis*-$[NiO_4N_2]$	Crystal structure study; $[NO_3]^-$ bidentate, pyrazole rings *cis*	74
5-(pyridin-2-yl)-tetrazole (pttH)	$Ni(ptt)_2 \cdot 1.75\ NH_3 \cdot H_2O$	Pseudo-O_h	NH_3-bonded	75
3Me-pttH (LH)	$NiL_2 \cdot 2\ NH_3 \cdot H_2O$	Pseudo-O_h	NH_3-bonded	75
6Me-pttH (LH)	NiL_2	Pseudo-O_h		75
5-(R)-tetrazoles(LH) {R = 5-aminomethyl, 5-(β-aminoethyl), or 5-(γ-aminopropyl)}	NiL_2	—	Ligands possibly bidentate	76
2-amino-5-methyl-1,3,4-thiadiazole (28)	$NiLCl_2$	$\{NiL_2(\mu\text{-}Cl)_2NiL_2(\mu\text{-}Cl)_2\}_\infty$		77
	$NiL_{1.5}Br_2$	Involves both L and Br bridges		77
	NiL_2I_2	All-L bridging		77
	$NiL_4(NO_3)_2$	Pseudo-O_h	Only N atoms of ligand involved in coordination	77

TABLE 5 (continued)

Ligand	Complex	Stereochemistry assigned	Comments	Ref.
2-amino-5-phenyl-1,3,4-oxadiazole (29)	$[NiL_6]SO_4$	Pseudo-O_h	Coordination by N of NH_2 group (from IR spectra)	78
2-amino-5-phenyl-1,3,4-thiadiazole (30)	$NiL_2py_2(SO_4)$	Pseudo-O_h	Bridging L; $Dq = 823\ cm^{-1}$	79
2,5-dimethyl-1,3,4-thiadiazole	$NiLX_2$ (X = Cl or Br)	Pseudo-T_d	N_2X_2 coordination, with *N,N*-bridging ligand	80
	NiL_2X_2 (X = I or $[NO_3]^-$)	Pseudo-O_h	$[NO_3]^-$ bonding, monodentate ligands	80, 81
Quinoline	$NiL_2(NCS)_2$	Square-planar (red) and pseudo-O_h (green) isomers	Prepared by controlled thermal decomposition	82
2-Mequinoline	$NiL_2(NCS)_2$	Square-planar form only		82
4-Mequinoline, and 6-Mequinoline	$NiL_2(NCS)_2$	Square-planar (red) pseudo-O_h (green) isomers		82
4,4′-bipyridine	$NiL_2(NO_3)_2$	Pseudo-O_h	Bridging L, monodentate $[NO_3]^-$	83
p-benzoquinone diimine	$NiL(ClO_4)_2 \cdot 5H_2O$ $NiL_2I_2 \cdot 4H_2O$	—		84 84

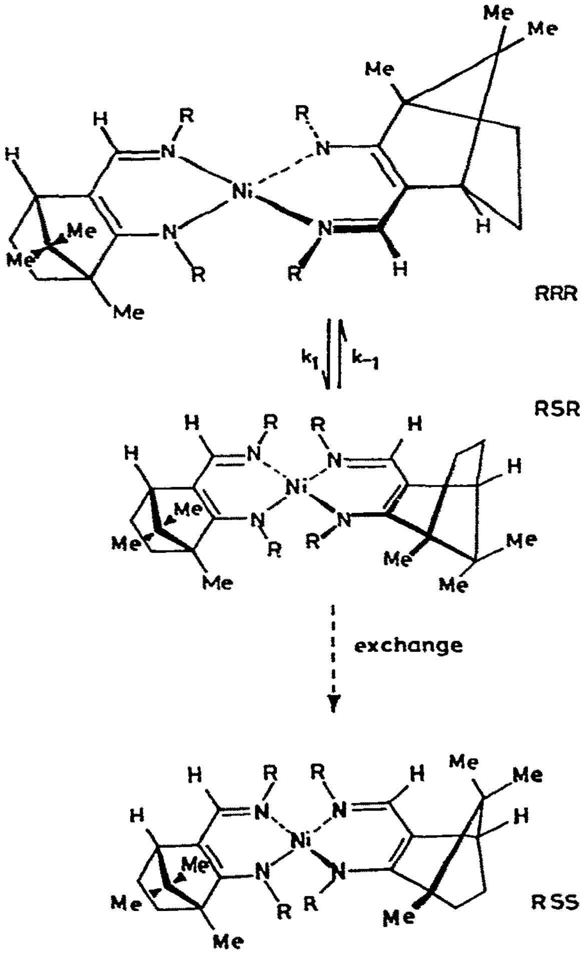
were assigned pseudo-tetrahedral structures. The crystal structure of bis{*N*,*N*′-1,3-dimethylpropanediylidine)dianilinato}nickel(II) (**32**), a related complex, shows it to have two independent molecules in the unit cell with differing distortions from tetrahedral stereochemistry [86]. The average Ni—N distances (=1.96 Å) are ca. 0.1 Å longer than $Ni—N_{square—planar}$ distances, and the inter-ligand N—Ni—N angles vary between 110.4 and 115°, with one in each molecule being particularly high (133.1 or 134.7°). There is extensive conjugation in the ring. The ^1H and ^{13}C NMR isotropic shifts and relaxation times of this complex have been measured (250 K, $CDCl_3$). The narrow NMR lines and long T_1 values underline the suggestion that intramolecular re-orientation between structurally equivalent molecular arrangements can be a powerful electron-spin relaxation process in solutions of transition metal complexes [87]. Analysis of the T_1^H/T_1^C ratios based on the Solomon—Bloembergen equation led to the conclusion that the basic structure of the solid state is retained in solution.



(32)

The barriers to rotation in a pseudo-tetrahedral Ni(II) complex can also be investigated using non-racemisable groups, as shown in Scheme IV [88]. In both (**33**) and (**34**) the gross structure is pseudo-tetrahedral between —80 and +137°C (in $Cl_2CDCDCl_2$ or tetralin) and conversion into (**35**) and (**36**) can be followed via integration of the two NMR signals for the two pairs of symmetry-related 4-H atoms and by time-dependent CD. The interconversion (**33**)↔(**35**) was found to be first order (in tetralin) : $\Delta H^{\ddagger} = 94 \pm 3$ kJ mol^{-1}, $\Delta S^{\ddagger} = 314 \pm 13$ J K^{-1} mol^{-1}. Such high barriers are unusual for open-shell tetrahedra, and no evidence could be found for perturbation by the bornane moiety. When diastereoisomerism of (**33**) was performed in the presence of a racemic ligand, the third, completely asymmetric isomer, was also observed (as the RRS isomer, the central symbol referring to the metal ion). Since (**37**) can be formed from (**33**) only by ligand exchange, the authors concluded that substitution can be faster than configurational inversion.

Not all recent work has been concerned with details of sterically induced tetrahedral coordination; there are still reports of more traditional work on Lifshitz-type complexes. Thus, $[NiL_2X_2]$ complexes, where X = $[CHCl_2CO_2]^-$ and L = *meso*-$H_2NCHPhCHPhNH_2$, provide further examples of low-spin↔high-spin behaviour [89]. Also, several complexes of *cis*-1,3-hexanediamine with Ni(II) have been reported, of formulation $[NiL_2X_2]$ (X = Cl, Br, $[NO_3]^-$, or $[ClO_4]^-$) [90]. Square planar structures were assigned, and it was



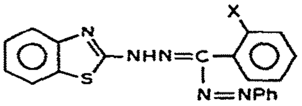
(33; R = Ph)
(34; R = Me)

(35; R = Ph)
(36; R = Me)

(37; R = Ph)

Scheme IV. Tetrahedral interconversions with a chiral anchored group [88].

confirmed that, as expected, the conformation of the ligand changes from diequatorial to diaxial on coordination. Although α-*N*-alkylimine arylhydrazones $RCOC(NNHC_6H_4X\text{-}4)C(=NR')Me$ contain three possible donor ligands, only the azomethine *N* and the α-*N* of the arylhydrazone coordinate to the Ni(II), giving a square-planar $\{NiN_4\}$ chromophore [91]. The same comments apply to the Ni(II) complexes of *o*-hydroxy(mercapto)phenyl benzothiazolylformazans (38), which were also assigned a square-planar $\{NiN_4\}$ chromophore [92].



(38; H_2L; X = OH, SH, OMe or H)

TABLE 6

Some properties of halogenated [Ni(dpg)$_2$] and [Ni(bqd)$_2$] [93,94]

Complex	r(Ni—Ni)/Å	r(Ni—N)/Å	Comments
Ni(bqd)$_2$ (unoxidised material)	3.856 (2)		Slipped-stack structure
Ni(bqd)$_2$I$_{0.018}$	3.180 (2)	1.88 (10)	Stacked along c-axis, each molecule staggered by 63° with respect to the next one
Ni(bqd)$_2$I$_{0.52}$ · S [a]	3.153		Maxima in reflectance electronic spectra at 775—730 nm (probably Ni—Ni ($d_{z^2} \rightarrow p_z$) in origin)
Ni(dpg)$_2$I	3.223 (2) (at —160°C)	1.868 (15)	

[a] S = solvent of crystallisation.

The materials obtained from the reaction of iodine with [Ni(dpg)$_2$](dpg = diphenylglyoximato ion) and [Ni(bqd)$_2$] (bqd = benzoquinone dioximate) have been re-investigated using a variety of physical methods (X-ray crystal structure determination at low temperature, Resonance Raman, ^{129}I Mössbauer spectroscopy, single-crystal conductivity measurements, and electronic spectroscopy). The major results are shown in Table 6. On the basis of these new results, Ni(dpg)$_2$I is shown to contain largely [I$_5$]$^-$, whereas the bqd-containing materials are formulated as containing [I$_3$]$^-$ [93,94]. The previously reported stoicheiometry for Ni(bqd)$_2$I$_{0.5}$ was found to be more closely formulated as Ni(bqd)$_2$I$_{0.52}$ · S, where S is the solvent of crystallisation [94]. The formal fractional oxidation states were found to be +0.20 (dpg) and +0.17 (bqd). The oxidation by iodine causes a shortening of the Ni—Ni separation and an increase in the c-axis conductivity. However, the ease of electron transport is still less than that of the well-known KCP, K$_2$Pt(CN)$_4$Br$_{0.3}$ · 3 H$_2$O, and it is still not known whether the charge carriers are transported through the nickel-atom chain (as in KCP) or through the π-systems of the stacked organic moiety. It was suggested that the latter was the case because of the relatively large Ni—Ni distance compared with that in KCP (2.89 Å) and the fact that the conductivity is relatively insensitive to changes in the metal. These are the first examples where the only feature of the donor crystal structure to change on halogenation is the interplanar spacing.

11.3.3.3 Multidentate ligands

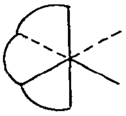
Empirical force field calculations have been used to show that the steady decrease in enthalpy change on complex formation as each nitrogen donor atom is added in complexes of polydentate ligands H(NHCH$_2$CH$_2$)$_x$NH$_2$ with Ni(II), as x increases from 1 (en) to 4 (tetren), is due to cumulative ring strain [95]. This effect is partly offset by the increase in Ni—N bond strength (in the absence of strain effects) as the nitrogen donor changes from primary to secondary to tertiary. These opposing effects produce a net decrease in ΔH on complex formation which almost exactly matches a term in ΔS present in the free energies of formation of monodentate ammine complexes..This matching of terms may go some way to explaining why the analysis of the chelate effect in these polyamines appears more complicated when separate enthalpy and entropy terms are considered.

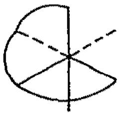
Using results for over forty complexes, a relationship between the thermodynamic heat of formation and electronic spectrum in aqueous solution has been established [96]. The most accurate spectroscopically derived function would be

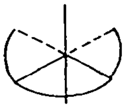
$$F = (3/4)N(\sigma_N - \sigma_O)$$

where N is the number of amine nitrogens bound in the molecular "plane", and σ_N and σ_O are the antibonding contributions to the energy of the acceptor $d_{x^2-y^2}$ orbital, derived using an angular overlap approach. Alternatively, instead of an F vs. ΔH^0_{aq} correlation, a $-\Delta H^0_{aq}$ vs. ${}^3E^b_g$ (i.e. the second observed "octahedral" band) is possible, although this means that different equations are necessary, depending on N. It was found that although a simple plot of $10Dq$ vs. $-\Delta H^0_{aq}$ was not utilisable, weighting $10Dq$ by the number of nitrogen atoms (i.e. plotting $N(\nu_1)$ vs. $-\Delta H^0_{aq}$) gave a useful plot for 29 complexes. The presence of differences in strain energies between very different amines such as en and tetradentates apparently are not reflected in poor behaviour as regards the correlation using the third method, and it was suggested that such strain must be partially or wholly compensated, decrease in ΔH^0_{aq} being paralleled by reduction in the spectroscopic parameter. It thus may become possible to obtain thermodynamic data (for σ-bonding systems, at least) directly from electronic spectra.

The configurational preferences of the well-known linear tetradentate ligands trien, 2,3,2-tet and 3,2,3-tet have been further investigated [97]. Trien shows a preference for *cis*-octahedral (or, in general, non-planar) configurations, i.e. (**39**) or (**40**), whereas the other two ligands have preferred *trans*-octahedral (or planar N_4) configurations, i.e. (**41**). Further study of the equilibria present, in various solvents (H_2O, dmf and dmso), confirms these preferences, but now shows that solvation effects can be important in conditioning them. The solid complexes $Ni(L)X_2 \cdot nH_2O$ (L = tetradentate ligand; X = a monoanion) are *trans* isomers, the only exception being $[Ni(2,3,2\text{-tet})(NO_3)][NO_3]$, necessarily *cis* because of a chelating $[NO_3]^-$. In solution, the


(**39**; *cis*-α)


(**40**; *cis*-β)


(**41**; *trans*)

most important equilibria established are (S = solvent)

(i) $3[Ni(L)(S)_2]^{2+} \rightleftharpoons [Ni_2(L)_3]^{4+} + [Ni(S)_6]^{2+}$

(ii) *trans*-$[Ni(L)(S)_2]^{2+} \rightleftharpoons$ *cis*-$[Ni(L)(S)_2]^{2+}$

(iii) *cis*-α-$[Ni(L)(S)_2]^{2+} \rightleftharpoons$ *cis*-β-$[Ni(L)(S)_2]^{2+}$

(iv)
$$\begin{tikzcd}[Ni(L)(S)_2]^{2+} + 2X^- \arrow[r, harpoons] & {[Ni(L)(S)X]^+ + X^- + S} \arrow[d, shift left] \\ & {[Ni(L)X_2] + 2S} \arrow[u, shift left]\end{tikzcd}$$

(v) *trans*-$[Ni(L)(S)_2]^{2+} \rightleftharpoons [Ni(L)]^{2+} + 2S$

octahedral　　square planar
(high spin)　　(low spin)

Most of these solutions have the ionisation equilibrium to the left (*cis*-α and *cis*-β cannot be distinguished). It was concluded that equilibrium (i) can be neglected for 2,3,2-tet and 3,2,3-tet, and that both have a more marked tendency to form coplanar $[NiN_4]^{2+}$ than does trien. For equilibrium (ii), it was found that all aqueous solutions of 2,3,2-tet complexes contain some *cis*-isomer(s) of high-spin $[Ni(2,3,2\text{-tet})(OH_2)_2]^{2+}$, and that the *cis* isomers are preferred over the *trans* isomers in the order

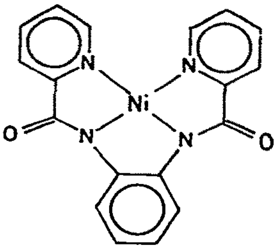
for solvent: $H_2O <$ dmf $<$ dmso

for amine: trien $\gg$ 2,3,2-tet $>$ 3,2,3-tet

The major factors are steric, and it appears that the values of thermodynamic parameters evaluated for such systems may be unreliable because of the various configurations possible.

