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1 NICKEL

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CONTENTS

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INTRODUCTION

This review is essentially a continuation of the previous article in this series[1], and attempts to cover the coordination chemistry of nickel appearing in 1983 and late 1982, including volumes 98 and 99 of Chemical Abstracts. The format adopted closely resembles that of the previous review[1], and the material has been organised by oxidation state, with further subdivision in terms of ligand donor type. However, a certain degree of overlap has been allowed in order to preserve continuity, and in all cases, including complexes with mixed ligands, compounds have been classified according to the fundamental theme of the article in which they appeared.

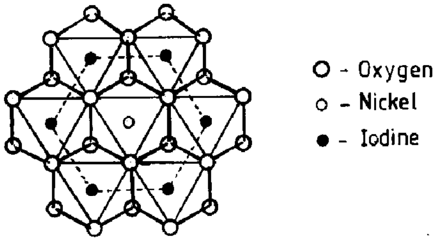
Articles of general interest which have appeared in the literature are a brief review of Fe, Co and Ni [2] and the development of a structure-reactivity relation for the complexation of various metal ions, including nickel [3]. The latter article predicts formation constants based solely on the structure of the organic ligand, which is analysed in terms of donor group, with a separate term being added to account for chelate ring formation.

1.1 NICKEL(IV)

The bulk of Ni(IV) compounds that have been synthesized, have ligands containing oxime functional groups. By way of introduction to the +4 oxidation state, a few unusual compounds containing nickel in this oxidation state have been included.

Raman and electronic spectroscopy have been used to characterize the compounds $Ni(en)_2X_3$, $Ni(dapn)_2X_3$ and $[Ni(en)_2Pt(en)_2X_2](ClO_4)_4$ (X= Cl, Br; en= 1,2-diaminoethane, dapn= 1,2-diaminopropane). Both $Ni(en)_2X_3$ and $Ni(dapn)_2X_3$ are mixed valence compounds with a Ni(II)---Cl-Ni(IV) chain [4].

Periodate ion, efficient as a strong oxidant and stabiliser of high oxidation states, has been used to isolate nickel(IV) in the complex $Li_2[Ni(IO_4)_6]\cdot 6H_2O$ [5]. A structure similar to that of $TeMo_6O_{24}^{2-}$ has been proposed, on the basis of spectroscopic evidence (1).

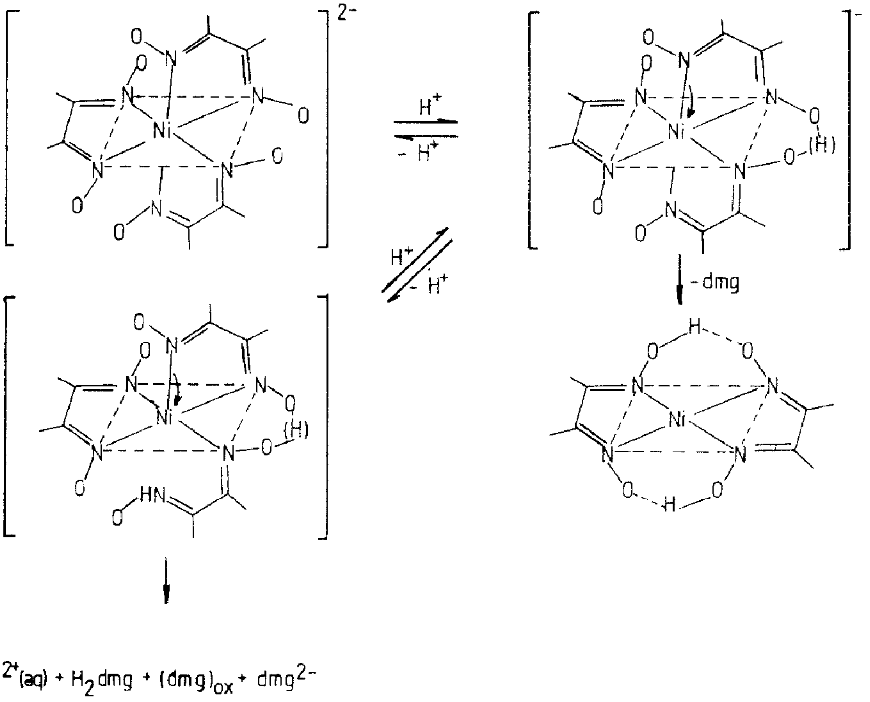


(1)

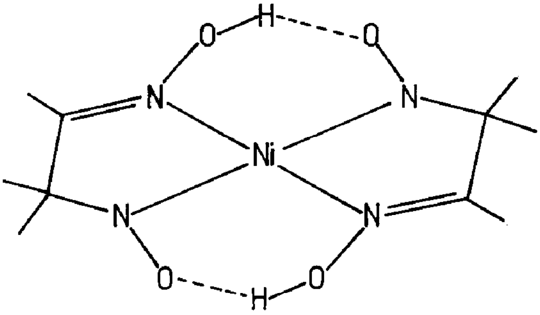
The decamethylnickelocene dication, $[(Me_5C_5H_5)_2Ni]^{2+}$, has been isolated as its PF_6^- salt. Nuclear magnetic resonance and UV-visible spectroscopy show that $[(Me_5C_5H_5)_2Ni]^{2+}$ is a diamagnetic, 18-electron complex, isoelectronic with $[(Me_5C_5H_5)_2Fe]$, $[(Me_5C_5H_5)_2Co]^+$, and $[(Me_5C_5H_5)_2Mn]^-$ [6].

1.1.1 Nitrogen-donor ligands

Potassium tris(dimethylglyoximato)nickelate(IV) has been prepared in aqueous alkaline medium from Ni(II) and dimethylglyoximate in the presence of hypoiodite [7]. The formation of the complex exhibits first-order kinetics, while ^{1}H-nmr indicates octahedral coordination through nitrogen donors. Confirmation of the +4 oxidation state was established by the absence of an e.s.r. signal. The proton-assisted decomposition of tris(dimethylglyoximato)-nickelate(IV) has also been studied [8]. The complex decomposes with dissociation and a concomitant intramolecular, or a subsequent very rapid, electron transfer to yield bis(dimethylglyoximato)nickelate(II) and/or Ni^{2+}(aq) as shown below.

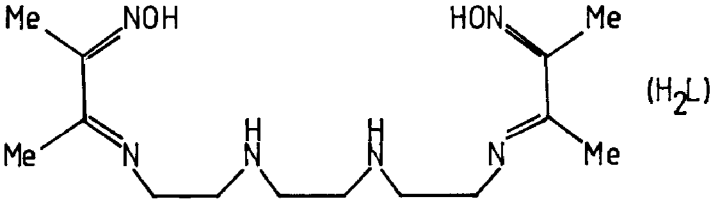


Further support that coordination occurs via nitrogen is provided by the crystal structure of bis[3-(hydroximino)-3-methyl-2-butanone oximato-(2-)-N,N']nickel (2) [9]. The ligand is very similar to dimethylglyoxime, differing only in the addition of a methyl group on one of the skeletal carbon atoms.



(2)

3,14-Dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dioxime (3) forms pseudooctahedral complexes with nickel in variable oxidation states which are reversibly interconvertible. As a result, the kinetics of the oxidation/reduction of these complexes have generated much interest.

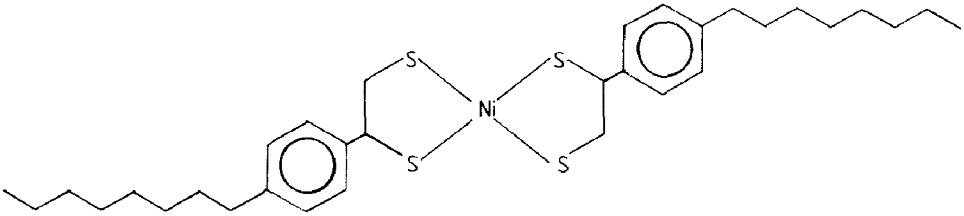


(3)

Macartney and McAuley [10] have studied the oxidation of $[Ni(H_2L)]^{2+}$ using a series of iron(II) phenanthroline and bipyridine cations as oxidant. In addition, the reduction of $[NiL]^{2+}$ using Fe(II), V(IV), Ni(II) cyclam ions in aqueous perchlorate media[11], as well as $Co(edta)^{2-}$ [12], as reductant, has been investigated. The crystal structures of the Ni(II) complex,$[Ni(H_2L)](ClO_4)_2$ and the Ni(IV) complex,$[NiL](ClO_4)_2$ have been determined.Both structures show a distorted octahedral environment for the Ni atom, with coordination taking place via the nitrogen atoms.Although the geometries are both very similar, the Ni-N bond lengths are very different with a considerable shortening as the oxidation state increases[13].

1.1.2 Sulphur-donor ligands

The structure of the mesogenic compound bis{[(octyl-4-phenyl)-1-ethylenedithiolato-1,2](2-)-S,S'}nickel (4)has been determined.The 1,2-dithiolatonickel and phenyl groups are nearly coplanar,while the average Ni-S and S-C distances are 2.12(1) and 1.692(7)Å respectively[14].



(4)

A series of complexes $[Ni(S_2C_2R_2)_2]$(R=CN,Me,Ph,H) have been prepared and their optical and electrical conductivities investigated,in an attempt to produce new one-dimensional metals based on them.However,attempts to oxidize or reduce these complexes failed to yield any metallic complexes[15].

1.2 NICKEL(III)

The bulk of complexes containing nickel in the +3 oxidation state consist of multidentate cyclic ligands with nitrogen being the principal donor atom.As a result of the relative instability of the d^7 electronic configuration,most of these complexes are associated with their more stable d^8 analogues and a wealth of information about the Ni(III/II) redox couple has been generated.

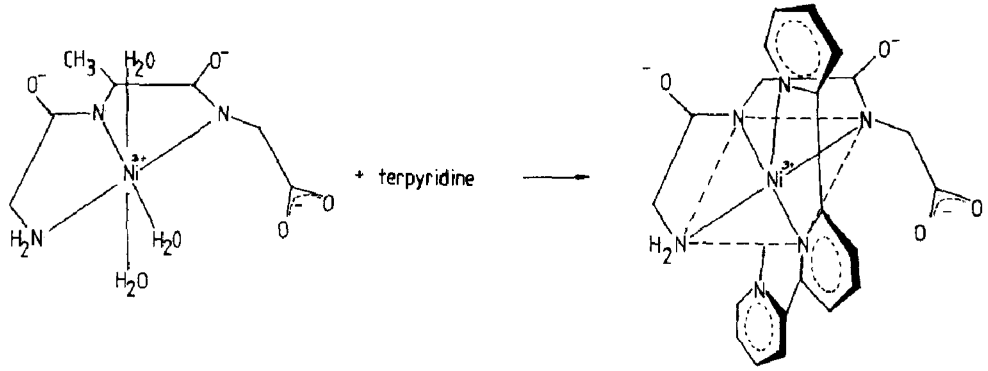
1.2.1 Nitrogen-donor ligands

The oxidation of tris(4,4'-dimethyl-2,2'-bipyridine)nickel(II) and tris-(1,10-phenanthroline)nickel(II) to their Ni(III) analogues,using tris-(2,2'-bipy)nickel(III)as oxidant has been investigated.In addition the reverse process,using $Ni(H_2A)^{2+}$ (H_2A=3,14-dimethyl-4,7,10,13-tetraaza-hexadeca-3,13-diene-2,15-dione dioxime),RuL_3^{2+} (L=5-nitro-1,10-phenthroline), and $Fe(H_2O)_6^{2+}$ as reductant has also been studied,and results indicate that the Ni(III)-complexes behave as strong, one-electron outersphere oxidants and possess moderate self-exchange rate constants[16].

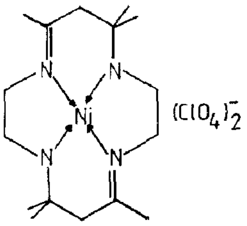
While on the subject of Ni(III)-bidentate N-donor ligand complexes it is interesting to note that $NiCl_2$ reacts with ethylenedimethacrylate-2,3-epoxypropylmethacrylatecopolymer (eda) to yield a polymeric complex material with general formula $[Ni(eda)_2Cl_2]Cl$. This structure was assigned with reference to the model complex $[Ni(en)_2Cl_2]Cl$ (en=ethylenediamine)[17].

The chemistry of 1,4,7-triazacyclononane([9]aneN$_3$) has been extended by Wieghardt and co-workers[18] who have isolated the complex $[Ni([9]aneN_3)_2](ClO_4)_3$ by oxidation of the corresponding Ni(II)-complex. The trivalent complex exhibits UV and magnetic data consistent with a low-spin d^7 configuration of a Ni(III) centre in a pseudooctahedral environment of six N donors. $[Ni([9]aneN_3)_2]^{3+}$ is a strong oxidant and exhibits a quasi-reversible one-electron redox process with a formal redox potential of +0.95V.