Moderately bulky triamines tend to give high-spin five-coordinate Ni(II) complexes, whereas those with less stringent steric requirements give pseudo-octahedral complexes. This generalisation has been put on a firmer empirical basis via an examination of stereochemical changes in complexes with $RN\{(CH_2)_nNR^1R^2\}_2$ (n = 2 or 3, R, R^1, R^2 = combinations of H, Me, and Et) [98], i.e. with alkyl-substituted dien and dpt. Me_3dpt gives high-spin five-coordinate $[Ni(Me_3dpt)X_2]$ (X = Cl, Br, $[NCS]^-$ or $[NO_3]^-$), whereas Me_3dien yields pseudo-octahedral $[Ni(Me_3dien)_2]Y_2$ (Y = I or $[ClO_4]^-$) and $[Ni(Me_3dien)(NO_3)_2]$, containing both mono- and bidentate $[NO_3]^-$. In solution, $[Ni(Me_3dien)(NCS)_3]$ remains six-coordinate, but the halide complexes give some five-coordinate species in solution. Conversely, unsubstituted dpt gives only six-coordinate complexes. It was concluded that five-coordination is promoted by increasing backbone length, and that methyl substitution at the N-trimethylene linkages is not sufficient in itself to promote five-coordination, whereas a long backbone together with a single methyl substitution (i.e. Medpt) or three methyl groups together (i.e. Me_3dpt) are sufficient. With dimethylene linkages, even three methyl groups do not promote five-coordination (e.g. Me_3dien), only full alkylation, as in Me_5dien, being able to do so. The larger steric requirements of triamines with longer backbones and bulkier substituents appears to be the determining factor in limiting the coordination number to five.

Other complexes with non-cyclic multidentate ligands reported are shown in Table 7. Of particular interest is the complex (42) formed with deprotonated *N,N*-bis(2′-pyridinecarboxamide)-1,2-benzene and Ni(II) [103]. Here, a picolinamide unit has been used to force amide nitrogen coordination on the metal ion. The complex probably has a highly conjugated structure.



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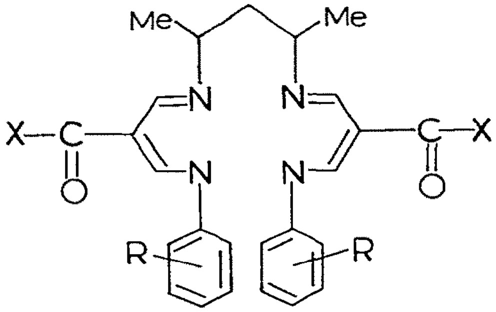

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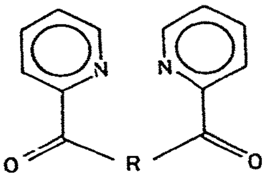
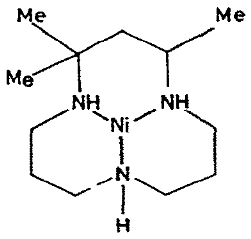


(44)

11.3.3.4 Macrocyclic ligands

Without doubt, macrocyclic ligands continue to provide some of the most interesting chemistry with Ni(II), and although the accent is still largely on solution thermodynamic properties, new systems also appear regularly.

(A) Tridentate macrocyclics. $[\mathrm{Ni(Me_3[12]aneN_3)}]^{2+}$ (45; $[\mathrm{Ni(L)}]^{2+}$) is readily obtained by reduction of the complex produced by Curtis-type condensation of propanone with nickel dpt complexes and is five-coordinate in aqueous

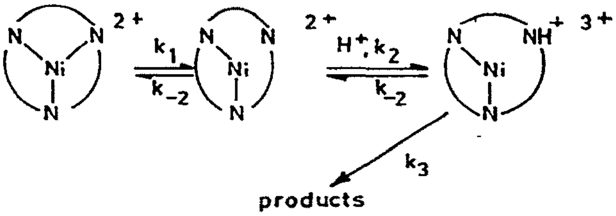


(45)

TABLE 7

Some multidentate ligand complexes

Ligand	Complex	Coordination suggested	Comments	Ref.
cis,cis-1,3,5-triaminocyclohexane	$[NiL_2][NO_3]_2$	$r(Ni{-}N_1) = 2.131$ Å $r(Ni{-}N_2) = 2.134$ Å	X-ray structure; C_{2h} site symmetry	99
trimethylenedi(biguanide)(H_2L)	$[Ni(H_2L)]X_2$	$[NiN_4]$square-planar	Dibiguanide acts as a quadridentate neutral ligand	100
β-arylhydrazone-imines (43; LH_2: R, X = H, Me; 2-MeO, Me; 4-Me, Me; H, Ph; or 2-MeO, Ph)	$[Ni(L)]$	$[NiN_4]$square planar	Diamagnetic complexes prepared by template reactions	101
1,4-bis{bis(2-aminoethyl)aminomethyl}benzene {L; $(NH_2CH_2CH_2)_2NCH_2 \cdot C_6H_4 \cdot CH_2N(CH_2CH_2NH_2)_2$}	$[Ni_2(L)(H_2O)_6]^{4+}$	Ligand bridges between two $[NiN_3(OH_2)_3]$octahedra	Potentiometric study shows 1 : 1 metal chelate stability constants are much lower than for penten and tetraen	102
N,N-bis(2′-pyridinecarboxamide)(1,2-benzene) (44; LH_2; R = $-NH(1,2\text{-}C_6H_4)NH-$)	$[Ni(L)]$ $[Ni(H_2L)Cl_2] \cdot 2H_2O$	$\{NiN_4\}$square planar Pseudo-O_h		103

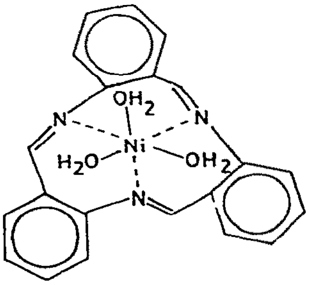


Scheme V. Mechanism for the hydrolysis of $[Ni([9]aneN_3)]^{2+}$ [105].

solution, forming a dihydrate [104]. The solution species readily loses a proton from a coordinated water molecule ($pK_a = 9.81$), and (presumably) dinuclear species were also detected in aqueous solution.

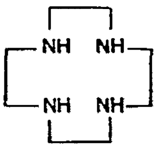
$2[Ni(L)(OH)]^+ \rightleftharpoons [Ni_2(L)_2(OH)_2]^{2+}$ ($\log K = 2.44$)

A comparison of the rates of acid hydrolysis of $[Ni([12]aneN_3)]^{2+}$ and $[Ni([9]aneN_3)]^{2+}$ underlines how macrocyclic or poly-substituted amines can coordinate in such a way as to hinder normal step-wise unwrapping of a ligand from a metal ion [105]. The mechanism of hydrolysis put forward is shown in Scheme V, and although $[Ni([9]aneN_3)]^{2+}$ is five orders of magnitude more stable thermodynamically than is $[Ni([12]aneN_3)]^{2+}$ ($\log \beta_f$ at 25° C = 16.2 or 10.9, respectively), the latter dissociates much more slowly. This was rationalised on the basis of a regular octahedral stereochemistry adopted by $[Ni([12]aneN_3)]^{2+}$, but a sizable distortion from regular geometry in $[Ni([9]aneN_3)]^{2+}$. The strain energy involved gives rise to weaker Ni—N bonds and hence greater lability. The kinetics of ligand substitution for (46), a complex of the related tridentate ligand tribenzo[*b*,*f*,*j*]-1,5,9-triazacyclododecine, with histamine, 3-Mehistamine, histidine, glycine, and histidine methyl ester have also been investigated [106].



(46)

(B) Tetradentate macrocycles. The rates of complex formation between macrocycles and various metal ions, including Ni(II), for the sequence of 12 to 16-membered tetraazamacrocycles (47)—(52) have been studied [107]. From a detailed study of the ligand protonation constants and metal ion complexation kinetics, it was concluded that:



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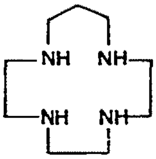

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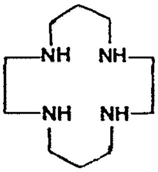

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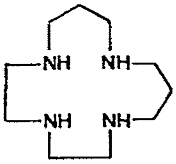

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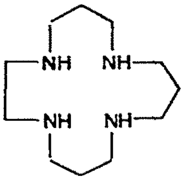

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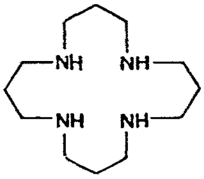


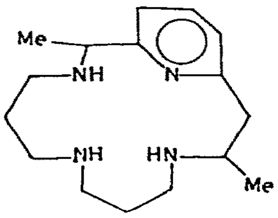
(52)

(i) For a given protonated species of a macrocycle, complexation rates follow the order $Cu^{2+} > Zn^{2+} > Co^{2+} > Ni^{2+}$, and parallel the sequence of solvent exchange rates;

(ii) For a given metal ion, the complexation rate constants with $[LH]^+$ all lie within one order of magnitude and do not vary regularly with ring size;

(iii) Complexation of cyclic ligands is slower than that of the corresponding open-chain tetraamine (for protonated species having the same charge).

On the basis of results (i) and (iii), it was concluded that an unfavourable step prior to the dissociation of a water molecule from the coordination sphere exists, in agreement with the fact that the positive charge of the metal ion and that of the protonated ligand are closer in cyclic tetraamines than in open-chain ones. A pH-dependence of k_{obs} was also found during complex formation with the ligands (53) and (54) and was explained in a similar way.



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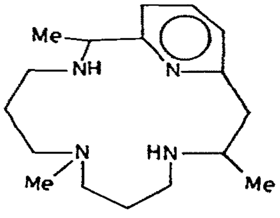
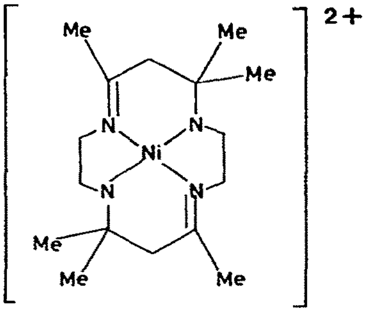


(54)

Because of the rigid structure imposed by the pyridine ring, (53) and (54) react more slowly with the metal ion than do (49) and (51) [108].

The equivalent conductance of the very stable, non-axially coordinating $[Ni([14]diene)][SO_4]$ (55) in water—dioxan solutions show it to be an anomalously strong electrolyte. This appears to be the first example of following changes in solvent structure using a transition metal macrocycle, and may have some relevance to hydrophobic interactions in porphyrin-containing biomolecules [109]. Nevertheless, configurational and conforma-



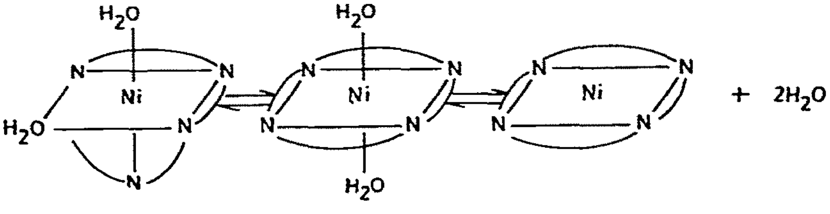
(55)

tional changes occurring when solvent molecules *do* coordinate attract much interest. For example, when the ligand L in the Lifshitz equilibrium

$[Ni(L)(OH_2)_2]^{2+} \rightleftharpoons [Ni(L)]^{2+} + 2\ H_2O$

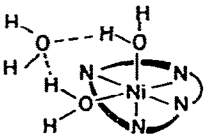
blue, high-spin	yellow, low-spin

is a macrocycle, its cyclic nature introduces an additional factor (other than temperature and concentration of inert salt) affecting the equilibrium; the match between the Ni^{2+} ion and the hole available in the macrocycle. Investigation of this aspect has continued, via solution studies on the 14-membered macrocycle (49) [110]. The hole in this ligand is suitable for high-spin Ni(II) {r(Ni—N) = 2.07 Å, all N atoms coplanar}, whereas the most appropriate ligand for low-spin complexes {$\bar{r}$(Ni—N) = 1.89 ± 0.03 Å} is (48) {the ideal r(Ni—N) distance is 1.92 Å}. The yellow form is indeed favoured by (48) rather than (49) and given that it cannot accommodate coplanar high-spin Ni(II), the equilibria



(56) (57) (58)

must be considered. No spectral evidence was found for (57). Two explanations were put forward to account for this observation: one was based on the fact that the entropy change (56) → (58) indicates that three water molecules



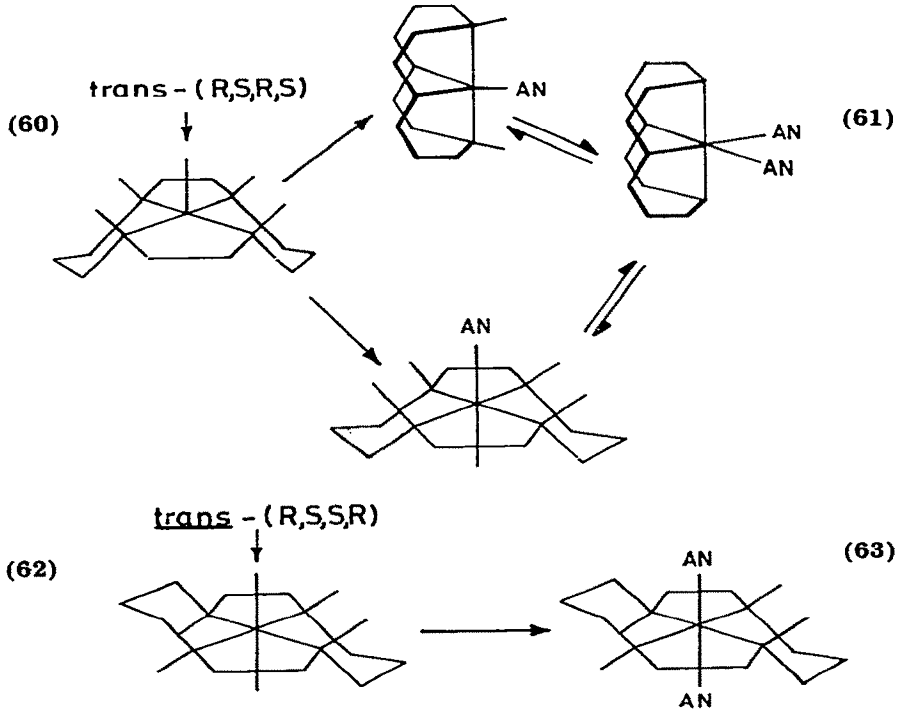
(59)

are liberated, so that structure **(59)** becomes possible, and the other on the more effective mobilisation of water molecules when **(48)** rearranges to **(58)**. Despite the much stronger in-plane interaction of **(48)** compared with **(49)**, conversion into **(58)** is much more endothermic for the 13-membered ring, **(48)**. This was ascribed to the increase in strain energy experienced by **(48)** during the rearrangements **(56)** → **(58)**, and to higher dehydration of second-sphere H-bonds. For **(47)** the equilibrium is well to the left (i.e. the blue form predominates), and it was inferred that the transformation occurring was also **(56)** → **(58)**, the very favourable entropy change being annulled by (among other terms) the rearrangement of **(47)** to give four, coplanar N atoms (believed to be a very endothermic process). **(51)** also favours the high spin blue-form, but this time the stable form is **(57)**, the equilibrium involving **(57)** → **(58)** [110].

$[Ni(L)]^{2+}$ {L = **(49)**} has also been the object of another study of solution behaviour, concerned with solvent adducts in dmf, dmso, H_2O, and MeCN [111]. The presence of a high-spin $\rightleftharpoons$ low-spin equilibrium was confirmed, but the stability order found (via the Evans susceptibility method) was

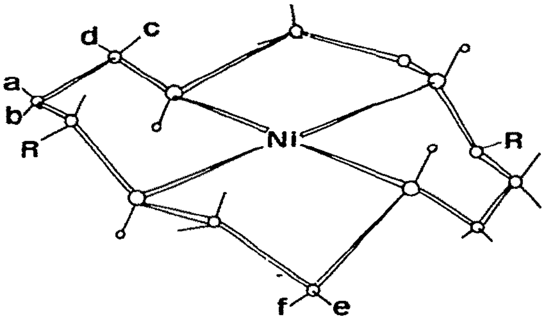
$$\text{dmf} > \text{MeCN} > \text{dmso} > H_2O$$

This is different from that predicted on the basis of electronic spectroscopy



Scheme VI. Possible structures for isomers of $[Ni(Me_4[14]aneN_4)]$ in MeCN(=AN) solution [112].

(i.e. from $10Dq^{xy}$), and the result was ascribed to the presence of five-coordinate adducts in solution. $[Ni(Me_4[14]aneN_4)]^{2+}$ provides clearer evidence for the formation of five-coordinate species with monodentate ligands [112], as the *trans*-(R,S,R,S) isomer **(60)**, at least (see Scheme VI). Conversely, the *trans*-(R,S,S,R) isomer **(62)**, which can be prepared only by direct methylation of the macrocyclic precursor complex $[Ni(cyclam)]^{2+}$, tends to give six-coordinate species. This difference in behaviour has been used to compare the ligand-substitution kinetics of five- and six-coordinate species [112]. Although rate parameters for MeCN exchange were very similar for the two complexes, the activation parameters differed considerably. The $\Delta S^{\ddagger}$ values were interpreted on the basis of an associative mechanism for solvent exchange on adduct **(61)** and a dissociative mechanism on adduct **(63)** (see Scheme VI). In further work on these complexes [113], it was found that they dissolve in coordinating solvents (H_2O, dmso, dmf, and MeCN) to give mixtures of high-spin paramagnetic and low-spin diamagnetic species. Unstable *bis*-solvento adducts, **(63)**, were isolated as perchlorates and, as



(64; R = H)
(65; R = Me)

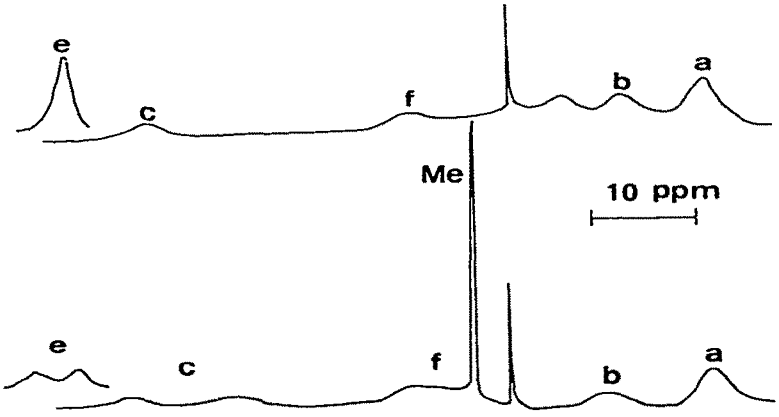


Fig. 5. ^1H NMR spectra of paramagnetic complexes (64) and (65) [114].

expected, are high-spin tetragonal octahedral in geometry, the most stable being those with the rod-like molecule MeCN [113].

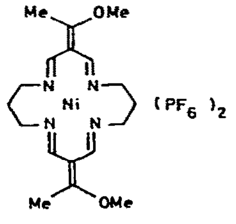
It has been convincingly demonstrated that conformational information can be obtained from the ^{1}H NMR of macrocyclic complexes by following isotropic shift signals [114]. Because of the high interconversion barrier of the chelate ring in $[\mathrm{Ni([14]aneN_4)}]^{2+}$, (64), and $[\mathrm{Ni(Me_2[14]aneN_4)}]^{2+}$, (65), "frozen" resonance signals are obtained (Fig. 5) and well-separated, widely spread signals are given, despite the paramagnetism of the complex. The ^{1}H NMR spectra of the *β-rac*-Me$_6$[14]aneN$_4$ and *α-rac*-Me$_6$[14]aneN$_4$ complexes were also assigned. In a slightly different vein, in a heterodinuclear system, the presence of a paramagnetic metal ion with a very short electronic relaxation time significantly reduces the line widths of the NMR signals of protons close to a second paramagnetic metal ion having a longer electronic relaxation time (and hence giving rise to broader, less-definable, signals) [115]. In an application to the heterodinuclear species produced in the equilibrium

$$[\mathrm{Ni_2(Me_6[14]aneN_4)_2(C_2O_4)}]^{2+} + [\mathrm{Co_2(Me_6[14]aneN_4)_2}]^{2+} \rightleftharpoons$$

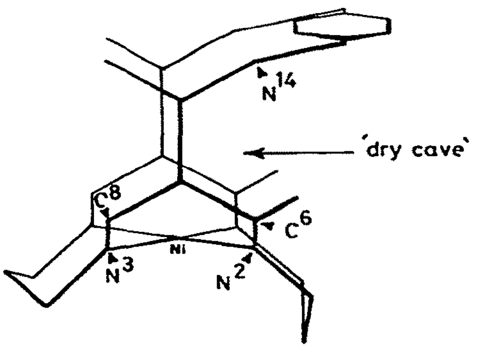
$$2\ [\mathrm{Ni(Me_6[14]aneN_4)(C_2O_4)Co(Me_6[14]aneN_4)}]^{2+}$$

it was possible to assign the spectrum due to the heterodinuclear species formed.

Turning now to the preparative aspects, of particular interest is the report of a designed macrocycle synthesis by Busch and co-workers [116]. Utilising the unusual intermediate (66), in which the vinylic carbon atom bearing the methoxy groups readily undergoes addition-elimination reactions (being very similar to an ester group), and the fact that the imine substituents adopt a saddle shape, it was possible to synthesize (67), by reaction with 1,4-diaminobenzene in MeCN. The complex (67) (systematic name {2,11,20,26-tetramethyl-3,10,14,18,21,25-hexaazatricyclo-10,7,7,2^{5,8}-octacosa-1,5,7,11,-13,18,20,25,27-nonaene(N$_4$)Ni} dihexafluorophosphate, abbreviated [Ni{*p*-xylyl(NHEthi)$_2$Me[16] tetraene N$_4$}][PF$_6$]$_2$) contains a hydrophobic cavity over the nickel ion. The interior walls of this cavity consist almost entirely

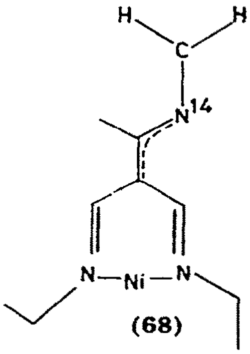


(66)



(67)

of filled π-orbitals and the name "dry cave" was coined. The p-xylyl group is displaced to one side of the Ni(II) and tilted with respect to the coordination plane, leaving a wide opening by the mouth of the cave (dimensions ca. 3.6 × 2.5 Å). In addition, there is an unusual type of isomerism. N(2)—C(6) and N(3)—C(8) are localised so that C(6)—C(7) and C(7)—C(8) are essentially single bonds, causing N(14) to be planar and sp^2 hybridised. The bridge may then either rise directly above the N(14) atoms ("lid-on" isomer) (68) or project rearward from N(14) ("lid-off" isomer) (69). The structure is that of the "lid-off" isomer (69).



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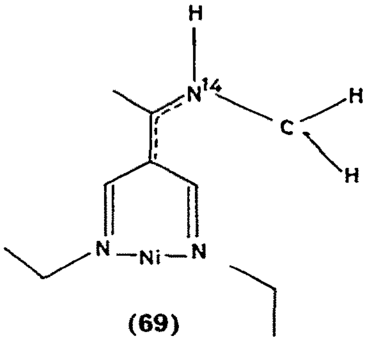
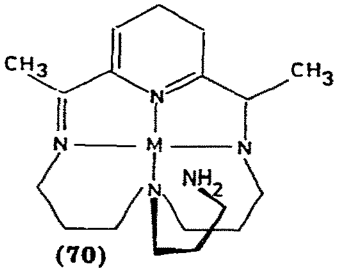


(69)

2,6-diacetylpyridine (dap) reacts with $N\{(CH_2)_3NH_2\}_3 \cdot 4H[ClO_4]$ in EtOH to give a macrocycle with a fifth pendant amine group, $[(\mathbf{70})][ClO_4]_2$ [117]. The macrocyclic complex is high-spin ($\mu_{eff} = 3.15\ \mu_B$) and a square-pyramidal coordination was assigned (electronic spectrum: bands at 25 000, 19 000, 13 000 and 9 200 cm^{-1}). Reaction with propanone led to a Curtis-type condensation giving a complex of suggested structure (71). The pendant NH_2 group of (70) has a pK of 6.25.



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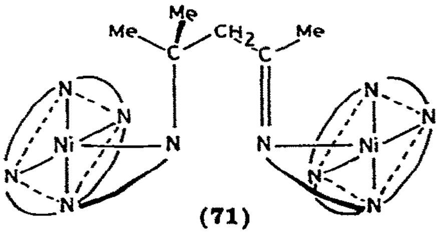
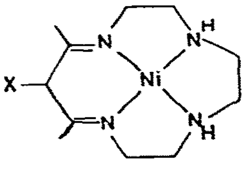


(71)

Pendant ligation can also be given via electrophilic substitution of (72).



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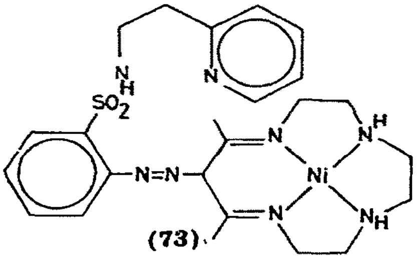
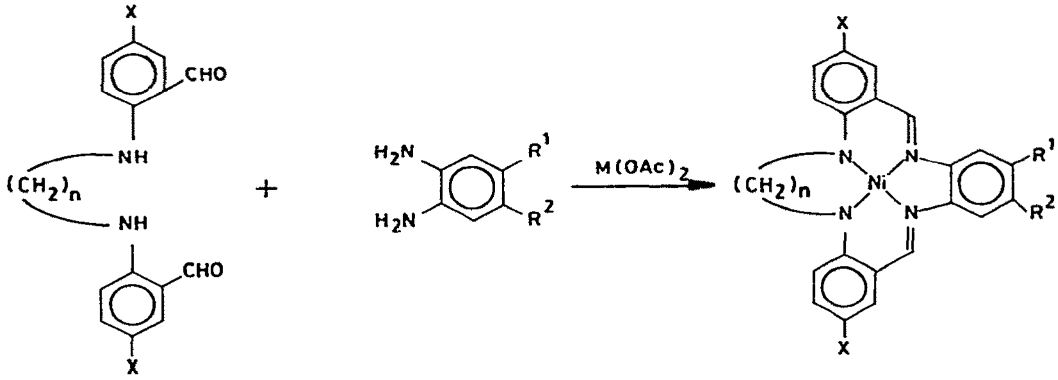
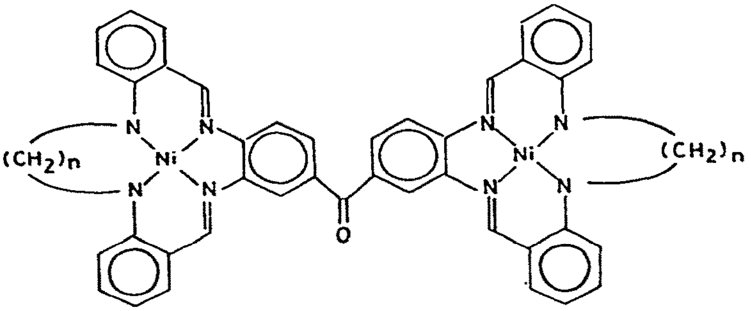


(73)

Various examples have been reported [118] (with X = —N=N-4-$C_6H_4NO_2$, H, or —N=N-2-$C_6H_4SO_3$) as well as the pyridine derivative, (73). Other complexes with tetraaza macrocycles reported are listed later in Table 8.