Nickel(III)-peptide complexes have been studied and characterized using chemical and electrochemical oxidation, redox stoichiometry, substitution reactions, UV-visible spectral shifts and e.s.r.[19-21]. The complexes were found to be six-coordinate with tetragonal distortion. Equilibrium constants for axial substitution and the kinetics of electron transfer for the Ni(III)-peptide complexes have been determined. The Ni(III/II) electron transfer reactions are rapid and it was generally found that Ni(III)-peptides will add a second peptide or other chelating agent to form stable bis-peptide or ternary complexes as shown below.



γ-irradiation has been used to convert rac-(5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate (5) and rac-(5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene)-nickel(II) perchlorate (6) to the corresponding nickel(III) species. On oxidation a change in geometry occurs from a square-planar Ni(II)-species to a tetragonally distorted octahedral Ni(III)-species, containing weakly coordinated perchlorate ions. Single-crystal EPR spectroscopy was used to monitor the structural and electronic changes [22].



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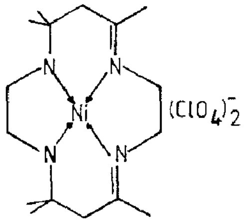
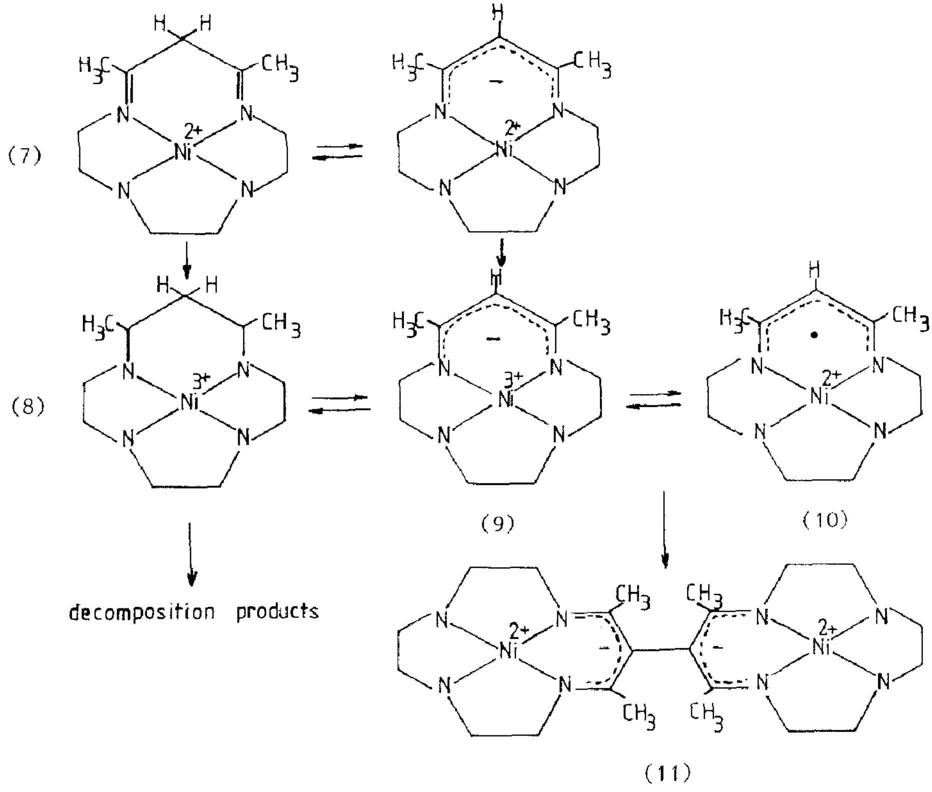


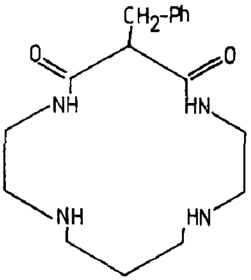
(6)

Pulse radiolysis has been used to study the oxidation of 11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-dienatonickel(II)diperchlorate (7) in aqueous solution. Oxidation of Br^- to $Br_2^{\bar{\cdot}}$ in the presence of (7) at low pH leads to the formation of the tervalent complex (8), which then decomposes. However, when the reaction is carried out at high pH the tervalent complex (9) is formed. This is followed by an intramolecular electron transfer to form a nickel(II) π-radical complex (10) which dimerizes to give (11). In all cases, oxidation from the +2 to the +3 state was accompanied by a change in structure from square-planar to octahedral coordination [23].



The extent of axial coordination of chloride ion in the complex $[Ni(III)L_3Cl](ClO_4)_2$ (L_3=β-*rac*-$Me_6[14]aneN_4$) has been examined using e.s.r. Even though the steric effects are great it has been shown that the macrocyclic complex contains two axially coordinated chloride ligands when dissolved in a concentrated solution of chloride ions [24].

Benzyldioxocyclam (12) has been prepared and reacted with Ni(II) in aqueous solution.Complexation occurs with simultaneous release of two protons from the amido groups.A comparison of the redox properties of this complex and the corresponding cyclam complex (13) was made.The $E_{1/2}$\{Ni(II)/Ni(III)\} values,calculated from CV profiles,were 0.47V vs SCE and 0.51V vs SCE for the cyclam and dioxycyclamato complexes respectively.This differs considerably from the Cu(II/III) system where the +3 oxidation state is substantially stabilized by complexation with dioxycyclam [25].



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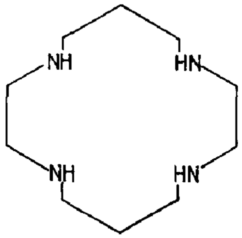
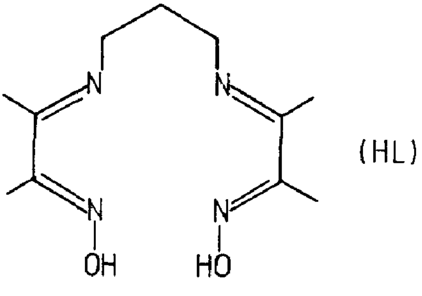


(13)

Nickel(III) complexes of 3,8-diene-2,10-dione dioxime (14) with two axial halide ligands have been prepared by oxidation of the corresponding Ni(II)-complex using persulphate as oxidant.E.s.r and near IR/visible spectra were used to confirm that the complexes contain nickel in the tervalent state in an octahedral environment.Of interest is the fact that the halide ligands are labile since the cross-exchange equilibrium

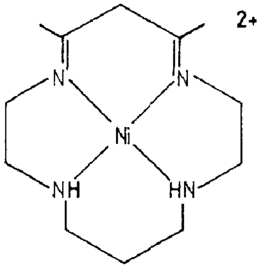
$$NiBr_2L + NiCl_2L \rightleftharpoons 2\ NiBrClL$$

is completely established in CH_2Cl_2/CCl_4 at -70°C after less than a minute [26].



(14)

Two reaction pathways have been found to take place during the oxidation of $[Ni(Me_2[14]4,7\text{-dieneN}_4)]^{2+}$ (15) and $[Ni(Me_2[13]4,7\text{-dieneN}_4)]^{2+}$ (16) using $Fe(phen)_3^{3+}$ as oxidant. In solutions of moderate acidity the rates of oxidation are first order in each reactant. The oxidation pathway however involves both oxidation of the metal centre as well as oxidation of the β-diiminato ligand [27]. Endicott *et al* have extended this work and examined the electron transfer reactions involving the Ni(II/III) couple in a variety of tetraaza macrocyclic complexes [28].



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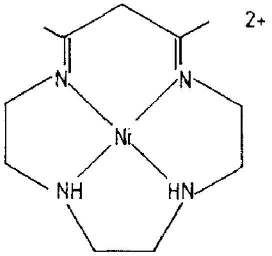
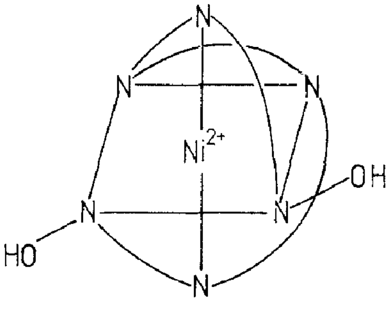


(16)

A single-crystal study of 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioximato nickel(III) using EPR spectrometry has been undertaken. The hexadentate ligand coordinates via six nitrogen atoms giving rise to a pseudooctahedral structure (17) [29].



(17)

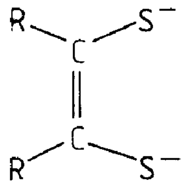
1.2.2 Sulphur-donor ligands

Interest in the chemistry of nickel(III) complexes containing unsaturated sulphur donor ligands of the general structure (18) has been maintained. This is manifested by a number of crystal structures, which show the complexes to be essentially square-planar with (18) acting as a bidentate ligand. Table 1 lists some of the important structural features of these complexes.

Table 1 Selected structural data of Ni(III)-*bis*-1,2-dithiolene complexes.

COMPLEX	Ni-S (Å)	C-S (Å)	C-C (Å)	S-Ni-S (°)	Ref.
$[(C_6H_5)_4As][Ni(S_2C_2(COOCH_3)_2)_2]$	2.129(6)	1.711(8)	1.327(8)	92.3(2)	[30]
$[TMPD]^a[Ni(S_2C_2(CN)_2)_2]$	2.152(4)	1.708(15)	1.315(18)	92.4(2)	[31]
$[N(CH_3)_3(C_6H_5)][Ni(S_2C_2(CN)_2)_2]$	2.142(2)	1.72(1)	1.338(20)	92.7(2)	[32]
$[t\text{-}Bu_4N][Ni(S_2C_2(S_2CS))_2]$	2.154(3)	1.73(1)	1.35(1)	93.4(1)	[33]

[a] $-TMPD^+$ =(*p*-(dimethylamino)phenyl)dimethyl ammonium

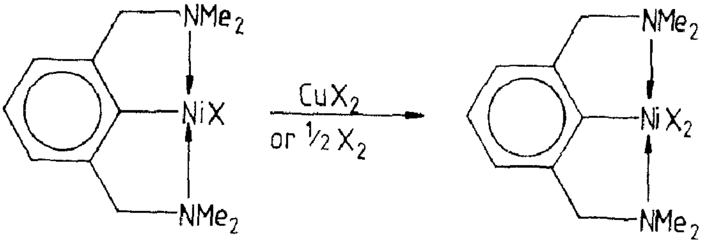


(18)

The Ni(III) diethyldithiocarbamate complex, $[Ni(N(C(S)OCH_2CH_3)_2)_2]^+$, has been prepared in solution by oxidation of the corresponding Ni(II)-complex. Cupric and ferric salts were used as oxidants, while the oxidation process proceeds via a common monoelectronic process [34].

1.2.3 Mixed-donor ligands

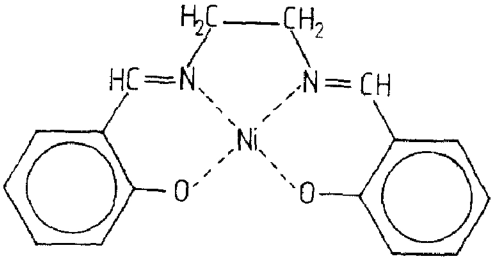
A unique series of penta-coordinate Ni(III)-complexes have been prepared using the method outlined below.



X = Cl, Br, I

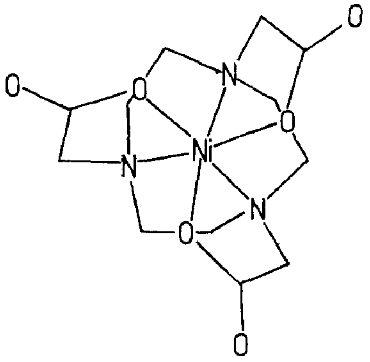
The crystal structure of $Ni\{C_6H_3(CH_2NMe_2)_2\text{-}o,o'\}I_2$ has been determined. The geometry at Ni has been described as square-pyramidal, with the Ni atom displaced approximately 0.34 Å out of the basal plane towards the apical I atom. ESR confirms the Ni(III) oxidation state, in which the unpaired electron of the low spin d^7 system is situated in the dz^2 orbital [35].

The electrochemical behaviour of [Ni(salen)] (19) has been studied in various solvents. The complex can be either oxidized or reduced to $[Ni(salen)]^+$ or $[Ni(salen)]^-$ respectively, while the effect of solvent on the standard potentials of oxidation and reduction have been discussed using the donor-acceptor approach [36].



(19)

The hexadentate ligand 1,4,7-triazacyclononane-N,N',N''-triacetate (TACNTA) reacts with Ni to yield the complex[Ni(TACNTA)] the structure of which has been determined (20).The base fragment 9-aneN$_3$ is chiral once coordinated to the metal ion,giving rise to two possible conformers depending on whether the acetate groups attach themselves in a clockwise or anti-clockwise fashion.Figure (20) depicts the acetate groups attached in a clockwise fashion and is more stable than the conformer where the acetate groups are attached in an anticlockwise manner [37].