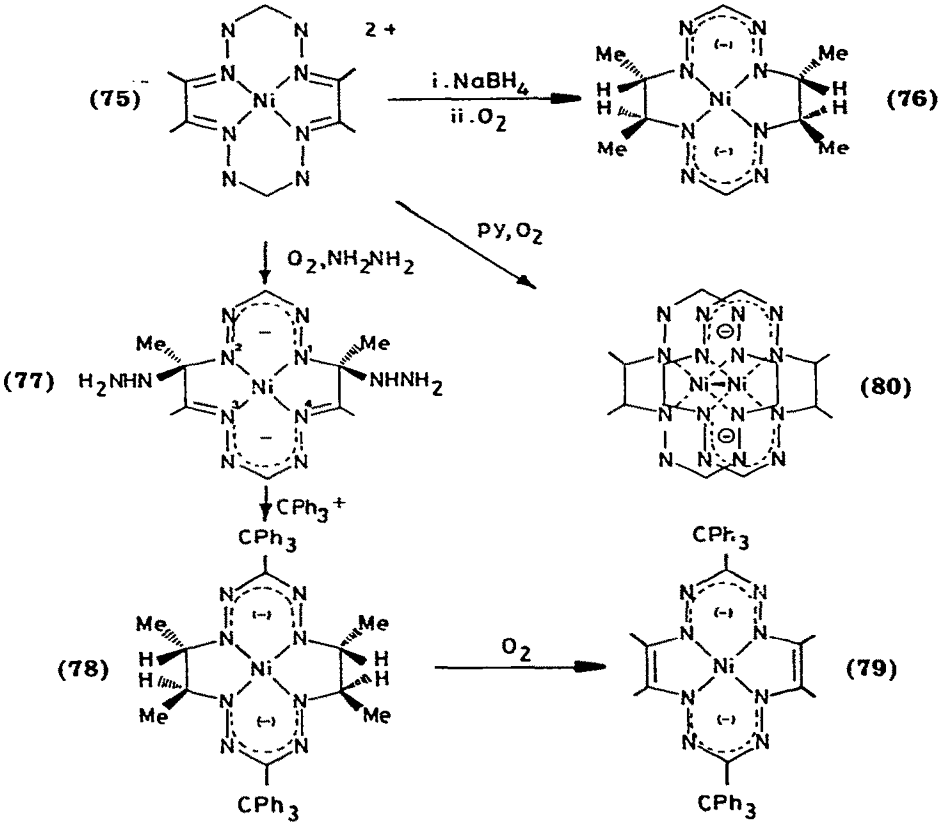
An extensive series of macrocycles, which contain the Würster-type chromophoric system N—C=C—C=N—C=C—N=C—C=C—N, has been prepared by metal template reactions, including several Ni(II) complexes [119]. When 3,3′,4,4′-tetraaminobenzophenone is the condensing amine, the dinuclear complexes (74; *n* = 2 or 3) are obtained. It is not known if there is any interaction via the π-systems between the two halves of the molecule.





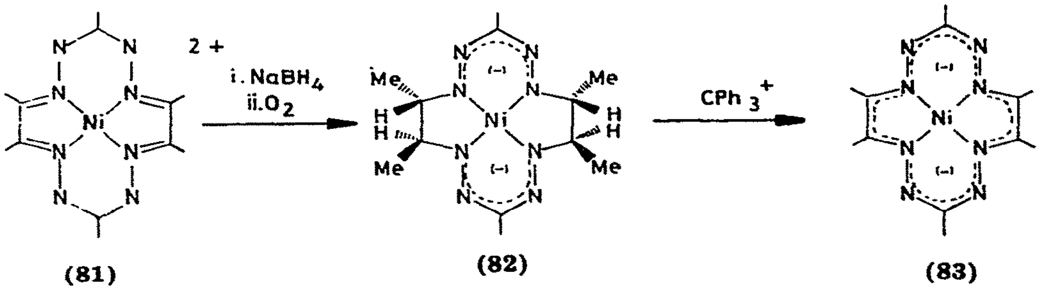
(74)

Macrocyclic ligand complexes are expected to give interesting redox and substitution chemistry, and this is borne out by a thorough study of the reactions of the octaaza*bis*-diimine complex, (75) [120] (see Scheme VII). (75) reacts with N_2H_4 and O_2 giving the dodecaaza complex (77), but with borohydride followed by air oxidation to give the isomer (76), in which the α-diimine functions have been reduced and double bonds introduced into the six-membered metallacycle rings. Initial attempts to oxidise (76) to the dihydrooctaaza[14]annulene complex, using trityl cation, led instead to electrophilic substitution on the 6-membered rings to give (78). In turn, (78) can be oxidized to the ditrityldihydrooctaaza[14]annulene, (79), which is monomeric, unlike the Ni—Ni bonded dimer (80). Methyl groups on the methine

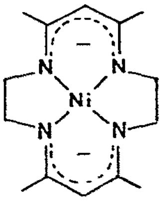


Scheme VII. Some reactions of the macrocyclic diimine complex, (75) [120].

carbons of the six-membered rings (e.g. as in (81)) block electrophilic attack by trityl cation, allowing oxidation of the dimethyldihydrooctaaza[14]-annulene, (82), to (83) (see Scheme VIII). The differences in reactivity from that found in (84) [121] were attributed to interference by the two methyl

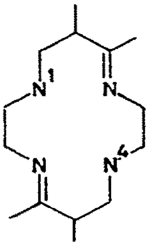


Scheme VIII. Oxidation of the macrocyclic diimine complex (81) [120].

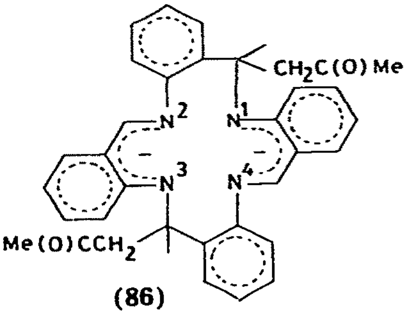


(84)

substitutents in (84) during addition of a bulky group, differing charge distribution over the 6-membered rings in (75) and (84) (affecting their relative nucleophilicities) and geometric requirements of saturated 5- or 6-membered rings. The crystal structures of (76) and (77) were resolved (Table 8) and show them to contain fully delocalised anionic 6-membered rings of the previously unknown β-diazonato type. The structures of the complexes with (85) and (86) were also determined [122,123] (see Table 8).



(85)



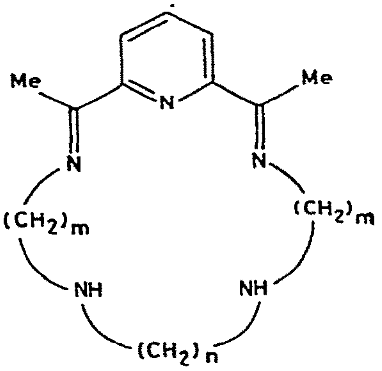
(86)

TABLE 8

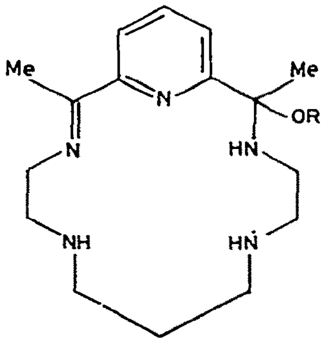
Crystallographically characterised Ni(II) macrocycles

Macrocycle	Complex	r(Ni—N)/Å	Comments	Ref.
(67)	$[Ni(L)][PF_6]_2$		Cavity varies in height (4.55—4.27 Å)	116
	(76)	1.809, 1.806	Crystallographically planar	120
	(77)	N^1, 1.809; N^2, 1.766; N^3, 1.869; N^4, 1.861	Both hydrazine residues are on the same side of the molecular plane	120
(85)	$[Ni(L)][ClO_4]_2$	1.926	No differentiation between Ni—N(H) and Ni—N(imino), *N*-meso-*C*-meso, centrosymmetric	122
(86)	[Ni(L)]	N^1, 1.921; N^2, 1.883; N^3, 1.912; N^4, 1.890	Ligand charge delocalised over rings remote from added enolate groups	123

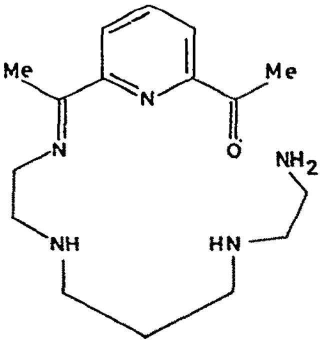
(C) Pentadentate macrocyclics. Unlike many other transition metal ions, Ni(II) is ineffective as a template for bringing about cyclic condensation of 2,6-diacetylpyridine with tetramines to give pentadentate ligands. However, a transmetallation technique has been developed to circumvent this problem [124]. The Ni(II) complexes of the ligands (87)—(89) were prepared by substitution of Ag(I) from the template-prepared macrocycle using a Ni(II) salt, usually the perchlorate. Addition of MeOH, or EtOH, across the methine linkage of complexed (88) gives adducts of (90), and addition of H_2O causes ring scission to (91). The only way in which these cyclic ligands can take up five octahedral positions (in $[Ni(L)X]^+$) is with one of the secondary amine groups in an axial position (for (90)), as seen in (92). A multidentate ligand



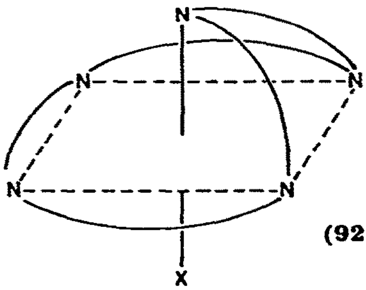
(87; $m = n = 2$)
(88; $m = 2, n = 3$)
(89; $m = 3, n = 2$)



(90; R = Me or Et)

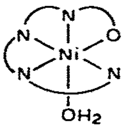


(91)



(92)

of unusual structure or conformation usually imposes irregular stereochemistry on the metal ion. In this case, it appears that the opposite effect occurs, i.e. a new conformation is imposed on the ligand because of the stereochemical preferences of the metal ion. The crystal structure of the open-ring complex of (89), $[Ni(L)(H_2O)]^{2+}$, confirms that it also is octahedral, as illustrated in (93) [124].



(93)

11.3.4 *Complexes with S- and Se-donor ligands*

11.3.4.1 *Monodentate ligands*

The few complexes reported during this period are listed in Table 9. The difficulty in preparing the Ni(II) analogues of $[(dppe)Pd(EH)_2]$ and $[(PPh_3)_2Pt(EH)_2]$ {E = S or Se} [125] has now been overcome by using Na[SH] instead of H_2S.

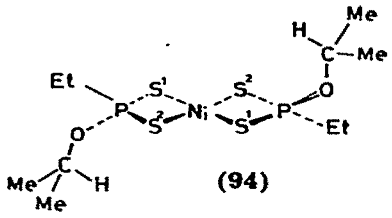
$$[(\text{dppe})\text{NiCl}_2] + 2\ \text{Na[SH]} \xrightarrow{\text{EtOH/benzene/N}_2} [(\text{dppe})\text{Ni(SH)}_2]$$

The Ni(II) complex is stable in air at room temperature, and is soluble in EtOH, but insoluble in hydrocarbons; in chlorohydrocarbons it decomposes rapidly to give black solids [126].

11.3.4.2 *Bidentate ligands*

The relative ease of preparation, and wide range of substituents which may be used, make the [*bis*(dithiocarbamato)Ni(II)] and [*bis*(phosphorodithioato)Ni(II)] complexes popular topics; recent new complexes are collected in Table 10.

All three of the crystal structures reported this year have interesting aspects. Thus, *bis*(*O*-isopropylethylphosphinodithioato)Ni(II) (94) gives the isomer with the two Et groups *trans* with respect to the molecular plane and, differently than is the case with all other phosphoro- and phosphino-dithioates investigated to date, the two Ni—S and two S—P distances are different [131]. The ligand thus appears to coordinate in the form with a more local-



(94)

$r(\text{NiS}^1) = 2.116$ Å; $r(\text{S}^1\text{P}) = 2.031$ Å
$r(\text{NiS}^2) = 2.262$ Å; $r(\text{S}^2\text{P}) = 1.901$ Å
$r(\text{PO}) = 1.668$ Å

TABLE 9

Monodentate sulphur-donor complexes of nickel(II)

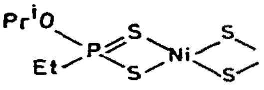
Ligand	Complex	Structure suggested	Comments	Ref.
$[SPh]^-$	$Ni(SPh)_2$	—	Decomposition gives Ni_3S_2, NiS, α-Ni_7S_6, β-Ni_7S_6, NiS_2 and $NiS_{1.03}$	127
N,*N*′-di-*o*-tolylthiourea	$[NiL_4X_2]$ (X = Cl, Br or I)	Tetragonal octahedral	X = Cl, paramagnetic; X = Br or I, diamagnetic. No conversion to pseudo-T_d	128
N,*N*′-di-*m*-tolylthiourea	$[NiL_4X_2]$ (X = Cl, Br or I)	Tetragonal octahedral	$[NiS_4]$ in solution ($CHCl_3$) because of bulky ligands	128
N,*N*′-di-*o*-anisylthiourea	$[NiL_4X_2]$ (X = Cl, Br or I)	Tetragonal octahedral		128
N-methylthiopyrrolidinone	$[NiL_2X_2]$ (X = Cl, Br or I)	Pseudo-tetrahedral $[NiS_2X_2]$		129
	$[NiL_4][ClO_4]_2$	Pseudo-tetrahedral $[NiS_4]$		129
Ethylenethiourea, thiazolidinethione, and thiohydantoin	$[L_4Ni(NCS)_2Hg(SCN)_2]$ $[NiL_6][Cd(SCN)_4]$	*cis*-$NiN_4(NCS)_2$ Pseudo-O_h $[NiS_6]$	Cation—anion complexes bond via S and bridged complexes have ligand bonding via imine NH	130

TABLE 10

Dithiocarbamates and phosphoro- and phosphino-dithioates of nickel(II)

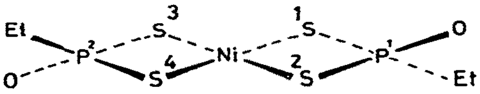
Ligand	Complex	Structure assigned	Comments	Ref.
$[S_2CN(CH_2CF_3)_2]^-$	$[NiL_2]$	Square-planar	—	134
$[S_2CNH(CH_2CF_3)]^-$	$[NiL_2]$	Square-planar		134
$[S_2CN(CH_2CF_3)_2]^-$	$[NiL_2(4\text{-Mepy})]$		First adduct of a dtc of Ni(II), due to strongly electron-withdrawing group	135
$[S_2P(OC_2H_4OPh)_2]^-$	$[NiL_2]$	Square-planar		136
$[S_2P(o\text{-}C_{10}H_7O)_2]^-$	$[NiL_2]$	Square-planar		136
$[S_2P(o\text{-}C_{10}H_7O)_2]^-$	$[NiL_2]$	Square-planar		136
$[S_2P(NHC_6H_5)_2]^-$	$[NiL_2]$	Square-planar		136
$[S_2P(O(CH_2)_7Me)_2]^-$	$[NiL_2]$	Square-planar	Soluble in alkanes	56
$[S_2CN\{(CH_2)_7Me\}_2]^-$	$[NiL_2]$	Square-planar	Soluble in alkanes	56
$[S_2P(OR)_2]^-$ (R = Me, Et or cych)	$NiL(PPh_3)_2$, $NiL(P\text{—}P)$	Binuclear Ni(I) complexes	$\{Ni_2S_2P_4\}$ coordination sphere (see text)	137

ised π-bond {cf. **(95)**}. In a similar vein, the ethylammonium salt of [*bis*-



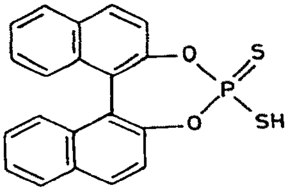
(95)

(ethylphosphorodithioato)Ni(II)]$^{2-}$ **(96)** also has the two *P* substituents *trans* with respect to the molecular plane and again gives a short Ni—S bond



(96)
$r(\text{NiS}^1) = 2.226$ Å; $r(\text{S}^1\text{P}^1) = 2.029$ Å
$r(\text{NiS}^2) = 2.221$ Å; $r(\text{S}^2\text{P}^1) = 2.025$ Å
$r(\text{NiS}^3) = 2.212$ Å; $r(\text{S}^3\text{P}^2) = 2.025$ Å
$r(\text{NiS}^4) = 2.239$ Å; $r(\text{S}^4\text{P}^2) = 2.036$ Å

(2.212 Å), suggesting the presence of contributions similar to **(95)** [132]. The third complex is the first axially chiral phosphorodithioato complex of Ni(II), formed from **(97)**, and its structure is shown as **(98)** [133].



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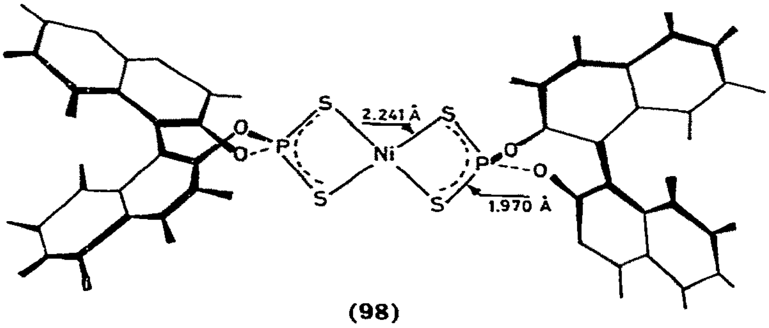


(98)

Interest in the thermodynamic behaviour of dithiocarbamates and phosphoro- and phosphino-dithioates remains sustained. An extensive investigation of the addition of py, 4-Mepy, and 2-Mepy to [Ni(S$_2$PPh$_2$)$_2$] [138] shows that at low L : Ni ratios only the 1 : 1 adduct forms, and 2-Mepy forms only the 1 : 1 adduct at all base concentrations. The formation of high-spin octahedral base adducts in such systems always occurs with an enthalpy change of —60 to —80 kJ mol^{-1}, despite very different adduct stability. Conversely, enthalpy change distributions between the two successive additions differ greatly (as does K_1/K_2) and there is no correlation between K_1 and ΔH_1. It was concluded that such reactions are solvent-dominated. From a similar study, but this time with mono- and bi-dentate phosphines, several complexes of stoicheiometry NiL(P—P) or $NiLP_2$ could be isolated, and it was suggested that they could be formulated as binuclear Ni(I) complexes, e.g. $[Ni_2\{S_2P(OMe)_2\}_2(dppe)_2]$ [137]. However, the stoicheiometry and diamagnetism of these complexes also fit a formulation based on a dealkylation reaction

$$[Ni\{S_2P(OMe)_2\}_2] + (P\text{—}P) \rightarrow [Ni\{S_2P(O)(OMe)\}(P\text{—}P)] + [MeS_2P(OMe)_2]$$

and the crystal structure of such a Ni(II) complex is known, the kinetics (of Co(III) analogues) have been followed, and products identified [139].

From a potentiometric study of a wide range of substituted phosphorodithioato- and xanthato-nickel complexes, it was concluded that the stabilities of these NiL_2 complexes increase with increase in the electron-donor characteristics of the substituents [140]. In an analogous solution study, the S—Ni bond in phosphonodithioates and phosphinodithioates was found to be more covalent than that in phosphorodithioates [141].

The considerable influence of substituents on adduct formation between $[NiS_4]$chromophores and *N*-bases is nicely illustrated in a study of the equilibria (at room temperature) between bis(dithiobenzoato)nickel(II) complexes and pyridine [142]. There was no evidence for formation of a five-coordinate intermediate, only 1 : 2 complexes being formed (when R = H or Me in $[(RC_6H_4CS_2)_2Ni]$). This reflects the higher acceptor character of the dithiobenzoato ion compared with that of xanthate, phosphorodithioate, or (particularly) dithiocarbamate (the first amine adduct of which has been reported only recently [135]). When R = Et_2N, however, there is no adduct formation even with a large excess of pyridine, in line with the high donor power of the Et_2N— group.

Previously undetected $Ni(S_2CNEt_2)^+$ is kinetically stabilised in dmso solutions containing low concentrations of $[S_2CNEt_2]^-$ and very high concentrations of $[Ni(dmso)_6]^{2+}$ [143]. Its electronic spectrum was reported, and the formation constant for $Ni(S_2CNEt_2)^+$, from Ni^{2+} and $[S_2CNEt_2]^-$ $\{(4 \pm 2) \times 10^5\ l\ mol^{-1}\}$ shows that it is quite stable; it has not been observed previously because $[Ni(S_2CNEt_2)_2]$ is much more stable.

A quantitative estimate has been made of substituent effects in the adduct formation reaction with substituted xanthates using Taft's σ^* parameter

$$[Ni(S_2COX)_2] + bipy \underset{k_r}{\overset{k_f}{\rightleftharpoons}} [Ni(S_2COX)_2(bipy)]$$

[144]. Alkyl groups (having only inductive effects) lie on roughly straight lines, but allyl and benzyl groups deviate, with k_f and k_r lower and higher, respectively, than expected. These deviations were accounted for on the basis of stacking interactions. Comparison between k_f's and k_r's for this reac-

tion and the analogous reaction between $[Ni\{(RO)_2PS_2\}_2]$ and phen showed the two sets to be correlated. In other words, the nature of the substituents is reflected in the rate constants for the two reactions. Given that the phosphorodithioate has two substituents whereas the xanthate has only one, then the substituent effect {i.e. inductive effect} and (to a lesser extent) mesomeric effects, are better transmitted in the xanthates. A detailed kinetic study of xanthate, phosphorodithioate, and pentanedithionate (pdt) substitution by dialkyldithiocarbamates shows that $[Ni\{S_2P(OEt)_2\}_2]$ and $[Ni\{S_2C(OR)\}_2]$ react with $[S_2CNEt_2]^-$ via a single process, to yield $[Ni(S_2CNEt)_2]$ (quantitatively) [145]. There was no evidence for the presence of intermediates. Conversely, $[Ni(pdt)_2]$ reacts with $[S_2CNEt_2]^-$ (and also with $[S_2CNPr_2]^-$ and $[S_2CNBu_2]^-$) via formation of a mixed ligand complex, which (for $[Et_2NCS_2]^-$) was isolated.

$$[Ni(pdt)_2] + [S_2CNEt_2]^- \rightarrow [Ni(pdt)(S_2CNEt_2)] + [pdt]^-$$

$$[Ni(pdt)(S_2CNEt)] + [S_2CNEt_2]^- \rightarrow [Ni(S_2CNEt_2)_2] + [pdt]^-$$

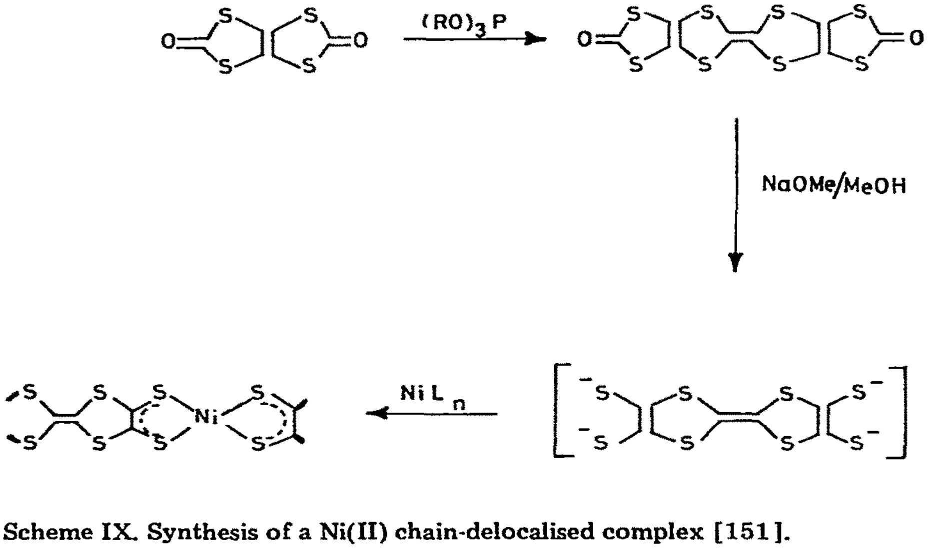
The authors concluded that rather than the stability of the five-coordinate adduct being the controlling factor in the substitution rate, it is the stability of the square-planar intermediate which is the important factor in such reactions. The ease of displacement of a given ligand is very sensitive to the nature of the second ligand, the order of increasing stability being $[Ni\{S_2P(OEt)_2\}_2] < [Ni\{S_2C(OR)\}_2] < [Ni(pdt)_2] < [Ni(S_2CNPr_2)_2]$, whereas the rates of substitution by $[S_2CNEt_2]^-$ (via competition reactions) decrease in the order $[Ni\{S_2C(OR)\}_2] > [Ni(pdt)_2] > [Ni\{S_2P(OEt)_2\}_2] > [Ni(S_2CNPr_2)_2]$ and there is no correlation between the two sets of parameters. Curiously, there was no evidence for the common substitution—dealkylation reaction [139]. A search for five-coordinate complexes with *S*-donors (rather than the more usual *N*-donors) seems called for.

Several Ni(II) complexes form part of a monumental paper correlating the ^{13}C NMR spectra of 71 dithiocarbamates with π-bonding in the $-CS_2^-$ moiety [146]. A high fractional oxidation number (ratio between oxidation state and coordination number) correlates with a high $\nu(CN)$ and low $\delta(N^{13}CS_2)$.

For $[M(S_2CNEt_2)_2]$ and $[M(Se_2CNEt_2)_2]$ (M = Ni(II), Pt(II) or Pd(II)), the ease of reduction follows the order ($E_{1/2}$) Ni > Pd > Pt, the Ni(II) undergoing quasi-reversible reduction [147]. Surprisingly, for each metal, the same reduction potential was observed for both $[S_2CNEt_2]^-$ and $[Se_2CNEt_2]^-$, and other energy terms (e.g. reorganisation energy) were invoked in order to rationalise coincidental $E_{1/2}$ reduction potentials. Conversely, the ease of oxidation of these complexes follows the sequence Ni < Pt < Pd, the bis(selenocarbamates) being more readily oxidised than their thio analogues. Only the Ni(II) complex quantitatively converted to the *tris* complex $[Ni(Se_2CNEt_2)_3]^+$, which in turn are reduced with greater difficulty going down the group: ($E_{1/2}$) Ni < Pd < Pt. In this case, the sulphur analogues are more easily reduced.

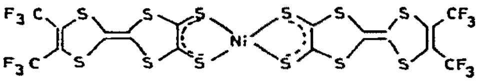
The Resonance Raman spectrum of an $[Ni(C_2S_2O_2)_2(SnI_4)_2]^{2-}$ complex ($[C_2S_2O_2]^{2-}$ = dithiooxalate) having an $[NiS_4]$ chromophore indicates that the two bands in the electronic spectrum lying at 15 000 and 18 500 cm^{-1} are assignable to MLCT (Ni → S) transitions. The third band (at 27 900 cm^{-1}) is, instead, due to an internal CT of the $\{SnO_2I_4\}$ unit and a fourth one (at 33 000 cm^{-1}) to the $\pi \rightarrow \pi^*$ transition of $[Ni(C_2S_2O_2)_2]^{2-}$ [148].

Whatever the predictions of the Peierls transition, partial oxidation of $[NiS_4]$ to give complexes with interesting "stacking" and conductance properties will be popular for some time to come. Partial oxidation of "red" $K_2[Ni(C_2S_2O_2)_2]$ with I_2/propanone or I_2/MeCN leads to formation of a 1 : 1 complex, $K_2Ni(C_2S_2O_2)_2I$, which loses iodine during the crystallisation process to give a polymorphic form of $K_2[Ni(C_2S_2O_2)_2]$ ("black form") [149]. The crystal structure of this form (obtained by "oxidation" of the red polymorph with $K_2[Cr_2O_7]$) shows that the major difference between the two forms is that the black polymorph has stacked molecules {with r(Ni—Ni) = 4.19 Å}. Otherwise, differences between the two forms are minor, the red form having a slightly tetrahedral distortion, whereas the black form is planar. The tetrathiosquarate dianion, $[C_4S_4]^{2-}$, seems more encouraging, dark red lustrous crystals being obtained by reaction of $NiCl_2$ with $K_2[C_4S_4]$ [150]. The material, of formula $Ni_{25}(C_4S_4)_{26}K_2 \cdot x\ H_2O$, is a semi-conductor {conductivity = 5×10^{-4} (ohm cm)$^{-1}$ (20°C, pressed disk)} in agreement with a chain-delocalised structure. In a similar vein, thiapendione can be coupled into a single conjugated molecular framework (Scheme IX), to yield insoluble amorphous complexes with M : L ≈ 1 : 1. The final products have intense IR bands at ca. 2000 cm^{-1}, characteristic of highly conducting crys-



Scheme IX. Synthesis of a Ni(II) chain-delocalised complex [151].

talline CT salts. The trifluoro analogues (99) are better characterised but are

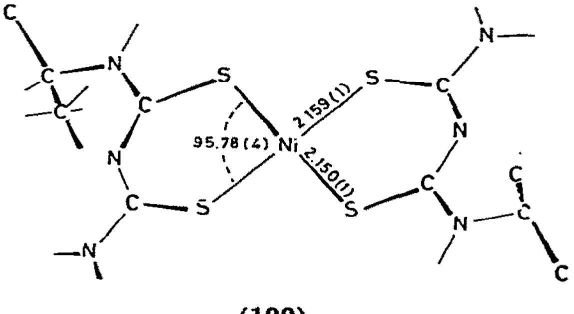


(99)

insulating materials, due to the strongly electron-withdrawing properties of CF_3 [151].