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1.3 NICKEL(II)

1.3.1 Oxygen-donor ligands

1.3.1.1 Monodentate ligands

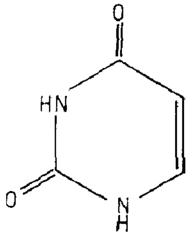
N-oxide complexes continue to generate interest. The effect of substituent in the bonding of variously-substituted pyridine N-oxide ligands with Ni(II) has been examined by means of UV/visible spectroscopy. Dq values obtained for the hexakis complexes $[NiL_6]^{2+}$ indicate that the position of the substituent is a dominant factor [38].

LIGAND	Dq(cm^{-1})
Pyridine N-oxide	794
4-Picoline N-oxide	794
2-Picoline N-oxide	785
2-Ethylpyridine N-oxide	781
2,6-Lutidine N-oxide	765

Natural-abundance ^{17}O-n.m.r. has been used to measure the rate of dimethyl sulphoxide exchange with $[Ni(dmso)_6]^{2+}$. The rate constant and activation parameters were found to be low for a purely dissociative mechanism, and the possibility of octahedral $\rightleftharpoons$ square-planar equilibrium is suggested [39].

2-Fluoro-5-nitroaniline and 4-fluoro-2-nitroaniline have been reacted with various nickel salts. Although both ligands bond via oxygen in a monodentate fashion, complexes of varying structure have been obtained depending on the ligand and metal salt used. 2-Fluoro-5-nitroaniline yields the octahedral complexes $[NiL_4X_2]$ (X=Cl, Br, NCS) and $[NiL_2(NCS)_2]$, with the latter containing bridging NCS groups. 4-Fluoro-2-nitroaniline yields the octahedral complexes $[NiL_4(NCS)_2]$and $[NiL_2(NCS)_2]$as well as the tetrahedral complex $[NiL_2Br_2]\cdot 2H_2O$ [40].

Depending on the pH of the reaction medium, uracil (21) may coordinate via a nitrogen or oxygen atom, depending on whether it is in its anionic or neutral form respectively. In the neutral form it has been found to complex via the carbonyl oxygen in the 4-position, and yields hexacoordinate complexes of the type $[NiL_4(H_2O)_2]X_2$ (X=Cl, NO_3). Dehydration of the chloro complex yields $[NiL_2Cl_2]$, in which the ligand is still coordinated via the same carbonyl group [41].

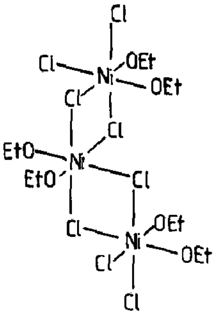


(21)

Trifluoroacetate has the capability of functioning as a monodentate or bidentate ligand as well as an anion. Reaction of $[Me_4N]_2NiCl_4$ with 4 $Ag(CF_3COO)$ affords the complex $[Me_4N]_2[Ni(CF_3COO)_4]$. Infrared data suggest that the trifluoroacetate groups are bonded in a unidentate manner, while magnetic data indicate a tetrahedral environment for the nickel ion [42].

The reaction of $N(CN)_2^-$ and $C(CN)_3^-$ with Ni in the presence of triphenylphosphine oxide has been investigated. Complexes of the type $[NiL_2X_2]$ (L=Ph_3PO; X=$N(CN)_2^-$or $C(CN)_3^-$) were obtained, in which Ph_3PO coordinates via oxygen and X via the nitrile nitrogen atoms [43].

The crystal structure of $[NiCl_2(CH_3CH_2OH)_2]$ has been determined [44]. The nickel ion is octahedrally coordinated by two ethanol molecules in <u>cis</u> positions, and by four chloride ions in a shared manner so as to form an extended zig-zag chain (22).



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1.3.1.2 Bidentate ligands

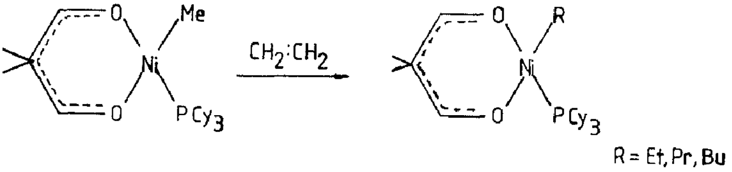
As is customary, much work has been concerned with the study of β-diketonato complexes of Ni(II). The kinetics and mechanism of the reaction of 2-thenoyltrifluoroacetone [45] and 1,1,1-trifluoropentane-2,4-dione [46], to form mono-complexes with Ni(II), have been studied in aqueous solution. The kinetic data obtained indicate a mechanism in which the metal ion reacts exclusively with the enol tautomer of the β-diketone ligands. In addition, the effect of various mixed aqueous solvents on the equilibrium and formation constants of Ni(II) with dibenzoylmethane have been studied and compared with those of the corresponding acetylacetonate complexes. The dibenzoylmethane complexes are found to be more stable than the acetylacetonate complexes regardless of the solvent used [47].

Various Ni-β-diketonate complexes have been isolated in the solid state. Selenoylthienoylmethane (STM) reacts in the presence of various bases to form complexes of the type [$Ni(STM)_2L_2$] ($L=H_2O$, pyridine, 3-picoline, 4-picoline). Thermal treatment of these complexes results in the bis-complex [$Ni(STM)_2$][48].

A new synthetic route to the direct synthesis of bis-(acetylacetonato)-nickel(II)dihydrate, in very high yield, has been developed [49]. The procedure involves the reaction of [NiO(OH)] with acetylacetone, which acts as a reducing and chelating agent:

$$[Ni(III)O(OH)] + 6\ C_5H_8O_2 \longrightarrow 2\ [Ni(II)(C_5H_7O_2)_2] + C_{10}H_8O_4 + 4\ H_2O$$

While on the subject of acetylacetonato complexes, it has been shown that ethylene can insert into the Ni-C bond of [$Ni(acac)(R)(PCy_3)$] ($R=CH_3$, PCy_3= tricyclohexylphosphine) to give new nickel-alkyl complexes [50].



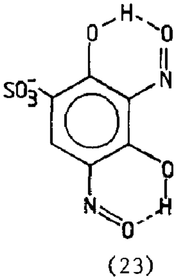
The tendency of β-diketonate-3d-transition metal(II) complexes to polymerize has been reinforced by the determination of the crystal and molecular structures of [$Ni_2(acac)_4$(pyridine)] and [$Ni_2(acac)_4$(piperidine)] [51]. The Ni atoms are octahedrally coordinated in both complexes. In addition, the structure of [$Ni_3(acac)_6$] has been redetermined.

β-hydroxy carbonyl and β-hydroxy carboxylic acid ligands have been the subject of some study. Formation constant data have been reported for the complexation of 4-hydroxy-3-aldehydobiphenyl [52], 8-formyl-7-hydroxy-4-methyl-2H-1-benzopyran-2-one [53], salycylic acid [54] and its esters [55], and N-(2-hydroxy-4-nitro)benzylglycine [56], with Ni(II). In addition, the equilibria, in aqueous solution, of Ni(II) and furan-2-carboxylate has been studied calorimetrically. Indications are that furan-2-carboxylate functions as a bidentate ligand with participation of both carboxylate and heterocyclic oxygen in complex formation [57]. Nuclear magnetic relaxation has also been used to study the complexation of Ni(II) with mandelic acid. Mono, bis and tris complexes are observed in the pH range 0-13 [58]. Apart from the solution studies, numerous complexes of the above ligands have been isolated in the solid state. Bis-chelates of Ni(II) with 2-acetyl- and 2-benzoyl-1,3-inandione have been isolated as tetrahedral complexes in which coordination occurs via the acyl and the hydroxyl oxygen atoms [59]. The reaction of o-hydroxy propiophenone with Ni(II), in the presence of quinoline, yields the mixed ligand complexes [NiLXQ] (HL=o-hydroxy propiophenone; X=Cl; Q=quinoline) and [NiL_2Q_2], the former being square-planar and the latter octahedral [60]. Mixed ligand complexes containing 3-acetyl-6-methyl-2H-pyran-2,4(3H)dione as primary ligand, and heterocyclic bases as secondary ligands, have also been synthesized [61]. Ascorbic acid has been complexed to Ni(II) in the presence of various amino acids [62] and pyridine [63], yielding hexacoordinate complexes in all instances.

Isotopic labelling has been used in the analysis of the infrared spectrum of Ni(II)benzilate. The ligand coordinates to the Ni ion via the carboxyl and α-hydroxy oxygen atoms [64]. Vibrational spectroscopy has also been used to study the nickel complexes of benzoylbenzamide (HL), which forms compounds of composition $NiL_2 \cdot 2H_2O$ and NiL_2. NiL_2 has been isolated in a red and green form, the former of which has been assigned a square-planar structure, while the latter has been assigned a tetrahedral or distorted tetrahedral structure [65].

The coordination properties of hydroxamic acid ligands have been studied in solution and in the solid state. Equilibrium and formation constants for the complexation of N-phenyl benzohydroxamic acid [66] and N-m-tolyl-p-methoxybenzohydroxamic acid [67] have been obtained in various solvents. Bis adducts of the general formula $[NiL_2(HA)_2]$ (HL=variously-substituted phenylbenzohydroxamic acid; HA=aliphatic carboxylic acid) have been isolated [68]. These hexacoordinate complexes are unusual in that the carboxylic acids behave as Lewis bases. Both monomeric and polymeric complexes have been observed in solution. In addition the crystal and molecular structure of diaqua bis(picolinato N-oxide)nickel(II) has been determined. The complex is hexacoordinate with a trans-octahedral configuration [69].

Nitroso-alcohol ligands, in particular ortho-nitroso napthols, are well known for their chelating properties. The formation kinetics of Ni(1-nitroso-2-napthol-6-sulphonate) (H_2L) have been reported. Both the acidic (HL^-) and basic (L^{2-}) form of the ligand react with Ni(II), the latter at a much faster rate [70]. 2,4-Dinitrosoresorcinol-6-sulphonate (23) (H_2L) reacts with Ni(II) to yield the square-planar complex $[Ni(HL)_2]$, while 1-hydroxy-2-nitroso-3,6-disulphonate napthalene (24) (HL) forms two square-planar complexes, $[NiL(NO_3)(H_2O)]H_2O$ and $[NiL_2]$ [71].



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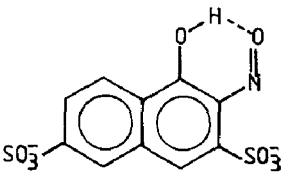

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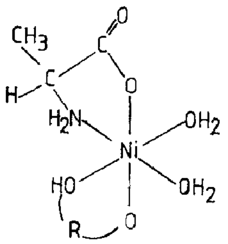
The complexes of Ni(II) with various nitrosolate ligands have been described. The nitroacetate ion, $[O_2CCHNO_2]^{2-}$, chelates with nickel in the presence of 2,2'-bipyridine and 1,10-phenanthroline to yield quasi-octahedral complexes of the type $[NiLB_2]$ ($L=[O_2CCHNO_2]^{2-}$, B=bipy or phen) [72]. The crystal structures of bis(nitrosocarbamylcyanomethanido)diaqua nickel(II) [73] and dinitro-bis(quinoline)nickel(II) [74] have also been determined.

Vitamin B_6 (pyridoxine) has been complexed with various nickel salts, and the resultant complexes have been analysed using differential thermogravimetric analysis [75]. Pyridoxine (HL) coordinates via the protonated or deprotonated phenolic group, and the alcoholic group in the α-position. All the complexes are octahedral and consist of $Ni(HL)_3X_2 \cdot nH_2O$ ($X=NO_3$, NCS, Br), $Ni(HL)_2(OAc)_2 \cdot 6H_2O$, $Ni(HL)SO_4 \cdot 5H_2O$, $NIL_2 \cdot 4H_2O$, and $Ni(HL)(L)(OAc) \cdot 4H_2O$ [76].

Coordination of nickel by diol-containing ligands has been studied by Misra and co-workers [77], who have synthesized ternary complexes of the type $[NiLB(H_2O)_2]$ (25), $[NiL_2B]$ (26), and $[NiLB_2]$ (27), (B= -alanine and L=ethanediol, propane-1,2-diol, 2-butane-1,4-diol, pentane-2,4-diol or hexane-1,6-diol).The complexes all exhibit octahedral geometry as indicated by spectroscopy.



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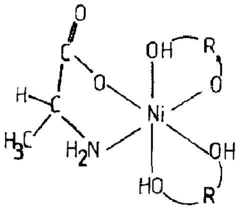

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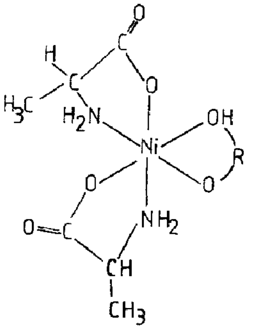


(27)

2,2'-Diphenylenedioxy-di-lithium (L) reacts with $NiCl_2$ in methanol to yield the highly reactive polymeric octahedral complex $NiL \cdot 2CH_3OH$, which reacts with a variety of bases. Complexes that have been isolated are $[NiL(bipy)_2]$, $[NiL(Ph_3P)(CH_3OH)]$, $[NiL(pyridine)_4]$ and $[NiL(Et_3N)_4]$ [78].

While on the subject of polymeric complexes, 4-methoxy- and 4-ethoxybenzofuro[3,2-d]pyrimidine react with $NiCl_2$ to yield polymeric complexes of the type $NiLCl_2 \cdot H_2O$(L=substituted benzofuro[3,2-d]pyrimidine). Magnetic and spectroscopic data indicate that coordination of L occurs via the methoxy/ethoxy and furan oxygen atoms, and that the structure is essentially octahedral with the chloride ions functioning as bridging groups [79].

Finally, a conformational study of the Ni(II)-phthalic acid complex has been reported. ^{13}C paramagnetic relaxation rates, contact shifts and INDO calculations have been used to determine the conformation , in which the Ni-O distance is estimated to be 2.1 Å [80].

1.3.1.3 Polydentate ligands

Folic acid and 7,8-dihydrofolic acid may function as dibasic or tribasic ligands, depending on the quantity of base used during complexation. Both ligands appear to function in a tetradentate fashion when dibasic, and in a tridentate manner when tribasic [81].

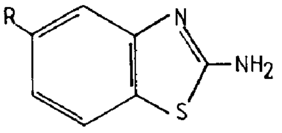
$$\begin{tikzcd}
\mathrm{Ni(II)} + H_3L \arrow[r, "KOH", "1:1"'] & {[Ni(HL)]} \arrow[r, "H_3L", "KOH\ 1:3"'] \arrow[dr, "HZ", "KOH"'] & K_4[NiL_2] \\
 & & K_2[NiLZ]
\end{tikzcd}$$

(H_3L = folic or 7,8-dihydrofolic acid; HZ = glycine)

1.3.2 Sulphur- and Selenium-donor ligands

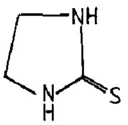
1.3.2.1 Monodentate ligands

2-Amino-6-methylbenzothiazole and 2-amino-6-chlorobenzothiazole (28) function as monodentate S-donor ligands when coordinating to Ni(II). Square-planar complexes of the type $[NiL_2X_2]$(L= substituted aminobenzothiazole) are obtained when X= Cl^-, NO_3^- and NCS^-, while tetrahedral complexes of the type $[NiL_4]X_2$ are formed when X is ClO_4^-. Coordination via the ring sulphur has been verified by a shift of 15 cm^{-1} in νC-S on complexation [82]. Imidazolidene-2-thione (29) , which is less sterically imposing, reacts with NiX_2 (X= Cl, Br), yielding the hexacoordinate complexes, $[NiL_4X_2]$ [83].



R= CH_3,Cl

(28)



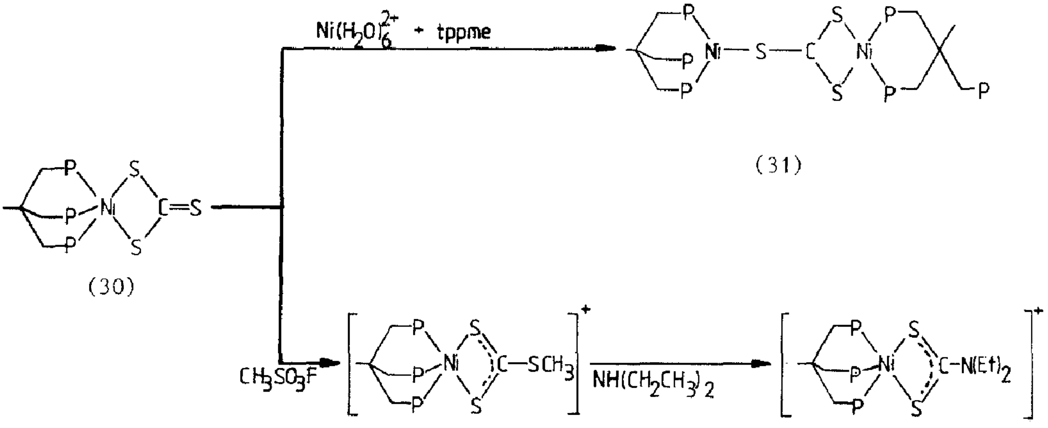
(29)

Various thiourea ligands have been used in the synthesis of mixed ligand complexes. A series of complexes, $[NiQ_2L_2]$(HQ= ethylacetoacetate; L= thiourea, allyl-, benzoyl-, methyl-, and diphenylthiourea) have been prepared. The complexes are all paramagnetic (μ= 3.02-3.27 Bm) and have been assigned trans-octahedral structures [84]. In addition, the dianionic complexes [NiL$_3$(NCS)X] (L= thiourea, o-tolylthiourea; X=Cl$^-$, NO$_3^-$) and [NiL$_4$(NCS)X] (L= o-chlorophenylthiourea; X=Cl$^-$, NO$_3^-$) have been synthesized. The former complexes are binuclear with thiocyanato bridges, while the latter complexes are hexacoordinate monomers [85].

1.3.2.2 Bidentate ligands

Interest in the complexation of dithiocarbamates with nickel remains sustained, and recent new complexes are listed in table 2. A striking feature is that the coordination geometry of the metal ion is square-planar, regardless of the number of dithiocarbamate and other ligands present in the complex.

The synthetic utility and potential of trithiocarbonate metal complexes has been investigated [92-94]. Sodium trithiocarbonate reacts with Ni(II) in the presence of 1,1,1-tris(diphenylphosphinomethyl)ethane (tppme) to yield the diamagnetic complex [Ni(tppme)(S$_2$CS)] (30). η^2-Coordination of the trithiocarbanato ion to the metal ion generates two active sites, namely the uncoordinated sulphur atom, which is susceptible to electrophilic attack, and the carbon atom which is susceptible to nucleophilic attack. The former is exemplified by reaction of (30) with $Ni(H_2O)_6^{2+}$ in the presence of tppme to yield [Ni$_2$(tppme)$_2$(μ-CS$_3$)]$^{2+}$ (31) , while the latter is exemplified by the reaction of (30) with CH_3SO_3F, followed by reaction with $NH(CH_2CH_3)_2$ to yield the complex [Ni(tppme)S$_2$CN(CH$_2$CH$_3$)$_2$] (32).



(31)

(30)

(32)

The synthetic versatility of these complexes is further emphasized by the reaction of (30) with [V(η^5-C$_5$H$_5$)$_2$], which leads to the formation of the Ni(0)

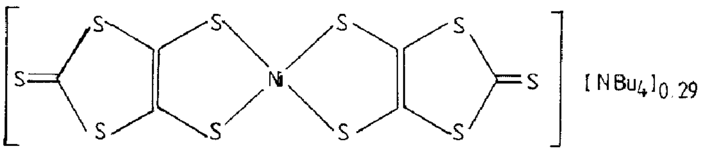
Table 2. Dithiocarbamate ligands and their Ni(II) complexes.

LIGAND (L)	COMPLEX	COMMENTS	Ref.
$[S_2CN(CH_2CH_2CH_2CH_3)_2]^-$	$[NiL_2]$	Square-planar	[86]
$[S_2CNCH_2CH_2CH_2CH_2]^-$	$[NiL_2]$	Square-planar;Crystal structure	[87]
4-Aminophenazone dithiocarbamate	$[NiL_2]$	Square-planar	[88]
$[S_2CN(CH_3)_2]^-$	$[NiL(COR)(PMe_3)]$ (R=CH_3, $SiCH_2$)	Square-planar; CO exchange	[89]
$[S_2CN(CH_2CH_3)_2]^-$	$[NiL(COR)(PMe_3)]$ (R=CH_3, $SiCH_2$)	Square-planar	[89]
	$[NiL(PMe_3)Cl]$	Square-planar;Crystal structure	[90]
$[S_2CN(R)_2]^-$ (R= alkyl)	$[NiL(PMe_3)(CH_2R)]$	Square-planar	[91]

complex $[Ni(tppme)(\eta^2\text{-}CS_2)]$, while the reduction of (32) with $NaBH_4$ affords the Ni(I) complex [Ni(tppme)(SH)] .

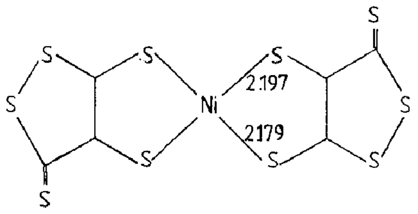
The infrared spectra of Ni-dithiooxamide complexes have been studied in great detail. NiX_2 (X=Cl, Br, I) reacts with planar dithiooxamide ligands in acid medium to yield the square-planar complexes $[Ni(H_2L)_2X_2]$ (H_2L=dithiooxamide, N-alkyl- or N,N'-alkyldithiooxamide). The ligands coordinate in a bidentate fashion with S,S-coordination, usually found in dithiolato complexes [95].

While on the subject of dithiolato complexes, a new two-dimensional, mixed valence compound, derived from a nickel bis-dithiolato complex has been synthesized [96]. The highly conducting,electrocrystallized, mixed valence complex $[NiL_2\ NBu_4]_{0.29}$ (HL= 4,5-dimercapto-1,3-dithiole-2-thione) (33) is interesting in that it shows an unusual two-dimensional structure, which is desirable to counter the Peierl's transition effect.



(33)

Variations on the dithiolate theme have manifested themselves in the form of some interesting crystal structures. The crystal structure of the Ni(II)-chelate of trithionedithiolate has been determined. As expected the $[Ni(C_3S_5)_2]^{2-}$ (34) anion is planar with the two Ni-S distances being 2.197(4) and 2.179(4) Å respectively [97].

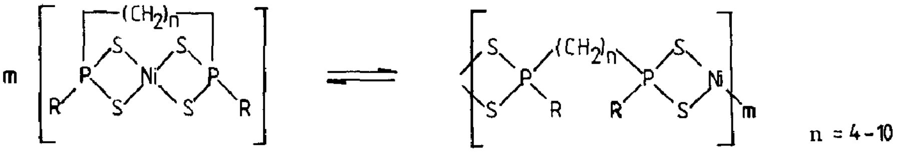


(34)

Direct- and alternating-current voltammetry have been used to study the electrochemical behaviour of a range of variously-substituted planar bis-

(dithio-β-diketonate) complexes $[Ni(S_2C_3RHR')_2]$. The complexes exhibit two succesive one-electron reductions, with the reduction potentials being dependant on the substituent present. Comparison with the isostructural diketonates reveals that these complexes are more difficult to reduce than their dithio-analogues [98]. Dithio Ni(II)-chelates have also been used as precursors to highly active olefin oligomerization catalysts. The complexes reported are $[Ni(L)(PR_3)X]$ (HL= variously-substituted dithio-β-diketonate; R= alkyl or aryl; X= halide). These complexes form extremely active catalysts under mild conditions, when activated by a suitable co-catalyst, such as alkylaluminium halide [99].

The Ni(II) complexes of variously substituted dithiophosphonic acids have been investigated by vapour pressure osmometry and ^{31}P-n.m.r. spectroscopy. Coordination polymers of the type $[S_2P(R)-R'-(R)PS_2Ni]_m$ are formed when R'= p-$(C_2H_4)_2C_6H_4$. However, when R'= o-$(C_2H_4)C_6H_4$ and o-$(C_3H_6)_2C_6H_4$, an equilibrium in solution, consisting of ansa-type and polymeric complexes, is found (35) [100].



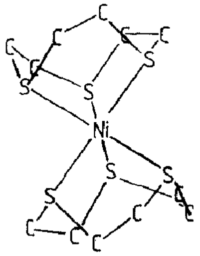
(35)

A novel method of anchoring nickel complexes within Zeolite cages, using bis(dialkyldithiophosphato)nickel(II) complexes, has been developed. The reaction involves the interaction of the above complexes with the basic AlO_4^- sites in the Zeolite system, with the possibility of a "phosphonium-like" intermediate [101].

Finally, the mixed S,Se-donor complex, bis(1,1-diethyl-3-selenobenzoylthioureato)nickel(II), has been prepared by the reaction of Ni(II)acetate with N-(diethylaminothiocarbonyl)benzimide chloride in the presence of sodium hydrogenselenide [102].

1.3.2.3 Polydentate ligands

1,4,7-Trithiacyclononane, a novel tridentate thioether ligand, has been complexed with Ni(II). The resultant complex, $[NiL_2](BF_4)_2$, has been characterized by single-crystal X-ray methods. The nickel ion occupies a slightly distorted octahedral environment of sulphur atoms provided by two facially coordinating thioether ligands (36) [103].



(36)

In conclusion, the tetradentate ligand, piperazine bis(dithiocarbamate), reacts with Ni(II) to form a polymeric complex $[NiL]_n$, in which the dithiocarbamate ligand acts as a bridging moeity. The coordination geometry is square-planar, with coordination occurring via the sulphur atoms of the CS_2^- groups [104].

1.3.3 Nitrogen-donor ligands

1.3.3.1 Monodentate ligands

Pyridine and its substituted analogues constitute the most widely used monodentate N-donor ligands found in nickel(II) complexes. Table 3 gives a brief summary of some pyridine-containing complexes.