The dependence of the conductivities of some $[mnt]^-$ complexes of Ni(II) on the size and redox character of the cation has been studied using the pressed disk technique [152]. As the cation radius decreases, the conductivity increases (κ : $[PPh_4]^+ > [PMePh_3]^+ > [NBu_4]^+ < [NEt_4]^+ < [NMe_4]^+ <$ (methylene blue)$^+$) as expected for increasing overlap down this series. The exceptions are the Ph-containing cations and this is believed to be due to the intrinsically higher CT interactivity of the Ph group. Comparison of the conductivities of two compounds differing only in the charge of an ion shows that they are related to the ease of disproportionation of those anions acting as transfer centres.

Alkyl or aryl *iso*-thiocyanates react with thiourea in the presence of base, and in a water-miscible solvent, to give compounds, LH, assigned an *S*- (or *N*-)-substituted thiocarbamyl-*iso*-thiourea formulation {e.g. $RNH \cdot C(=S)—S—C(NH_2)(=NH)$} [153]. A crystal structure analysis of the nickel complex $[Ni(L)_2] \cdot 2dmf$ {(100); R = $CHMe_2$} shows that this is not the case, and that the ligands should be re-formulated as 1-substituted 2,4-dithiobiuret compounds {e.g. $RNH \cdot C(=S)—NH—C(NH_2)(=S)$} [154]. The whole molecule is conjugated and the short (2.159(1) and 2.150(1) Å) Ni—S bonds indicate the presence of some double bonding. The dmf molecules do not coordinate, neither in the solid state nor in solution. Analogues with R = Et, Pr or *o*-tolyl have a similar, square-planar, structure.



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11.3.5 Complexes with P- and As-donor ligands

11.3.5.1 Monodentate ligands

A definitive study (^{31}P, ^{1}H, FT NMR and electronic spectroscopy) of stereochemical interconversions of PMe_3 complexes in solution (CH_2Cl_2 or $CHClF_2$) between 114 and 295 K has appeared [155]. $[NiX_2L_3]$ (X = CN, Cl, Br or I), $[NiXL_4]X$ (X = Cl, Br or I), and $[NiL_5]^{2+}$ give rise to the following equilibria in solution (L=PMe_3):

$[NiX_2L_3] \rightleftharpoons [NiX_2L_2] + L$ (X = halide)

$[NiX_2L_2] + L \rightleftharpoons [NiX_2L_3]$ (X = CN or halide)

$[NiX_2L_3] + L \rightleftharpoons [NiXL_4]^+ + X^-$ (X = halide)

$[NiXL_3][BF_4] + L \rightleftharpoons [NiXL_4][BF_4]$ (X = halide)

$[NiL_4][BF_4]_2 + L \rightleftharpoons [NiL_5][BF_4]_2$

The intra-molecular ligand exchange in $[NiL_5][BF_4]_2$ and $[NiXL_4][BF_4]$ proceeds via a Berry pseudo-rotation (low $\Delta G^{\ddagger}$, <38 kJ mol^{-1}) whereas for $[NiXL_4]X$ the exchange rate is faster, proportional to $[X^-]$, and increases in the order Cl < Br < I; an I_a mechanism was suggested. In $[NiX_2L_3]$, energy barriers for the axial-equatorial phosphine exchange are higher (38.5—54.5 kJ mol^{-1} at 230 K) and a *D* mechanism involving loss of axial PMe_3 to form a four-coordinate intermediate was proposed. Finally, the intermolecular exchange reactions

$[Ni(CN)_2L_3] + {}^*L \rightleftharpoons [Ni(CN)_2L_2{}^*L] + L$

and

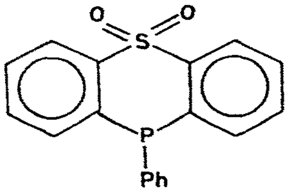
$[NiXL_4]^+ + {}^*L \rightleftharpoons [NiXL_3{}^*L] + L$ (X = Cl or Br)

are dissociative *D* in type.

^{31}P NMR has also been used [156] to follow phosphorus ligand exchange in *trans*-$[Ni(2\text{-}MeC_6H_4)X(PPh_3)_2]$ (X = Br or I). In chlorobenzene, the phosphine is readily replaced in the order $PPhMe_2 \approx PPh_2Me >> P(4\text{-}C_6H_4OMe)_3 > P(4\text{-}C_6H_4Me)_3 > P(4\text{-}C_6H_4F)_3 > P(4\text{-}C_6H_4Cl)_3 >>> P(2\text{-}C_6H_4OMe)_3 \approx P(2\text{-}C_6H_4Me)_3$. Phosphine ligand is replaced by phosphites in the order $P(OMe)_3 > P(OEt)_3 > P(OCHMe_2)_3 > P(OPh)_3$. It was concluded that steric factors rather than electronic factors are more important in such exchange reactions.

11.3.5.2 Bidentate and multidentate ligands

New complexes are listed in Table 11 (and new structural determinations



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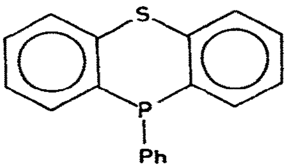

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TABLE 11

Phosphorus-donor complexes

Ligand	Complex	Suggested structure	Comments	Ref.
PPh_3	$[NiL(Y)X]$ (Y = 4-Me-8-mercapto-quinoline; X = Br, SCN)	—		157
PPh_3	$[NiL_2Cl(NO)]$	—	NO/Cl interchange reaction	158
(101)	$[L_2NiBr_2]$	Square-planar		159
(102)	$[L_3NiBr_2]$	Five-coordinate		159
$Ph_2P(2\text{-}Cl\text{-}C_6H_4)$	$[L_2NiBr_2]$	Square planar		159
$Ph_2P(2\text{-}MeO\text{-}C_6H_4)$	$[L_2NiBr_2]$	Tetrahedral		159
$Ph_2PCH{=}C(X)PPh_2$ (X = Ph, Me_3C or CF_3)	$[\hat{L}NiCl_2]$	Square-planar	Constrained *cis*- by *cis*-ligand; obtained by stereospecific template reaction	160
dmpe	L_2NiCl_2			161
$P(CH_2CH_2CN)_3$	$Ni_{0.5}Co_{0.5}Cl_2L_2$	Polymeric$[NiN_2P_2X_2]_n$	Four crystallographically identical products; "lattice strain" invoked	162
2-pyridylaminodiphenylphospine	$[L_2NiX_2]\cdot n$MeOH (X = Cl or Br, $n = 3$; X = NCS, $n = 1$)	Pseudo-octahedral		163
	$[L_3Ni]X_2$ (X = I or $[ClO_4]$)	Pseudo-octahedral $\{NiN_3P_3\}$		163
	$[NiL_2][ClO_4]_2$	Planar		163
	$[NiL_2I]I$	Five-coordinate		163
$(HO_2CCH_2P(Ph)CH_2)_2\{LH_2\}$	$[Ni(LH_2)_2]X_2$ (X = Cl, Br or I)	Strongly distorted tetragonal $NiP_4^{2+}\cdots 2X^-$		164
$N(CH_2CH_2PMe_2)_3$	$[Ni_3L_4][BF_4]_6\cdot 4$dmf $[Ni_3L_4]Br_3[BPh_4]_3$	Trigonal-bipyramidal $\{NiNP_4\}$ bridged by flattened central L	Diamagnetic	165

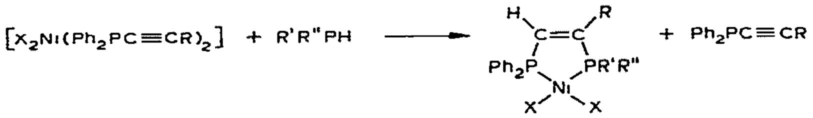
TABLE 12

Structures of some phosphine complexes

Complex	Stereochemistry	$\bar{r}$(Ni—P)/Å	Comments	Ref.
$[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6][BPh_4]_2$	Ni_3S_2 trigonal-bipyramidal unit; square-planar $[NiP_2S_2]$	2.27(4)	r(Ni—Ni) = 2.91(2) Å, r(Ni—S) = 2.15(2) Å; no Ni—Ni interaction	166
$[Ni\{Me_2C(OH)CH_2COMe\}_2]\text{-}[Ni(NCS)_4\{P(CH_2CH_2CN)_3\}_2]$	Square-planar $\{NiO_4\}$ cation; *trans*-$[NiN_4P_2]$ anion (distorted)	2.42	μ_{eff} = 3.17 μ_B; *P*-donor monodentate	167
$[Ni_2(\mu\text{-}P_3)(triphos)_2][BPh_4]_2$	μ-*cyclo*-P_3 unit; ca. trigonal-bipyramidal $\{P_3Ni_2\}$	2.24 (Ni-triphos) 2.34 (Ni-P_3)		168

in Table 12). Results on mixed donors containing phosphorus are included, because there have been few reports. Particularly interesting is the "triple-decker" structure found for $[(\text{triphos})\text{Ni}\text{-}\mu\text{-}(\eta^3\text{-E}_3)\text{Ni}(\text{triphos})]^{2+}$ complexes (E = P or As). In these, a triangle of P, or As, atoms is held between the two Ni—P donor units [168]. A MO scheme for the complexes was suggested, and a complete electrochemical study carried out to investigate how the *cyclo*-E_3 unit influences the energies of the redox levels [168].

The unsymmetrical *cis*-diphosphinoalkenes can probably only be obtained by addition of a secondary phosphine to a coordinated phosphinoalkyne [160]. Non-template base-catalysed addition of diphenylphosphine



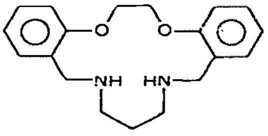
to a phosphinoalkyne gives, stereospecifically, the *trans*-1,2-bis(phosphino)-alk-1-ene [169]. The syntheses of some new functional phosphines, Ph_2PCH_2COOEt and Ph_2PCH_2CN, in which the formation of *P*-bonded nickel was involved in the various steps, has also been reported [170].

11.3.6 Complexes with mixed-donor ligands

11.3.6.1 (O, N) ligands

These complexes are legion, and the Schiff base reaction is ubiquitous, which combine to make much of the work reported fragmentary. Solution studies have been made, mainly by potentiometry upon complexes of Schiff bases [171—175], erotic acids [176], oximes [177], 2-pyridine carboxaldehyde [178], and diaminoethane-*N*,*N'*-di(*o*-hydroxyphenylethanoic acid) [179], and protonated Ni(II)-edta complexes have been re-investigated [180].

Crystal structures are listed in Table 13. Of particular note is the report of another pentagonal bipyramidal complex derived from diacetylpyridine [187]; the evidence is accumulating that this unusual geometry is favoured with such linear ligands rather than with macrocycles.



(103)

$[\text{Ni}(\text{dacoda})(\text{OH}_2)]$ (dacoda = 1,5-diazacyclooctane-*N*,*N'*-diacetate), known since 1972, has been found to undergo a Lifshitz equilibrium

$$[\text{Ni}(\text{dacoda})(\text{OH}_2)] \rightleftharpoons [\text{Ni}(\text{dacoda})] + \text{H}_2\text{O}$$

blue,	yellow,
square pyramidal	planar

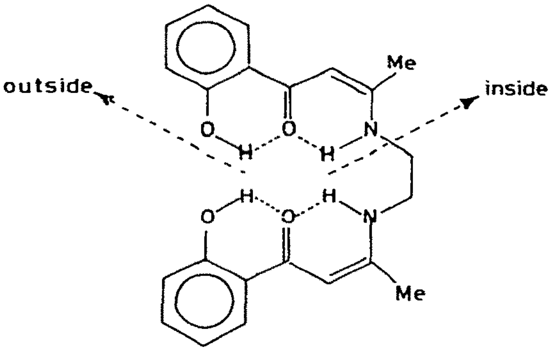
TABLE 13

Crystal structures of mixed (O, N) donor ligands

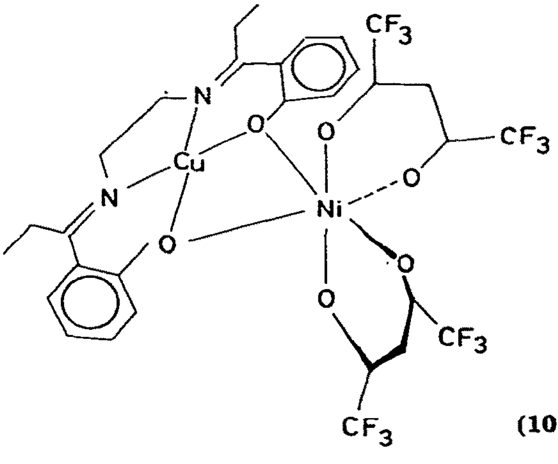
Ligand	Complex	Geometry	Comments	Ref.
2-aminoethanol (LH)	$[Ni_2(L)_2(LH)_4][ClO_4]_2$	Distorted pseudo-O_h- $\{NiO_3N_3\}$ units joined by H-bonds		181
N-(methoxyphenyl)-5-nitrosalicylald-iminate (LH)	$[Ni_2L_4(OH_2)]$ 2 H_2O	Distorted pseudo-O_h; dimeric; bridging H_2O	Ni ··· OH_2 (bridge) long (2.24 Å)	182
1-Me-3-(2-chloro-6-MePh)-triazine-1-oxidate (LH_2)	$[NiL_2]$ (propanone) $[NiL_2]C_6H_6$ (benzene)	Planar Planar	green	183
N,*N'*-*Bis*((2-hydroxy-5-MePh)-(4-MePh)methylene)-3-azahexane-1,6-diamine (LH)	$[Ni(L)(OH_2)]_2$	Pseudo-O_h $[NiN_3O_2(OH_2)]$	Ligand penta-dentate	184
2-(*p*-nitrophenylimino-methyl) (phenolate) (LH_2)	$Ni_2L_2(NO_3)_2(EtOH)_2$	Dimeric	Ferromagnetic	185
1-(2-HOPh)-3,5-diphenyl formazanate (LH_2)	$[NiL(NH_3)]$			186
2,6-diacetylpyridine-bis(benzoic acid hydrazone)	$[NiL(OH_2)_2][NO_3]_2 \cdot 2 H_2O$	Pentagonal bipyramidal $[NiN_3O_2(OH_2)_2]$		187
(103)	$[NiLCl_2]$	Pseudo-O_h; *trans*-Cl_2		188

claimed to be the first case for a five-coordinate complex. The high $\Delta S^{\ddagger}$ for the equilibrium was rationalised on the basis of de-solvation of the planar complex [189].

Mono- and di-ketones readily condense with amines (in 2 : 1 ratio) to give compartmental (or "binucleating") ligands and several more examples have appeared [190—192]. For (**104**; H_4aapan), several mixed NiM′ (M′ = Cu(II), Co(II), Fe(II) or Mn(II)) complexes were prepared. The Ni(II) was always in the "inside" compartment, and was square-planar (and, hence, diamagnetic) [190]. More interesting is the case were a paramagnetic Ni(II) is close to another paramagnetic transition metal ion. What are apparently the first examples of such complexes have now been reported. They are prepared by using bis{*N*,*N*′-ethylenebis(2-hydroxypropiophenoneiminato)}M(II), [M(prp)en], as a ligand for a hexafluoropropanedionato complex M(prp)en + [M′(hfpd)$_2$] → (**105**).



(**104**)

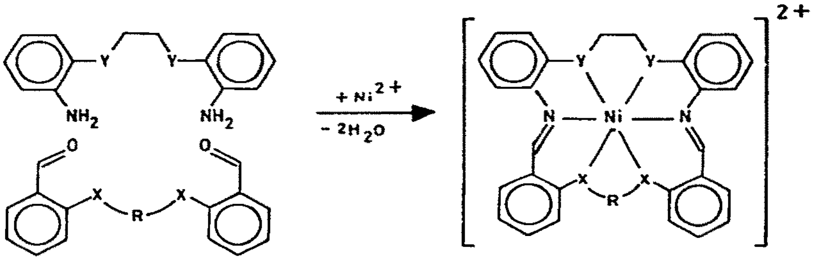


(**105**; M = Cu, M′ = Ni)

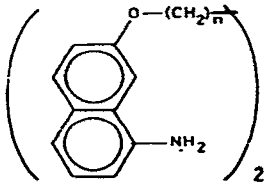
A thorough study of their crystal structures (M = Ni, M′ = Cu, Co or Mn; M = Cu, M′ = Ni) has been reported [192]. The magnetic susceptibility was studied for (**105**) as a function of temperature. A drop in effective magnetic moment at lower temperatures was explained in terms of depopulation of excited S_T spin states. It appears that the generalisation that as M—Ô—M increases J becomes more antiferromagnetic, also holds for mixed binuclear complexes.

An alternative way of observing Ni—Cu pair effects is to dope small amounts of Ni^{2+} into a dimeric Cu^{2+} complex almost diamagnetic at room temperature which becomes diamagnetic at low temperature. In this way, Ni—Cu signals were observed in the EPR spectrum of a macrocyclic compartmental-ligand Cu^{2+} complex (chromophore $[\mathrm{Cu}_2N_4O_2Cl_2]$), with the Cu(II) in a distorted square pyramidal geometry [193].

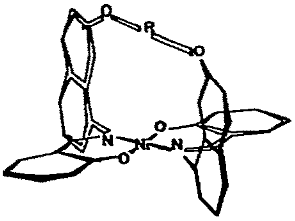
Complexes of the Schiff base formed by condensation of substituted *o*-hydroxyaceto- and *o*-hydroxybenzo- phenones are monomeric and five-coordinate [194]. Schiff base formation, but this time with simultaneous cyclisation, can also be used to prepare hexadentate macrocyclic ligands, and the steric requirements of the ligands prepared as Ni(II) complexes (**106**) have been discussed [195]. Schiff base ligands now have their "fly-overs", to compete with "capped" and "strapped" porphyrins but, unlike the latter, have the take-off point at the ligating atoms. A rigid α-naphthyl unit was chosen because it would lie perpendicular to the $\{\mathrm{Ni}O_2N_2\}$ plane and impose a less accessible axial position than would a saturated carbon chain [196]. The ligand was prepared by condensation of (**107**) with salicylaldehyde after proection of the amine group. This square-planar diamagnetic Ni(II) complex 108) reacts with bidentate bases (phen or bipy) to give the corresponding



(**106**; Y = NH, O or S; X = NH)



(**107**; *n* = 2)



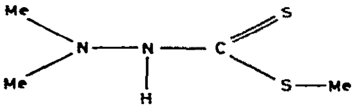
(**108**; R = $(CH_2)_4$)

1 : 1 adducts, thus indicating that the $\{NiO_2N_2\}$ complex is stereochemically flexible. However, py adds only with difficulty and the bis-adduct is formed only in neat py. A crystal structure analysis of **(108)** has confirmed its structure, although two crystallographically independent discrete molecules exist [197]. Both have *trans*$\{NiO_2N_2\}$chromophores with a fly-over tetramethylene diether moiety and differ only in the conformation of the $(CH_2)_4$ chain. In turn, this changes the orientation of the α-naphthyl group approximately orthogonal to the molecular plane, and hence the size and shape of the cavity.

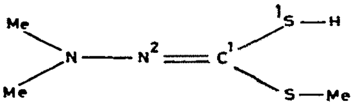
A single-crystal magnetic susceptibility study of diaqua(2,6-diacetylpyridine)bis(semicarbazone)Ni(II) nitrate, the only seven-coordinate Ni(II) complex known before this year (see ref. 187), has been reported [198]. Other complexes with (*O*,*N*) ligands are listed in Table 14.

11.3.6.2 (N,S), (O,S) and other mixed-donor ligands

Few structures have appeared this year. Bis(*N*,*N'*-dimethyldithiocarbazato)Ni(II) has a *trans*$\{NiN_2S_2\}$chromophore [218] and an MO calculation (STO-3G basis set) has been used to rationalise why form **(109b)** is present in the complex, whereas form **(109a)** usually predominates in the free ligand and its analogues. From an energy minimisation along the antisymmetric $N^2—C^1—S^1$ stretching coordinate in the complex, it was found that the structure of this unit in the optimised ion was similar to that found experimentally for form **(109b)**.

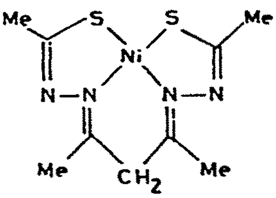


(109a)



(109b)

Thioacethydrazide $\{MeC(S)NHNH_2\}$ cannot be isolated as the free ligand, but exists complexed to transition metal ions. Some further derivatives, prepared by Schiff-base condensation with pentane-2,4-dione ($tahacacH_3$) have been reported, formulations being confirmed by crystal structure analysis [219] for [Ni(tahacacH)] · MeCN **(110)**, $[Bu_4N]$[Ni(tahacac)] **(111)** and [Ni(tahacacO)] **(112)**. The ligand in **(111)** appears to be present in the dipolar form, and the conjugated complex has shorter Ni—N and Ni—S bond



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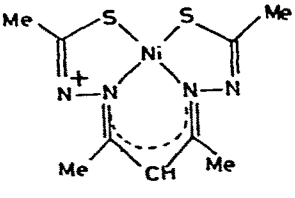

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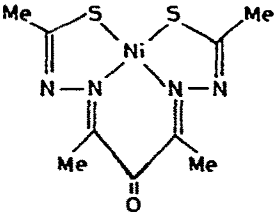


(112)

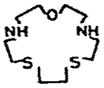
TABLE 14

Mixed-donor ligand complexes of (*O*, *N*), (*S*, *N*) and (*O*, *S*) ligands

Ligand	Complex	Comments	Ref.
Pyrazine-2,5-dicarboxylate (LH_2)	$NiL \cdot 2.5\ H_2O$ $NiL \cdot 2\ NH_3$	Hydrated polymers, high resistivities	199
Salicylaldehyde hydrazone (LH)	$Ni(LH)_4Cl_2$ $NiL_2 \cdot 2\ H_2O$	Ligand monodentate Ligand bidentate	200 200
Ethyl picolinate	$[NiL_2Cl_2]$	Pseudo-O_h	201
Picolinoyl hydrazide	$[NiLCl_2] \cdot 2EtOH$ $[NiL_2(EtOH)_2][NO_3]_2$	Pseudo-O_h	202
β-aminoketoximates (LH_2)	$[Ni(HL)]Cl$	Oxime—oximate bonding, potentiometric study	203
Alcoholaminates (2-aminoethanol + pentanediones) (LH_2)	$[Ni_2L_2]$ $[NiL(ROH)]_4$ (R = Me, Et, Pr or Bu)	Binuclear, diamagnetic β-cubane structures, ferromagnetic	204 204
Glyoxylimine-aryl hydrazonates (LH_2)	$[NiL]$		205
Benzoin + amine Schiff bases	$[NiL]X_2$	Tetradentate ligands	206
4,8-dihydroxy-1,5-naphthyridine (and thiol analogue) (LH_2)	$[NiL]_n$	Polymers of high resistivity	207
Pyridine-2,6-dicarboxaldehyde		MeOH-addition reactions	208
DL-2,6-diaminopimelic acid		Solution study	209
Semicarbazones and thio-analogues: $R^1{=}N{-}NH{-}C({=}X){-}NR^2R^3$ (LH)	$[NiL_2]$	Various	210—212
Dithiocarbazates: $R^1{=}NNR^2CS_2R^3$ (LH)	$[NiL_2]$ or $[NiLX]$ (X = NCS or NO_3)	Square-planar, diamagnetic	213—214
1,4-diaza-7-thianonanes (L)	$[NiL]^{2+}$, $[NiL_2]^{2+}$	L is tridentate in $[NiL]^{2+}$	215
1,5-diaza-8-thianonane (L)	$[NiL]^{2+}$	L is tridentate; solution study	215
Monothio-β-diketones:	$[NiL_2]$	Square-planar	216
$R^1C(SH)CH_2C(O)CF_3$ (LH)	$[NiL_2] \cdot B$ (B = py or 4-Mepy)	Isotropic shifts measured	217

lengths. The green (**112**) is prepared from form (**110**) or (**111**) by oxidation with air in a Ca[CO_3]-buffered slurry. An analysis of the electronic spectra indicated that σ-interactions in (**112**) are very different from those in (**110**) or (**111**).

The mixed pentadentate macrocyclic and open ligands (**113**)—(**115**) form


(**113**)


(**114**)


(**115**)

octahedral complexes in both solid state and solution, the sixth position being occupied by water. The macrocyclic effect between (**115**) and the macrocyclic analogues, as given by $\Delta\beta = \log \beta_{101}(\text{macr}) - \log \beta_{101}(\text{linear})$ is strong ($\Delta\beta = 3.20$ for (**113**) and 3.28 for (**114**)), but slightly lower than found for polyamines [220]. Examination of the entropy/enthalpy relationships between these ligands led the authors to conclude that it was not possible to define which of the many parameters involved is responsible for the large difference in complexation entropies between these mixed pentadentate ligands and pentaamines.

The unusual hydrazidothiophosphorus derivatives $P(NHNH_2)YZS$ (Y, Z = OEt, OC_6H_4Cl-4, OPh, Ph) have several potential donor sites (*N*, *O*, *S* or P) and form [NiL_4X_2] complexes (X = Cl or Br) [221]. The complexes are tetragonal octahedral, paramagnetic ($\mu = 2.92$—$3.15\ \mu_B$) and undissociated in solution (in $MeNO_2$). A crystal structure analysis shows that only the hydrazido amine-*N* bonds in [$Ni\{P(NHNH_2)(OEt)_2S\}_4Br_2$] and that the configuration is *trans*.

11.3.7 Complexes with ligands of biological interest

There are few reports, reflecting the relatively unimportant rôle of Ni(II) in biological systems (as far as is known). Scattered reports are collected in Table 15.

Electronic spectra have been used to suggest a $\{NiO_5N\}$ chromophore for an adenosine-5′-phosphate (ATP) complex of formula $Na_2Ni(ATP) \cdot 8\ H_2O$ (Dq^{xy} 700 cm^{-1}; Dq^{z} 940 cm^{-1}). Bonding appears to be via three phosphate oxygen atoms, the adenine N(7) and two water molecules [238]. The complex appears to be different from that reported by Bhattacharyya and Bhaduri [239]. To allow energy to be passed between the adenine base and the triphosphate in ATP, the molecule must fold (a ribose sugar group, which does not pass energy, lies between them) and it is believed that metal ions facilitate this folding. This has been investigated using UV spectroscopic methods, with Ni(II) tripolyphosphate and adenine as a model system [240], for following coordination by adenosine mono-, di- and tri-phosphate. The stability constant for interaction with adenosine is greater (eleven times) for $[HOP_3O_9]^{4-}$ than that with aqueous Ni^{2+}, and the phosphate group tends to

TABLE 15

Ligands of biological interest

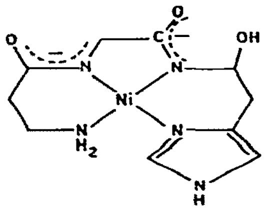
Ligand	Complex	Comments	Ref.
Adenine (=AH)	$Ni(AH)_2X_2$	Pseudo-O_h; X-bridged polymer	222
9-Me-adenine	$NiL(NO_3)_2 \cdot 2\,H_2O$	Pseudo-O_h	222
	$NiLX_2$	Pseudo-O_h, $\{NiCl_5N\}$chromophore double-chain polymer	
Inosine-5′-monophosphate (LH_2)	$[Ni(L)(OH_2)_5] \cdot 2\,H_2O$	$\{NiNO_5\}$	223
Uridine	$NiL_2X_2 \cdot nH_2O$ (X = Cl or Br)	Ribose chelate	224
Thymidine	$NiL_2Br_2 \cdot H_2O$	C_4-carbonyl oxygen bonding	224
Cytosine	Ternary complexes with phen or bipy	Potentiometric study	225
Glycine + histamine Glycine + histidine		Potentiometric study, 1 : 1 : 1 gly + histamine formation favoured	226
Glutamine	$NiL_2Cl_2 \cdot 6\,H_2O$		227
O-phospho-DL-serine (LH_2)	Ni(L)(B-B) (B-B = histamine, phen or bipy)	L tridentate	228
D-penicillamine	Ternary complexes with histamine or histidine	No mixed-ligand formation with gly	229
L-cysteine (LH_2)	$Ni[Ni(L)_2]$		229
L-phenylalanine (LH)	$Ni(L)_2 \cdot 2\,H_2O$	Bridging-CO_2^-	230
N-acetyl-DL-tryptophanate (LH)	$NiL_2 \cdot 3\,H_2O$		231
	$NiL_2 \cdot 2B$ (B = py, 3-Mepy or 4-Mepy)	Amino-acid bonds with $-CO_2^-$ alone	
2,4-(1H,3H)-pteridinone (LH)	$Ni(LH)_2Cl_2 \cdot H_2O$ $Ni_2(LH)_3Br_4 \cdot 3\,H_2O$ $Ni(L)_2 \cdot 2\,H_2O$		232
1,4,6-trimethylpyrimidine-2-thione	NiL_2X_2 (X = Cl or Br) NiL_3Br_2	*N*-coordinated, X-bridged polymers	233

TABLE 15 (continued)

Ligand	Complex	Comments	Ref.
Trimethoprim (2,4-diamino-5-(3′,4′,5′-trimethoxybenzyl)pyrimidine	Ni_2LCl_4	NH_2 coordination	234
Valium (7-chloro-1-methyl-5-phenyl-3H-1,4-benzodiazepine-2-one)	$[Ni_2L_3X_4]$ (X = Cl, Br or I)	Pseudo-T_d Ni(II), bridging L	235
Cycloserine			236
Riboflavin-2′,3′,4′,5′-tetraacetate	$NiL_2X_2 \cdot nH_2O$ (X = Cl, Br or I)	Pseudo-O_h $[NiN_2O_2X_2]$	237
	$NiL_2(NO_3)_2$	Pseudo-O_h $[NiN_2O_2O_2']$	237

bind to N(7) of the adenosine rather than N(1). For Ni^{2+}, intramolecular macro-chelate formation occurs to the extent of 29, 65 and 80%, respectively, for $[ATP]^{4-}$, $[ADP]^{3-}$ and $[AMP]^{2-}$. Increasing the number of phosphate groups (and, hence, their denticity) reduces the ability of the nucleic base portion of the molecule to give inner-sphere coordination (in a monomeric complex).