The reaction of pyridine and substituted pyridines with $Ni(NCS)_2$ has generated much interest [105 - 111]. Different coordination geometries have been obtained depending on the substituent and the reaction conditions employed. Of interest are the complexes, trans-$[Ni(NCS)_2L_4]$ and trans-$[Ni(NCS)_2L_2L'_2]$ (L= 4-methylpyridine, L'= 4-phenylpyridine), both of which are clathrates. The crystal structures of both complexes have been determined, revealing that the former complex is host to methyl cellosolve, while the latter is host to p-cymene [109].

The effect of temperature on the reaction between 4-methylpyridine and $Ni(NCS)_2$ has been studied [111]. When the reaction is carried out at a low temperature, trans-$[Ni(NCS)_2L_4]$ is obtained, as manifested by a single infrared active band at 2070 cm^{-1}. However, when the reaction is carried out at 55-60°C, three infrared bands at 2060, 2070 and 2120 cm^{-1} respectively are observed. The latter complex, having the same composition as trans-$[Ni(NCS)_2L_4]$ has been assigned the molecular structure, $[Ni(NCS)_2L_3]\cdot L$, in which a pyridine ligand has left the coordination sphere. Complexes having a

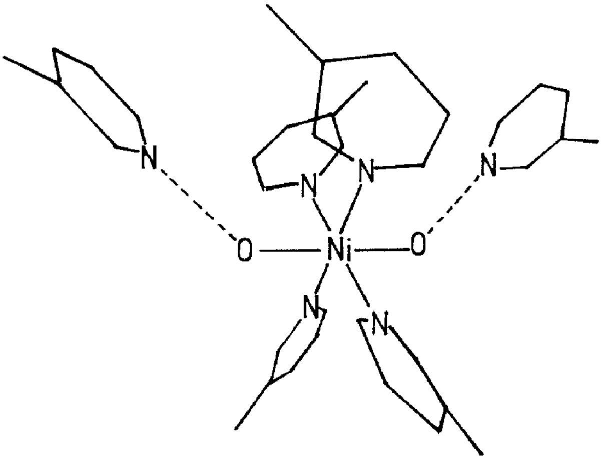
Table 3. Some pyridine and substituted pyridine complexes of Ni(II).

COMPLEX	LIGAND	COMMENTS	Ref.
$[Ni(NCS)_2L_2]$	2,5-dimethylpyridine	*Trans*-square-planar; Crystal structure	[105]
	2-benzoylpyridine	Octahedral; Bonds via N and O	[106]
	4-benzoylpyridine	Octahedral; Bridging NCS group	[106]
$[Ni(N_3)_2L_2]$	pyridine; 3-substituted pyridine	Octahedral; Bridging azide groups	[107]
$[Ni(O_2CH_2)_2L_2]$	2-aminopyridine	Octahedral; Bridging formato groups	[112]
$[Ni(O_2CR)_2L_2]$	3-, 4-substituted pyridine	Octahedral; Study of *cis*— *trans* interconversion.	[115]
$[Ni(NCS)_2(H_2O)_2L_2]$	pyridine; 3-substituted pyridine	*Trans*-octahedral	[107]
$[Ni(NCS)_2L_3]$	2-amino-3-methyl-, 2-amino-5-methylpyridine		[108]
$[Ni(NCS)_2L_2L'_2]$	4-methyl- , 4-phenylpyridine	Clahtrate; Crystal structure	[109]
$[Ni(NCS)_2L_4]$	4-methylpyridine	Clathrate; Crystal structure	[109]
	pyridine; 4-methylpyridine	Octahedral	[110]
	4-methylpyridine	Isomers	[111]
	3-substituted pyridine	*Trans*-octahedral	[107]
	3-benzoylpyridine	Octahedral	[106]
$[Ni(H_2O)_2L_4](PF_6)\cdot L_2$	3-methylpyridine	Octahedral; Crystal structure	[114]
$[Ni(SO_3Cl)_2L_4]$	pyridine	*Trans*-octahedral	[113]

similar composition have been isolated by other workers [108].

In addition to the above, pyridine complexes containing azide [107], and formato [112] ions as bridging moeities have been prepared. The complexes have the general formula, $[\mathrm{NiB_2L_2}]$ ($\mathrm{B}= \mathrm{N_3}^-$ or $\mathrm{CH_2O_2}^-$; L= pyridine or substituted pyridine), and are octahedral with the pyridine ligands occupying the trans-axial positions.

Siddiqi et al have synthesized the tetragonally distorted complexes, trans-$[\mathrm{Ni(SO_3Cl)_2L_4}]$ (L= pyridine, acetonitrile, pyridine N-oxide). In each case the chlorosulphate ion functions in a unidentate fashion occupying trans-axial positions [113]. The related complex, trans-$[\mathrm{Ni(H_2O)_2L_4}](\mathrm{PF_6})\cdot 2\mathrm{L}$ (L= pyridine) (37), is unusual in that two pyridine molecules are strongly associated, via hydrogen bonding, with the two coordinated water molecules ($-\mathrm{OH_2}\cdots\mathrm{NC_5H_5} = 2.718$ Å), as can be seen from the crystal structure [114].



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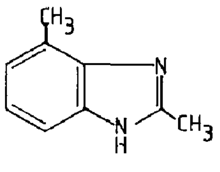
^{1}H-n.m.r. spin dynamics have been used to study the cis ⟷ trans interconversion of the complexes $[\mathrm{NiL_2(O_2CR)_2}]$ (L= 3-methyl-, 4-methyl- and 4-ethylpyridine; R= $\mathrm{CF_3}$, $\mathrm{CF_2H}$, $\mathrm{CFH_2}$, $\mathrm{C_2F_5}$ and $\mathrm{C_3F_7}$). The mechanism is dependent on the carboxylate ligand, and varies from associative to dissociative, in the sequence $\mathrm{R}= \mathrm{CF_3} < \mathrm{CF_2H} < \mathrm{CFH_2} < \mathrm{C_2F_5} < \mathrm{C_3F_7}$. Isomerism in the related $[\mathrm{NiL_4(O_2CR)}]$ complexes, where the $\mathrm{O_2CR}$ ligands are monodentate, was also studied and a more facile dissociative process was observed [115]. In contrast, a purely dissociative mechanism was found for the complexation of isoquinoline with Ni(II) in various solvents [116].

Imidazole and imidazole-type ligands have been used extensively in the formation of Ni(II) complexes. Cyanato nickel(II) complexes containing various substituted imidazoles have been prepared. These complexes vary in structure from trans-$[Ni(NCO)_2L_4]$(L= imidazole, 2-methyl- and 2-ethylimidazole) to trans-$[Ni(NCO)_2L_2(H_2O)_2]$(L= 1,2-dimethylimidazole), probably due to steric effects [117]. The steric effects of substituted imidazoles are further highlighted by a series of complexes,$[Ni(pnf)_2L_2]$ and $[Ni(pnf)_2L_2(H_2O)]$ (pnf= substituted phenolate; L= substituted imidazole), in which only two imidazole ligands coordinate [118]. In addition, the crystal structure of trans-$[Ni(NCS)_4L_2]$ (L= 5-{2-aminoethyl}imidazole-N^3) has been determined. The complex is remarkable in that only two imidazole ligands coordinate in a monodentate fashion, even though three coordination sites per ligand are available [119]. The effect of steric hindrance is exemplified in the extreme by the complexation of lophine (lophine= 2,4,5-triphenylimidazole) with Ni(II) perchlorate. The resultant complex, characterized spectroscopically, has been assigned a dimeric structure, $[(H_2O)_5Ni(L)Ni(OH_2)_5]$, in which a single lophine ligand coordinates in a bridging manner [120].

The interaction of 2,4(or 7)-dimethylbenzimidazole (38) with Ni(II) has been studied potentiometrically. The resultant complexes are less stable than their corresponding imidazole analogues. This instability has been assigned to the steric hindrance offered by the benzene ring [121]. A similar ligand, 2-methyl-5-nitrobenzimidazole (39), reacts with Ni halides yielding $[NiL_2Cl_2]\cdot H_2O$ and $[NiL_2Br_2]$ respectively. These complexes, although appearing similar, are quite different. The chloro complex is six-coordinate with bridging chloride moieties, while the bromo complex is four-coordinate with tetrahedral geometry [122]. In contrast, 3,4-dihydro-1-phenyl-1H-[1,4]-oxazino[4,3-a]benzimidazole (40) reacts with a variety of nickel salts yielding complexes of the type $[NiL_2X_2]$ (X= Cl^-,Br^-,$NO\ ^-$,NCS^-). These complexes are all essentially tetrahedral, with the exception of the thiocyanato analogue, which is square-planar [123].



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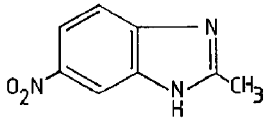

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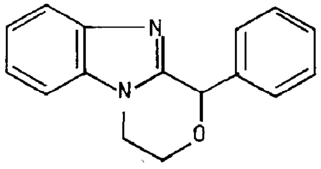
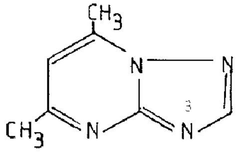


(40)

Pyrazole and tetrazole complexes have elicited some interest. The far infrared spectrum of $[NiSO_4L_2]$ (L= pyrazole) has been examined. The complex has the unusual feature of SO_4^{2-} functioning as a bidentate ligand, as well as exhibiting strong hydrogen bonding with the coordinated pyrazole molecules [124]. The hexakis complexes, $[NiL_6](BF_4)_2$ (L= pyrazole [125] and 2-methyl-tetrazole [126], have been prepared and characterized using single-crystal X-ray analysis. Both complexes exhibit an almost perfect octahedral array of ligands coordinated to the Ni(II) ion. In addition, pyrazine carboxamide reacts with the appropriate nickel salt, yielding the tetrakis complexes *trans*-$[NiL_4X_2]$ (L= pyrazine carboxamide; X= Cl, Br, I, NCS) [127].

5,7-Dimethyl 1,2,4 triazolo 1,5-a pyrimidine (41) reacts with $Ni(NCS)_2$ in aqueous solution to form $[Ni(NCS)_2(H_2O)_2L_2]$ (L= 41). The complex has a distorted octahedral geometry in which the pyrimidine ligands are *trans* to each other, while the thiocyanate and water ligands are *cis*. It was also shown that (41) has a clear preferance for coordination through N(3) [128].

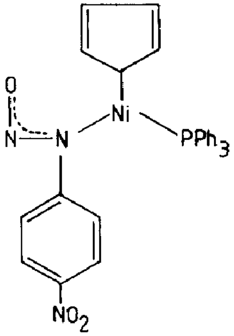


(41)

The synthesis and crystal structure of the Ni(II)-saccharin complex, $[Ni(H_2O)_4L_2]$ (HL= saccharin), has been described. Saccharin, being a bulky ligand, coordinates in the *trans*-axial positions, while the four water ligands occupy the square of the plane. Contrary to earlier speculation about the bonding, it has been shown that each saccharinato anion coordinates via nitrogen (average Ni-N distance of 2.154(1) Å),and not via the carbonyl oxygen atom [129].

Various aspects of the chemistry of Ni(II)-nitro complexes have been examined. Figgis *et al* have studied the electron distribution [130] and covalent bonding [131] in *trans*-$[Ni(NH_3)_4(NO_2)_2]$. In addition, the oxygen atom transfer reactions to CO of the nickel-nitro complexes, $[Ni(NO_2)_2L_2]$ (L= phosphine) [132] and $[Ni(NO_2)(S_2CNHR)(PBu^n_3)]$ (R= alkyl) [133], have been analysed using infrared and ^{31}P-n.m.r. spectroscopy.

Sodium *anti*-*p*-nitrobenzenediazoate reacts with $[Ni(\eta^5-C_5H_5)(PPh_3)Cl]$ to yield $[Ni(\eta^5-C_5H_5)(PPh_3)(ON_2C_6H_4NO_2-p)]$, which appears to be the first authenticated example of an arenediazato complex. The crystal structure reveals that the arenediazato ligand has an *anti* configuration and is coordinated to nickel via N(1) in a monohapto fashion (42). The coordination geometry of the Ni(II) ion is essentially planar with Ni-N(1)= 1.901(4), Ni-P = 2.166(1), Ni-C (cyclopentadienyl)= 2.103(6)-2.187(7), and Ni···O(1) = 2.784(4) Å [134].



(42)

In conclusion, hydrazinium complexes of the formula $(N_2H_5)_2Ni(C_2O_4)_2 \cdot nH_2O$ (n= 3, 2, 1) have been prepared,and their spectral, magnetic, and thermal properties investigated [135], while the complex [$NiLCl_3$] (L= N-methylbipyridine) has been proposed as a model for the intermediate formed during chelation of 2,2'-bipyridine [136].

1.3.3.2 Bidentate ligands

Ligands containing two nitrogen atoms have the ability to chelate or bridge, depending on the location and geometrical environment of the donor atoms. In this discussion, the chelating ligands are discussed first, followed by those that bridge.

The most widely studied bidentate nitrogen ligand is probably ethylenediamine (en), and its substituted analogues. Although most of the present work is concerned with the synthesis of mixed-ligand complexes of nickel(II) (see table 4), it is interesting to note that the structure of [$Ni(en)_3$]SO_4 has been determined at 110 K , in the presence of twinning. A reversible phase change has been observed during cooling, whereupon the crystal symmetry is lowered from $\bar{3}$m to $\bar{3}$, with twinning and superposition of the nonequivalent <u>hkl</u> and <u>khl</u> reflections occuring [137]. In addition to the above solid state work, the kinetics of chelate ring opening in $Ni(en)^{2+}$, catalyzed by hydrogen phosphate, has been studied. The rate of dissociation is first order in the nickel complex and depends upon the acidity and phosphate concentration [138].

Substituted ethylenediamine ligands have the added interest of steric interactions. N,N-diethylethylenediamine reacts with $Ni(NCS)_2$ yielding [$NiL_2(NCS)_2$] (L= $NH_2C_2H_4N(C_2H_5)_2$). The complex is all-trans, with significant

Table 4. Ethylenediamine and substituted ethylenediamine complexes of Ni(II).

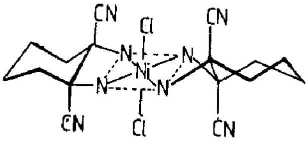
LIGAND (L)	COMPLEX	COMMENTS	Ref.
$H_2NCH_2CH_2NH_2$	$[NiL_3]SO_4$	Crystal structure	[137]
	$[NiL_2X_2]$ (X=$[NCC(O)NH_2]^-$, $[ONC(CN)C(CO)NH_2]^-$)	Distorted octahedral	[139]
	$[NiL_2XX']$ (X,X'= $ONC(CN)_2^-$, $N(CN)_2^-$,	Pseudooctahedral	[140]
	$[NiL_2XY]$ $C(CN)_3^-$; Y= NCS^-, $NCSe^-$)		
	$[NiL_2XY]\frac{1}{2}H_2O$ (X=*o*-Phthalato, Y= H_2O)	Distorted octahedral; Crystal structure	[141]
	$[NiL_2X]Y$ (X= NO_2^-; Y= NO_3^-)	*Cis*-octahedral	[142]
	$[Ni_2L_4C_2O_4]X_2$ (X= NO_3^-, ClO_4^-)	Dimeric octahedral	[142]
	$[Ni_2L_4(NCS)_2]X_2$ (X= I, ClO_4^-)	Dimeric octahedral	[142]
$H_2NCH_2CH_2N(C_2H_5)_2$	$[NiL_2(NCS)_2]$	All-*trans* configuration	[143]
$RHNCH_2CH_2NHR$ (=H_2L)	$[NiL_2(H_2O)_2]$ (R=*o*-aminobenzenesulphonyl)		[144]
$(i\text{-}C_3H_7)HNCH_2C(CH_3)_2NH_2$	$[NiL_2](ClO_4)_2$	*Trans*-square-planar configuration	[145]
$(CH_3)_2NCH_2CH_2N(CH_3)_2$	$[NiLL']$ (L= 3,4-dimethyl-pent-3-ene-carboxylic acid)		[146]

distortion due to bent Ni-NCS coordination, short Ni-NH_2 bonds (2.081 Å), and long Ni-$(C_2H_5)_2$ bonds (2.304 Å) [143]. Bis(o-aminobenzenesulphonyl)-ethylenediamine (H_2L) reacts with $NiCl_2$ in alcoholic KOH to give the octahedral complex $K_2[NiL_2(H_2O)_2]$, in which the NH_2 groups do not participate in coordination [144]. In addition, a potentiometric study of the complexation of N'-isopropyl-2-methyl-1,2-propanediamine with Ni(II) has been undertaken in aqueous perchlorate solution. Both the mono and bis complexes were observed, while the absence of the tris complex indicates the steric limitation of the ligand [145].

Tetramethylethylenediamine (tmen) and 2,2'-bipyridine have been used as stabilizing ligands in the oxidative coupling of CO_2 and olefins [146-148], CO_2 and azaolefins [149], CO_2 and alkynes [150-152], and alkynes and isocyanates [153]. Reaction takes place in the presence of electron-rich Ni(0) centres (e.g. $Ni(tmen)_2$ and $Ni(bipy)_2$), and yields novel nickela(II) heterocycles of the general formula [NiLQ] (L= tmen, bipy; Q= cyclic ligand formed in reaction), in which Ni-C, Ni-O and Ni-N bonds are present. Analagous nickela(II) cycloalkane complexes have been obtained when the Ni(0) centres are reacted with organic dihalides [154] and methylcyclopropane [155].

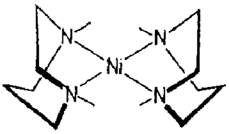
o-Aminobenzylamine reacts with NiX_2 (X= Cl, Br) to yield a variety of complexes with metal:ligand ratios of 1:1, 1:2, 1:3. According to spectroscopic evidence, the complexes $[NiLX_2]$(L= o-aminobenzylamine) are tetrahedral, while the complexes $[NiL_2X_2]$ and $[NiL_3]X_2$ are octahedral. In addition, an insoluble complex $[Ni_2L_3Cl_4]$ was also isolated. Indications are that this complex is octahedral and may involve ligand and chloro bridging moieties [156].

The complexation of the isomers of 1,2-dicyano-1,2-cyclohexanediamine with Ni(II) has been investigated. Only the trans isomer complexes to yield the suggested six-coordinate complex $[NiL_2X_2]$ (43) as shown below [157].



(43)

The crystal structure of bis(1,4-diazacycloheptane)nickel(II)chloride dihydrate is of interest since it is possible for the seven membered cyclic diamine ligand to coordinate in three different ways viz. the cis form (44), the trans form with the carbon chains pointing away from the metal ion (45), and the trans form with the three carbon chains pointing towards the metal ion (46). The crystal structure reveals that (45) exists in the solid state, and that octahedral coordination is prevented by steric hindrance of the axial sites by the hydrogen-carbon backbone of the ligand [158].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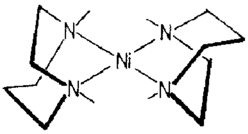
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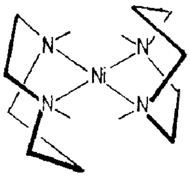
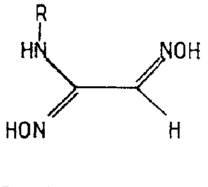
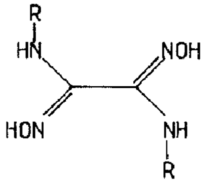

(46)

Dioxime ligands have been used extensively to complex with Ni(II) salts. Ethanedioldioxime reacts with anhydrous NiX_2 (X= Cl, Br) in non-aqueous medium to yield the mono adduct $[NiLX_2]$ (L= ethanedioldioxime). These complexes are diamagnetic having square-planar geometry [159].

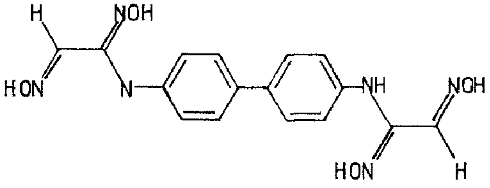
Many *bis* complexes have been synthesized using the basic dioxime framework to which various adducts have been attached. Sixteen Ni-complex pigment derivatives of 2,3-dioximes of arylides of 2,3-dioxobutyric acid have been synthesized [160], while the structure of *bis*[*bis*(diethylamino)glyoximato]nickel(II), which also has square-planar geometry, has been determined [161]. Bekâroglu *et al* have synthesized a number of Ni(II)-dioxime complexes. They have reacted 5,6-dihydrocyclopent[f,g]acenphthylene-1,2-dione dioxime (L) with $NiCl_2$ to yield the square-planar complex $[NiL_2]$ [162]. In addition, they have examined the stereoisomers of the nickel complex of 1,3-diphenyl-2-thioxo-4,5-*bis*(hydroxyimino)-imidazoline. Both the *anti* and *amphi* forms were separated and their structures identified spectroscopically. A mechanism for the interconversion of the two forms is suggested [163]. They have also synthesized a series of substituted amino and diaminoglyoximes of general formula (47), (48) and (49). Ligands (47) and (48) coordinate via the oxime



R = phenyl, 1-napthyl,
2-napthyl,
4-amino-1,1'-biphenyl
(47)



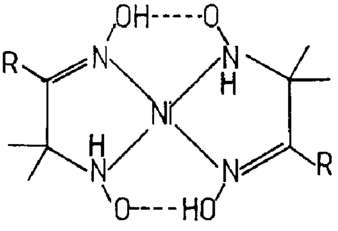
R= 1-napthyl, 2-napthyl
(48)



(49)

groups to yield monomeric square-planar complexes $[NiL_2]$, while ligand (49) yields square-planar polymeric complexes of the type $[NiL_2]_n$ [164].

α-Hydroxylamino-oximes (H_2L) react with Ni(II) yielding the inner-complex compounds $[Ni(HL)_2]$ (50). These complexes have been dehydrogenated resulting in complexes of the type $[NiL_2]$ (51). Magnetic and spectroscopic measurements indicate that both types of complex have square-planar geometry, and that the ligands in the latter complexes exist as aminyl (nitrosyl) radicals [165].



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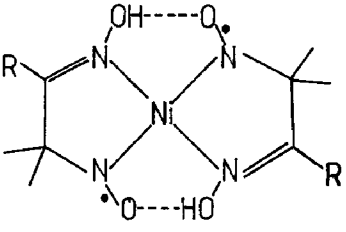


(51)

R= CH_3, C_6H_5

Pyridine-2-amidoxime (HL) reacts in its free form with various nickel salts yielding pseudooctahedral complexes of general formula $[Ni(HL)X_2]$ (X= Cl^-, Br^-, NO_3^-, ClO_4^-). The ligand coordinates via the nitrogen atoms of the pyridine ring and the oxime group. In its deprotonated form, the ligand complexes to form the square-planar complex $[NiL(OH)(H_2O)]$ [166].

Diacetylhydrazone-oxime reacts with $NiCl_2$ in absolute alcohol, resulting in the octahedral bis-oxime complex cis-$[NiL_2Cl_2]$. Coordination occurs via the nitrogen atoms of the oxime groups, with two chlorine atoms occupying the fifth and sixth coordination sites in a cis configuration as determined in the crystal structure [167].

The effect of bulky substituents on structure is demonstrated in the complex bis[N-methyl-1-(methylamino)-9-phenaleneaminato]nickel(II). The crystal structure shows distorted tetrahedral geometry for the nickel atom, with the two planar ligands perpendicular to each other [168].

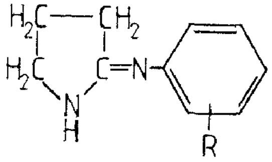
Positive ion electron-impact mass spectrometry has been used to study the nickel complexes formed with dimethylglyoxime, diphenylglyoxime, and α-furildioxime. The molecular ions were found to be very stable and a full analysis of the somewhat complicated spectra was done [169].

Another interesting analytical technique, laser Raman spectroscopy, has been used in the study of nickel α-diimine complexes. It was found that Raman spectroscopy is a sensitive technique for accurately determining the imine stretching frequency in α-diimine complexes of the type $[NiL_3](PF_6)_2$ (L= α-diimine ligand) [170].

Hydrazine and in particular substituted azines have been used extensively as ligands in the formation of nickel(II) complexes. An immersion analysis of the reaction products in the reaction of $[Ni(C_2O_4)(H_2O)_2]$ with N_2H_4 shows that the complexes $[Ni(C_2O_4)(N_2H_4)_n]$ (n= 1,2,3) were formed, with hydrazine being added via a topochemical mechanism [171]. Hydrazinium hydrazidocarboxylate, $N_2H_5COON_2H_3$, has been reacted with various metals. Reaction with Ni(II) yields the complex $N_2H_5[Ni(N_2H_3COO)_3]\cdot H_2O$, which exhibits a Ni-N stretching frequency of 415 cm^{-1} in its infrared spectrum [172].

Hexacoordinate complexes of Ni(II) containing substituted hydrazine ligands have been synthesized by Saha and Mallick [173], Rana and Shah [174], Rai et al [175], and Narang and Dubey [176], while tetracoordinate complexes have been prepared by Mishra et al [177,178], Kvitko et al [179], Lipunova et al [180] and Pokhodenko et al [181]. The hexacoordinate complexes are mostly octahedral containing one or two azine ligands, while the tetracoordinate complexes are planar, with the exception of $[NiL_2]$ (L= 5-amino-3-methyl-1-phenyl-4-[(phenylamino)methyl]pyrazole) [179], which has a tetrahedral structure.

A series of Schiff bases, produced by the condensation of 2-pyrolidene with aromatic amines (52), has been reacted with $NiSO_4\cdot 2H_2O$. The resultant complexes are square-planar, with coordination occurring via the NH and azomethine groups [182].