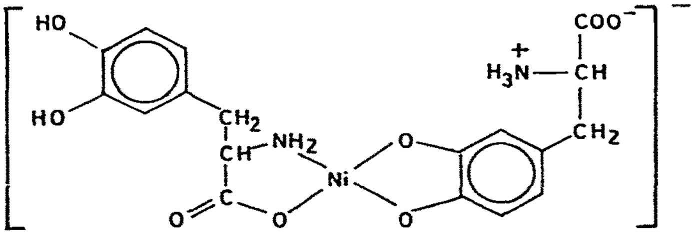
Turning to amino-acids, it has been found that Ni(II)-glycylglycyl-L-histidine is, unexpectedly, very sensitive to O_2, especially at neutral pH [241]. The reaction product was isolated, and characterisation by NMR showed that a decarboxylation had occurred, the structure suggested being (**116**).



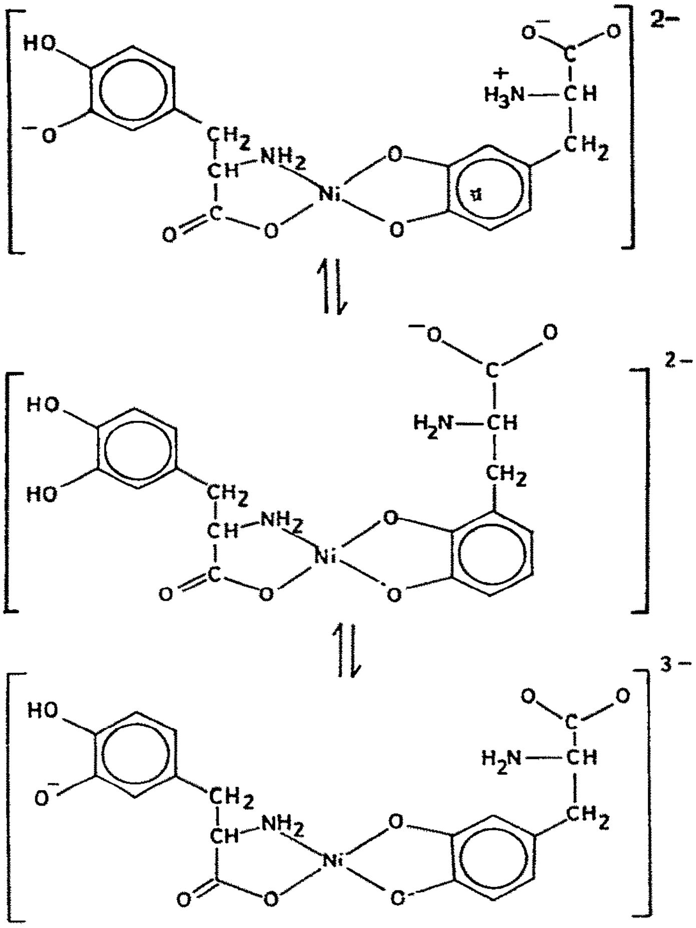
(**116**)

A thorough solution study of the Ni^{2+}—DOPA system has appeared [242], utilising model experiments on the ternary complex Ni(II)-L-alaninato-pyrocatecholate (in which the potential donor groups of DOPA belong to two different ligands). The following conclusions were drawn: (i) the complex $[Ni(LH_2)]^+$, with amino-acid type bonds, is present in fairly significant concentration; (ii) the complex [Ni(LH)] contains a pyrocatecholate-type bond and a protonated side-chain amino group; (iii) there is strong evidence that the species $[Ni(H_3L_2)]^-$ has structure (**117**) whereas $[Ni(H_2L_2)]^{2-}$ has structure (**118**) (in equilibrium with (**119**)); (iv) species $[Ni(HL_2)]^{3-}$ is also mixed-bonding in type, as in (**120**).

A thorough study of bonding by several dipeptides and tetrapeptides with Ni(II) has been carried out. For the dipeptides {e.g. Cl^-H^+-Gly-Gly-OH, and Cl^-H^+-(*O*-Bzl)-L-Tyr-(*O*-Bzl)-L-Tyr-OH}, no 1 : 2 Ni(II) : dipeptide complexes are formed. This was attributed to either steric hindrance of bulky *O*-Bzl-L-Tyrosine residues or to the formation of neutral species incapable of attacking other ligand species in the mixed solvent (80 : 20, dmso : H_2O)



(**117**)



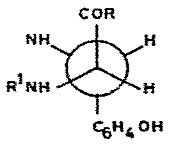
(118)

(119)

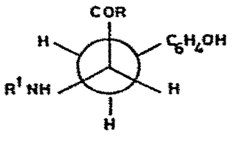
(120)

used. Conversely, the tetrapeptides {e.g. Cl^-H^+-(*O*-Bzl)-L-Tyr-Gly-Gly-(*O*-Bzl)-L-Tyr-OH} gave only complexes of 1 : 1 composition, suggesting bonding to the nickel by sites other than the terminal *C*- or *N*-atoms [243]. An octahedral structure with a {$NiN_4O(OH_2)$} chromophore was advanced to account for the potentiometric results.

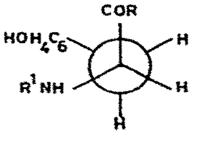
In the tripeptides Tyr-Gly-Gly (**121**; R = $NHCH_2CONHCH_2COOH$, R^1 = H) and Gly-Leu-Tyr (**121**; R = OH, R^1 = $COCHCHMe_2NHCOCH_2NH_2$), the rotamer (**121a**) predominates through a wide range of pH, although rotamer (**121c**) increases in extent with increase in pH (that of (**121b**) remaining more or less constant). When these tripeptides react with Ni(II) in water, the rotamer



(**121a**)

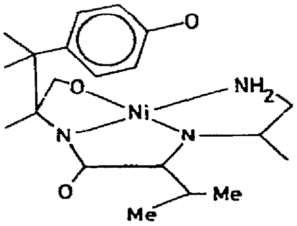


(**121b**)

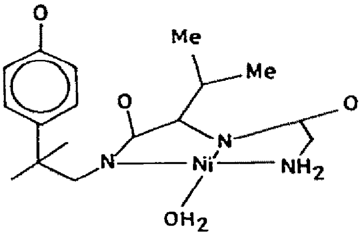


(**121c**)

(**121c**) population increases considerably (NMR, pH 7), up to 0.79, and that of the other two decreases to 0.21. A square-planar geometry is present for both tripeptide complexes at just above pH 7, with an octahedral one growing in between pH 7 and 9. Ni(II)-Gly-Leu-Tyr has an even higher rotamer (**121c**) population (0.92) for the square-planar form [244]. Up to pH 11, the ligands act as tetradentates and it was suggested that the changes in rotamer populations are due to aromatic-ring—metal interactions observed when Gly-Leu-Tyr acts as a tetradentate ligand, coordinating through NH_2, two deprotonated peptide nitrogen atoms and the carbonyl group (**122**), rather than when it is tridentate (**123**). Tyr-Gly-Gly gives a similar tetradentate structure. Such interactions may be of importance in the functioning of certain enzymes (e.g. tyrosinase).



(**122**)

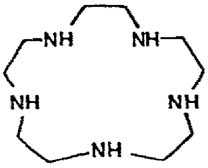


(**123**)

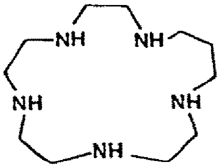
A complete account of the first example of α-amido acid complexes of transition metal ions with low-dimensional properties has appeared [245]. The complex Ni(hippurate)$_2$(OH$_2$)$_3$ has the Ni(II) in essentially octahedral coordination (Dq= 975 cm^{-1}, B = 855 cm^{-1}). A crystal structure analysis shows these octahedral units to be bridged by water molecules. The complex is antiferromagnetic; anisotropic super-exchange occurs along the chain (c axis) and inter-chain exchange is restricted to dipolar interactions along b. The system is then a pseudo-1D system in which 3-dimensional ordering is not predicted to occur until $T \rightarrow 0$ K.

11.4 NICKEL(III) COMPLEXES

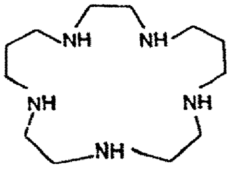
Most well-characterised Ni(III) complexes known to date involve macrocyclic ligands, so these will be treated first. The new complexes reported this year have been with the new pentadentate macrocyclics (**124**)—(**126**) [246].



(**124**)



(**125**)



(**126**)

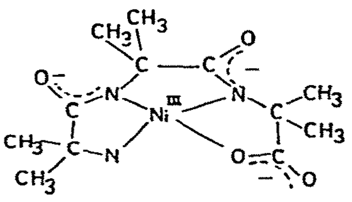
The Ni(II) complexes of these ligands have distorted O_h structures (as the perchlorates, the sixth position is occupied by a solvent molecule) with progressive weakening of the Ni—N interactions in the order [Ni(**124**)] > [Ni(**125**)] > [Ni(**126**)]. Reversible one-electron oxidation (Pt electrode in MeCN/0.1 M $[Et_4N][BF_4]$) gave the Ni(III) analogues with EPR spectra characteristic of octahedral low-spin Ni(III) systems ($g_\parallel < g_\perp$ and $g_\parallel \approx 2$). The half-wave potentials were very low (ca. 0.82—0.74 V) and it was concluded that insertion of a further nitrogen atom into a tetraaza-ligand framework facilitates attainment of the Ni(III) oxidation state. A similar comparison of electrochemical properties for the tetraaza-analogues [247] finished with the conclusion that attainment of the Ni(III) oxidation state depends only on the Ni—N bond strength [248].

That axial interaction is, indeed, important in stabilising the Ni(III) state can be seen in another report [249]. Addition of polydentate anions ($[SO_4]^{2-}$ or $[PO_4]^{3-}$) to Ni(II) complexes of the well-known macrocycles [14]aneN_4, cyclam and [14]-4,11-dieneN_4 stabilises Ni(III) in mildly acidic solution, after controlled-potential electrolysis. The complexes gave EPR spectra with $g_\parallel = 2.03$ and $g_\perp = 2.23$, unequivocal evidence for the presence of Ni(III). The complexes with [14]aneN_4 and cyclam are the first Ni(III) complexes with saturated ligands which are stable in mild, aqueous acid solution.

There have also been two interesting reports on Ni(III) complexes (again in solution) with peptides. Most Ni(III) peptides reported over the years undergo self-oxidation, the ligand being oxidised and the metal reduced (e.g. Ni(III) tetraglycine undergoes oxidation at the methylene groups). It has now been found that substitution of these methylene groups, as in the amino-acid α-aminoisobutyric acid (Aib_3H_2), gives thermally very stable Ni(III) complexes [250]. However, the complex obtained is photochemically unstable (visible radiation), photolysis causing decarboxylation of the tripeptide with the formation of propanone.

$$2[Ni^{III}(Aib_3)] \xrightarrow[H^+]{h\nu} 2Ni^{II} + H_4Aib_3^+ + H_3Aib_2\text{-amide}^+ + CO_2 + Me_2CO$$

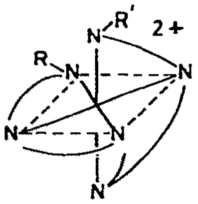
The asymmetry in the *g* values (EPR spectrum) was explained in terms of the presence of one carboxylate group and three *N*-donor ligands in a square-planar structure (**127**). In the second report, the EPR spectra of solutions of



(127)

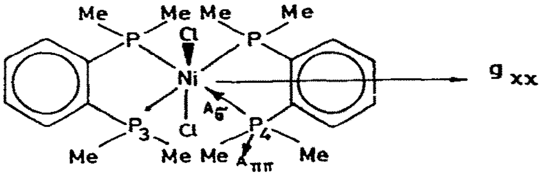
bleomycin-Ni(III) at —196°C were followed (1 : 1 Ni(II) : L; freshly oxidised Ni(II) complex) and compared with those of model tripeptides [251]. Tetragonal ($g_{xx}, g_{yy} > g_{zz}$) rather than square-planar ($g_{zz} > g_{xx}, g_{yy}$) spectra were given, with high field splitting characteristic of bonding by a single nitrogen atom.

However, not all Ni(III) complexes reported are solution species. A stable Ni(III) complex can be prepared using the 1 : 1 condensation product of biacetyloxime with tetraethylenepentamine and oxidising the Ni(II) complex with aqueous alkaline $[NH_4]_2[S_2O_8]$ [252]. From the EPR spectrum, a tetragonal structure (128) with an unpaired electron in the d_{z^2} orbital was suggested. A second interesting compound isolated in the solid state is $[Ni(TCNQ)_2]$, obtained from the reaction of $[Ni(cp)_2]$ with $[TCNQ]^-$. Of the three possible formulations $\{[Ni^{2+}(TCNQ^-)_2]$, $[Ni^{3+}(TCNQ^-)(TCNQ^{2-})]$ and $[Ni^{4+}(TCNQ^{2-})_2]\}$ the evidence (mainly from XPES spectroscopy) is in favour of a mixed Ni(III)—Ni(IV) formulation (of which ca. 15% is Ni(III)). The material is a semi-conductor ($K = 1.7$ (ohm cm)$^{-1}$) [253].



(128)

Finally, a definitive EPR study of $[Ni(dp)_2X_2]Y$ {dp = 1,2-phenylenebis-(dimethylphosphine); X = Cl or Br; Y = $[ClO_4]^-$ or $[PF_6]^-$} has appeared [254]. The orientation of the axes of the g and A tensors is shown in (129).



(129)

The presence of an almost isotropic $^{31}P_A$ tensor is an artifact caused by almost equal spin density distribution in the 3p orbitals of P, i.e. the in-plane π; σ and the out-of-plane π. The in-plane p-orbitals of σ and π symmetry are a_g (i.e. they directly acquire unpaired spin density by overlap). The authors concluded that in the bromide there is considerable back-bonding between the bromine p_x and p_y orbitals (and also the d orbitals) and the out-of-plane p_z orbitals of the phosphorus.

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