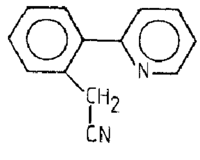
R= H, o-, m-, p-CH_3

(52)

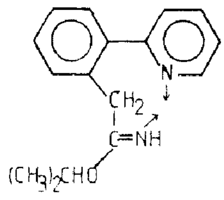
The reaction of $NiCl_2$ with 2-(2'-pyridyl)phenylacetonitrile in isopropanol has been studied. Of interest is the fact that the acetonitrile carbon atom is activated during coordination and reacts with solvent to form an azomethine group, as shown below [183].

$$NiCl_2 + L \longrightarrow [NiCl_2L_2] \xrightarrow{\text{i-propanol}} [NiCl_2L'_2]$$

L =



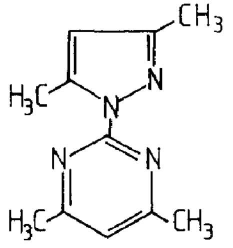
L' =



The chemistry and structural elucidation of nickel tetraazadiene complexes have been studied in great detail. The complexes,$[Ni(R_2N_4)_2]$ (R= aryl group), have been prepared by the reaction of *bis*(1,5-cyclooctadiene)nickel, or of *bis*(cyclopentadienyl)nickel with the aryl azides, $R{-}N_3$ (R= 4-MeC_6H_4, 4-MeO-C_6H_4 , 4-ClC_6H_4, 3,5-$Me_2C_6H_3$) [184-187]. The crystal structures of *bis*-1,4-*bis*(3,5-dimethylphenyl)tetraazabutadiene nickel [184] and 1,4-*bis*-(4-tolyl)tetraazabutadiene (cyclopentadienyl)nickel [185] have been determined. The former complex has pseudooctahedral geometry with two planar R_2N_4 ligands perpendicular to each other, while the latter has a planar NiN_4 ring, with the aryl substituents twisted 45° out of this plane. Finally, the Ni(II)/azide system has been studied potentiometrically , with the observation that a binuclear $Ni_2N_3^{3+}$ species coexists with the monoazide NiN_3^+ species at high nickel concentration [188].

Various 5,7-dihalo-8-aminoquinoline ligands have been complexed with Ni(II). The ligands coordinate via the amine and quinoline nitrogen atoms to form both monomeric and polymeric complexes, depending on the ligand and the nickel salt used. Monomeric octahedral structures have been assigned to $[NiL_2X_2]$ (L= 5,7-dibromo-8-aminoquinoline; X= Cl, Br, I, NCS), whereas polymeric structures have been proposed for the complexes $[NiL_2(NO_3)_2]$(L= 5,7-dihalo-8-aminoquinoline) and $[NiLCl_2]{\cdot}H_2O$ [189]. In addition, the coordination properties of 8-quinolinylmonoethylorthophosphate have been examined [190].

In a series examining the metal complexes of pyrimidine-derived ligands, 3,5-dimethyl-1-(4',6'-dimethyl-2'-pyrimidyl)pyrazole (53), a potential antitumour agent, has been reacted with NiX_2 (X= I^-, ClO_4^-, BF_4^-). The resulting *tris* complexes have the composition $[NiL_3]X_2$ with coordination occurring via N(1) and either N(1') or N(3') (see 53) [191]. In a similar series, the transition metal complexes of 6-methyl-2-aminobenzothiazole (54), have been studied. The ligand functions in a bidentate and monodentate fashion giving rise to the two series of complexes,$[NiL_2X_2]$and$[NiL_4X_2]$(X= I^-, NCS^-, OAc^-) respectively [192].



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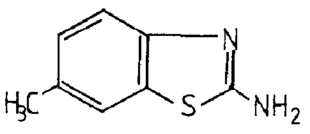
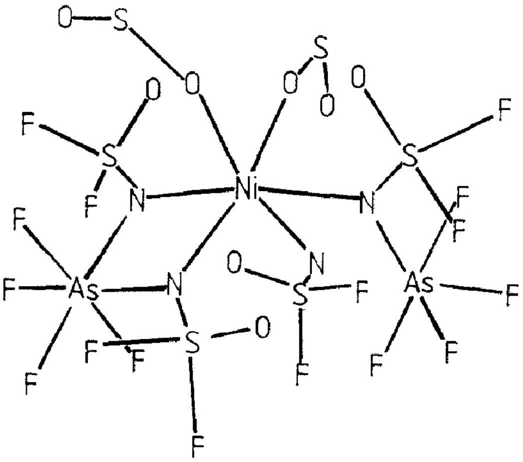


(54)

The reaction of $[Ni(SO_2)_2](AsF_6)_2$ with $R_3SiNSOF_2$ in liquid SO_2 , yields the *bis*(imidodifluorosulphate) complex $[Ni(NSOF_2)_2]$. An interesting intermediate, $[Ni(SO_2)_2\{AsF_4(NSOF_2)_2\}_2]$, was isolated during the reaction. The crystal structure confirms an octahedral configuration with an unusual bidentate nitrogen-donor ligand (55) [193].



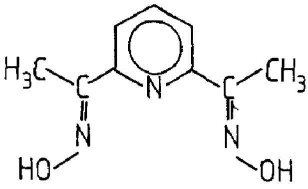
(55)

Azoles represent a class of ligand which, apart from their ability to act as monodentate ligands, have the ability to function as bridging ligands. 1,2,4-Triazole, 5-aminotetrazole and 4-n-butyl-4H-1,2,4-triazole have been reacted with $NiCl_2$, yielding the polymeric complexes, $[NiL_2Cl_2]$[194], $\{NiLCl_2\}$ [195] and $\{NiL_4Cl_2\}$ [196], respectively. In addition, 5-nitrobenzimidazole reacts with $Ni(OAc)_2$ in the presence of base, to yield the polymeric octahedral complex $[NiL_2(H_2O)_2]$ [197]. The azole ligand functions as the bridging moeity in all of the above complexes.

1.3.3.3 Polydentate ligands

2,6-Diacetylpyridine dioxime (56) coordinates to Ni(II) in a tridentate fashion, giving rise to a variety of coordination geometries, depending on the nickel salt used. The *mono* complexes $[NiLX_2]$ (L= 56) are pentacoordinate when X= Cl^- , Br^- , I^- , and hexacoordinate when X= NCS^- , $NCSe^-$, NO_3^- , whereas the *bis* complexes $[NiL_2]X_2$ all involve octahedral coordination [198]. A similar ligand, 2-(α-pyridylmethyl)imino-3-butanone oxime (57) yields octahedral complexes of the type NiL_2X_2 (X= Br^-, I^-, NCS^-, NO_3^-, ClO_4^-) [199].

Potassium hydrotris(1-indazolyl)borate (58) reacts with $NiCl_2$, yielding the ionic complex $[NiL]Cl$ (L= 58), in which (58) functions as a negative tridentate ligand. Infrared spectroscopy suggests that coordination occurs via both the pyridyl and pyrrole nitrogen atoms, while the magnetic moment is slightly lower than that expected for octahedral coordination [200].



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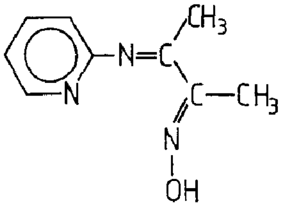

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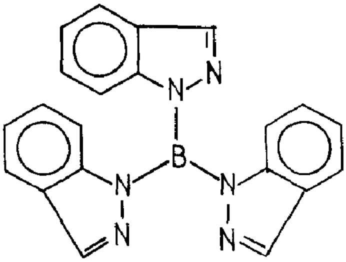
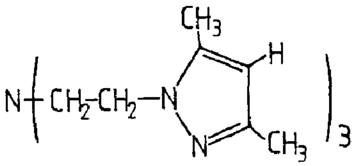


(58)

The effect of ring size on the kinetics of ternary complex formation at Ni(II) has been investigated. Stopped-flow and temperature jump relaxation methods were used to measure the rate constants for the formation and dissociation in aqueous solution of the ternary complexes NiL (L= diethylenetriamine, ethylenepropylenetriamine, dipropylenetriamine) with L' (L'= 2,2'-bipyridine, pyridine-2-azo-p-dimethylaniline, 5-nitrosalicylic acid, 8-quinolinol) [201]. In addition, potentiometric techniques have been used to study the complexation of 1,1,1-tris(N-methylaminomethyl)ethane with Ni(II). The chemical model that was found to fit the experimental data best involved the formation of a single complex, $[NiL_2]^{2+}$ [202].

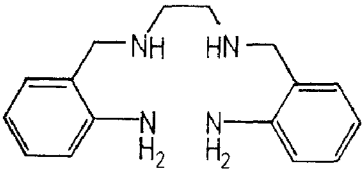
Tripod ligands and their metal complexes have generated much interest recently. The tetradentate ligand, tris(3,5-dimethyl-1-pyrazolylethyl)amine (59), has been reacted with Ni(II). Distortional isomerism has been observed for the pentacoordinate complex cation $[NiBrL](BPh_4)$(L=59) via the X-ray analysis of the two compounds, $[NiBrL](BPh_4)\cdot C_2H_5OH$ and $[NiBrL](BPh_4)\cdot(CH_3)_2CO$. The two isomers have trigonal bipyramidal and square-based pyramidal structures respectively [203].



(59)

In addition, the X-ray crystal structure of [$NiL(NCS)_2$], where L= 2,2',2''-triaminotriethylamine, has been redetermined. Quasi-octahedral coordination is observed with average Ni-N(L) and Ni-NCS bond lengths of 2.12 and 2.09 Å respectively [204].

Two tetramines, 2,3:10,11-dibenzo-1,5,8,12-tetraazadodecane (60) and 3,4:9,10-dibenzo-1,5,8,12-tetraazadodecane (61), have been synthesized and reacted with $Ni(NCS)_2$. Both ligands form octahedral complexes,[$NiL(NCS)_2$], in which the thiocyanato groups are trans to each other [205].



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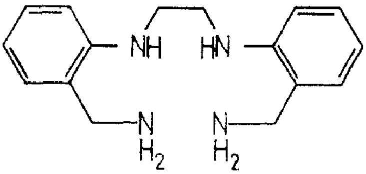
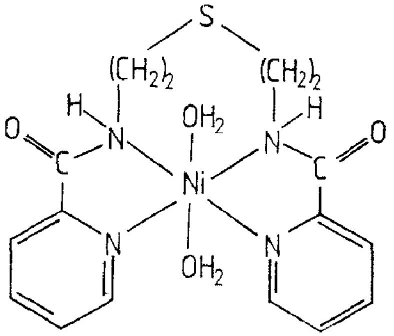


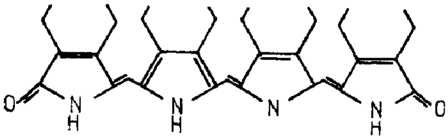
(61)

The synthesis and complex formation of bis(2,2'-picolinoylaminoethyl)-sulphide has been investigated. The potentially pentadentate ligand functions as a tetradentate ligand to form the complex [$NiL(H_2O)_2$] (62) in which coordination occurs via the pyridyl and amide nitrogen atoms [206].



(62)

Octaethyl-21H,24H-bilin-1,19-dione (63), a linear tetrapyrrole,complexes with Ni(II) to yield a 1:1 complex, the crystal structure of which has been determined. The nickel atom is coordinated to four pyrrole nitrogen atoms in a severely distorted square-planar arrangement, while the bilindione ligand has a helical conformation [207].



(63)

1.3.4 Phosphorous-donor ligands

1.3.4.1 Monodentate ligands

Apart from their interest as ligands, trialkyl- and triarylphosphine compounds have been used with great effect in the stabilization of complexes containing nickel-carbon σ-bonds. New synthetic methods have resulted in an expansion of the number of well-characterized alkyl-nickel(II)-phosphine complexes (see table 5).

$[Ni(CF_3)Br(PEt_3)_2]$ and $[Ni(CF_3)_2(PEt_3)_2]$, have been prepared by the reaction of $[NiBr_2(PEt_3)_2]$ with $(CF_3)_2Cd\cdot(CH_2OCH_3)_2$ [208]. Co-condensation of nickel metal vapour with CF_3 radicals, generated by radio-frequency glow discharge, yields the unstable complex $[Ni(CF_3)_2]$, which has been stabilized by trapping with $P(CH_3)_3$ to give $[Ni(CF_3)_2(PMe_3)_3]$ [209]. In addition, four new alkylnickel(II)-phosphine complexes, $[NiL_2(PR_3)_2]$ (L= CH_3, CH_2CH_3; R= ethyl, n-butyl), have been prepared by the reaction of $[Ni(acac)_2]$ with $AlL_2(OC_2H_5)$ in the presence of the phosphine ligands [210].

Complexes of the type $[NiLX(PR_3)_2]$ (L= C_6Cl_5, 2-Br-C_6H_4; X= halide or pseudohalide; R= alkyl) have been prepared by various routes [211,212],and have proved to be useful as synthetic intermediates. Cyclic α-alkoxyvinyl-nickel(II) complexes of the type trans-$[NiL(C{:}CHCH_2CH_2O)(PR_3)_2]$ and trans-$[NiL(C{:}CHCH_2CH_2CH_2O)(PR_3)_2]$ have been synthesized from $[NiLX(PR_3)_2]$ and 2,3-dihydro-5-lithiofuran and 2,3-dihydro-6-lithiopyran respectively. Treatment of these complexes with $HClO_4$ yields the corresponding cationic cyclic carbene complexes, trans-$[NiL(C{:}CH_2CH_2CH_2O)(PR_3)_2](ClO_4)_2$ and trans-$[NiL(C{:}CH_2CH_2CH_2CH_2O)(PR_3)_2](ClO_4)$[213]. The crystal structures of trans-$[Ni(C_6Cl_5)(C{:}CHCH_2CH_2O)(PMe_3)_2]$ and trans-$[Ni(C_6Cl_5)(C{:}CH_2CH_2CH_2O)(PMe_3)_2]$-$(BF_4)$ have been determined. Comparison of these structures suggests strong π-bonding in the nickel-carbene bond [214].

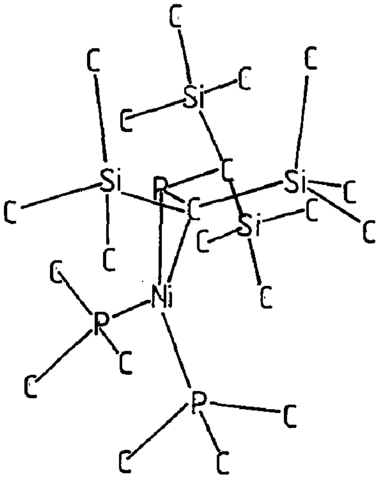
^1H- and ^{31}P-n.m.r. have been used to study the intermolecular exchange of the tertiary phosphine and halide ligands in trans-$[NiLX(PR_3)_2]$ (L= C_6Cl_5, $ClC{:}CCl_2$, $C_6H_2Me_3$-2,4,6; X= Cl, I, N_3, NCS; R= Me, Ph) [215]. In addition, the intermolecular exchange occuring in trans-$[NiL_2(PR_3)_2]$ has been investigated, and a dissociative mechanism involving a three-coordinate inter-

Table 5. Ni(II) complexes containing monodentate phosphorous-donor ligands.

COMPLEX	COMMENTS	Ref.
$[Ni(CF_3)Br(PEt_3)_2]$		[208]
$[Ni(CF_3)_2(PEt_3)_2]$		[208]
$[Ni(CF_3)_2(PMe_3)_3]$		[209]
$[NiL_2(PR_3)_2]$ (L= Me, Et; R= Et, n-butyl)		[210]
$[Ni(C_6Cl_5)X(PCy_3)_2]$ (X= Cl^-, I^-, NCS^-, NCO^-, N_3^-: Cy= cyclohexyl)		[211]
$[Ni(2\text{-}Br\text{-}C_6H_4)Br(PPh_3)_2]$	Electrogenerated species	[212]
$[NiL(\overline{C:CHCH_2CH_2O})(PR_3)_2]$ (L= C_6Cl_5, $C_6H_2Me_3$-2,4,6; R= Me, Ph)	Square-planar; Crystal structure	[213]
$[NiL(\overline{C:CH_2CH_2CH_2O})(PR_3)_2]BF_4$ (L= C_6Cl_5, $C_6H_2Me_3$-2,4,6; R= Me,Ph)	Square-planar; Crystal structure	[214]
$[NiLX(PR_3)_2]$ (L= $ClC:CCl_2$, C_6Cl_5; X= Cl^-,I^-,N_3^-,NCS^-; R= Me, Ph)	N.m.r. exchange study	[215]
$[NiL_2(PR_3)_2]$ (L= $C_6H_3(OMe)_2$-2,6; R= Me, Ph)	*Trans* configuration	[216]
$[NiLCl(PR_3)_3]$ (L= $C_6H_3(OMe)_2$-2,6; R= Me, Ph)	*Trans* configuration	[216]
$[Ni(\eta\text{-}C_5H_4PPh_3)(PPh_3)_2](PF_6)_2$		[217]
$[Ni(C_5H_5)X(R_2PX)]$ (X= Cl, Br; R= t-Bu)		[218]
$[NiH(succinimido)(PCy_3)_2]$	*Trans* configuration; Ni hydride	[219]
$[Ni\{(Me_3Si)_2CPC(H)(SiMe_3)_2\}(PMe_3)_2]$	η^2-phosphaalkene complex; Crystal structure	[220]
$[NiX_2(Ph_2PCH_2SR)_2]$ (X= Cl^-,Br^-,I^-,NCS^-; R= Me, Ph)	Isomers in solution	[221]
$[NiX_2(\overline{B_{10}H_{10}CHC}PPh_2)_2]$		[222]
$[Ni(Se_2CNEt_2)Cl(PEt_3)]$		[223]

mediate suggested [216].

Phosphaalkenes, RP:CR$'_2$, have the ability to function as η^1 (P donor) or η^2 (P=C π-donor) ligands. To date only the η^1 behaviour has been demonstrated. However, this has been rectified by the synthesis and structural determination of the η^2-phosphaalkane complex [Ni{(Me$_3$Si)$_2$CPC(H)(SiMe$_3$)$_2$}(PMe$_3$)$_2$] (64). Coordination occurs via a P=C π-donor and two PMe$_3$ moeities, while the geometry at nickel is square-planar [220].



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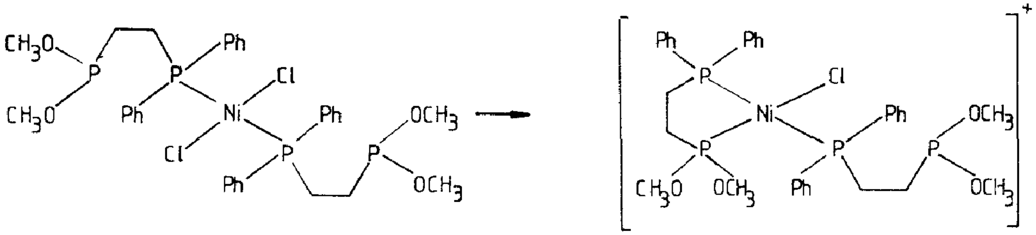
In an ongoing study, the coordination properties of phosphinomethylthioethers with Ni(II) have been reported. Complexes of the type [NiX$_2$(Ph$_2$CH$_2$SR)$_2$] (X= Cl, Br, I, NCS; R= CH$_3$, Ph) in which the phosphinomethylthioethers function as monodentate phosphorous donor ligands, have been isolated. The isothiocyanate complexes are diamagnetic, both in solution and the solid state and are assigned a <u>trans</u>-square-planar configuration. The halide complexes are square-planar or distorted tetrahedral in the solid state, while in solution they exhibit square-planar ⟷ distorted tetrahedral equilibrium [221].

1.3.4.2 Bidentate ligands

Ph$_2$PCH$_2$CH$_2$P(OCH$_3$)$_2$ reacts with Ni(II) yielding the square-planar complex [NiL$_2$Cl$_2$] (65). This complex undergoes a metathetic reaction with NH$_4$PF$_6$ to form the diamagnetic complex [NiL$_2$Cl PF$_6$] (66), in which the less basic (CH$_3$O)$_2$P-phosphorous arm of one of the diphosphines has displaced one of the chloride ligands [224].



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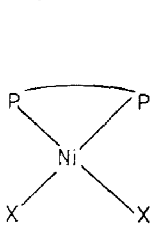
The long chain diphosphine, 1,8-bis(diphenylphosphine)octane, has been reacted with various nickel salts, yielding complexes of the type $[NiLX_2]$ ($L = Ph_2P(CH_2)_8PPh_2$; X= Cl, Br, I, NCS). The coordination sphere of the nickel atom is pseudotetrahedral for the halide complexes, and square-planar for the thiocyanate complex. Molecular-weight data indicate that $[NiLI_2]$ exists as a dimer in chloroform, with bridging diphosphine ligands [225].

The use of nickelocene as a reagent in the synthesis of complexes of the type $[Ni(\eta^5\text{-}C_5H_5)(L)]X$ (L= diphosphine or diarsine; X= halide or pseudo-halide) has been thoroughly investigated [226-230]. Nickelocene itself provides a direct route, while the reduced complex $[Ni(\eta^5\text{-}C_5H_5)(C_5H_6)]BF_4$, formed by the reaction of HBF_4 with nickelocene, provides a reactive and versatile intermediate.

Far infrared spectroscopy has been used to determine the stereochemistry of the diphosphine complexes $[NiLX]$ (67), $[NiL_2X]ClO_4$ (68), and $[NiL_2](ClO_4)_2$ (69) ($L = Ph_2PN(Ph)PPh_2$; X= Cl, Br, I, NCS). (67) is square-planar with C_{2v} symmetry, (68) is square-based pyramidal with C_{4v} symmetry, while (69) is square-planar with D_{2h} symmetry [231]. Square-based pyramidal geometry has also been observed for bromo-bis(bisdiphenylphosphinoethylene)nickel(II) tetraphenylborate, the crystal structure of which has been determined [232].



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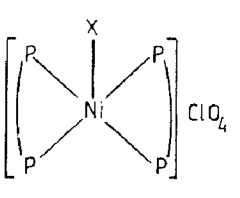

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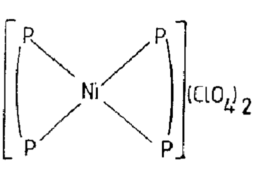
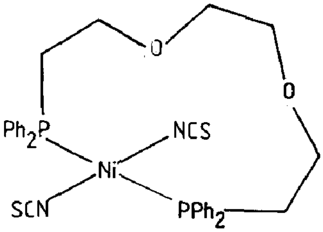


(69)

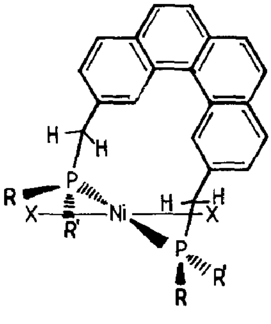
The preparation of the square-planar nickel(II)-dichloro complexes containing (R)-1,2-bis(diphenylphosphino)propane, (2S,3S)-2,3-bis(diphenylphosphino)butane and (R)-1,2-bis(diphenylphosphino)-1-phenylethane has been reported [233]. The complexes have been characterized using circular dichroism and ^{1}H- and ^{31}P-n.m.r. spectroscopy. In addition, the use of (-)-(S,S)-2,3-bis(diphenylphosphino)butane nickel(II)chloride as a catalyst in the synthesis of optically active olefins has been described [234] and the crystal structure of the essentially square-planar complex [$NiBr_2L$] (L= trans-bis-1,2-(diphenylphosphino)cyclopentane) determined [235].

Diverse donor properties have been exhibited by the facultative diphosphine diether ligand, 1,8-bis(diphenylphosphino)-3,6-dioxaoctane. Reaction with various nickel salts leads to the isolation of [$NiLX_2$] (X= Cl, Br, I, NCS). In the solid state these complexes are pseudotetrahedral (X= Cl, Br) or distorted square-planar (X= I), while in CH_2Cl_2 they are all planar. A single-crystal X-ray analysis of the thiocyanate complex reveals that the complex exists as a monomeric planar species with the diphosphine coordinating in a trans-bidentate manner (70). The pseudooctahedral complex [$NiLCl_2$]·$4H_2O$ and the planar complex [$NiL(H_2O)_2$]$(BF_4)_2$ have also been isolated [236].



(70)

The ditertiary phosphine ligands, 2,11-bis(dialkyl- or diphenylphosphinomethyl)benzo[c]phenanthrene, which have the ability to span trans positions, have been reacted with various nickel salts. The resulting complexes, [$NiLX_2$] (X= Cl, NCS) have been assigned structures of the type shown (71). An n.m.r. study of the complexes provides evidence for a "fan-like" motion of the benzo[c]phenanthrene moeity over the plane of the complex [237].



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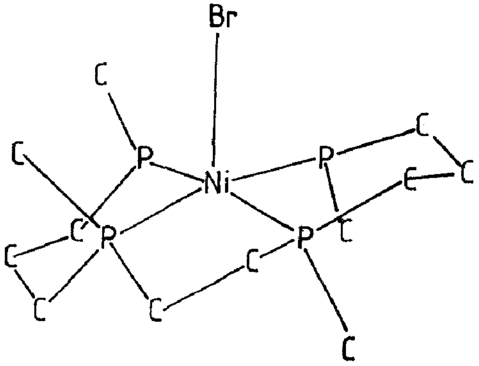
1.3.4.3 Polydentate ligands

The triphosphine ligands $RP[CH_2CH_2P(OCH_3)_2]_2$ (R= CH_3, C_6H_5) readily form complexes of stoichiometry $[NiLCl_2]$ (L= triphosphene). Conductivity measurements indicate that the complexes are tetracoordinate having molecular formula [NiLCl]Cl, while near infrared spectroscopy indicates a square-planar geometry [224].

$NiBr_2$ and the tetraphosphaalkane ligands RR'-$(CH_2)_3$-PCH_3-$(CH_2)_m$-PMe-$(CH_2)_3$-PRR' (R=Me, R'= H, Me; m= 2,3) react to form complexes of the type [NiLBr]Br , in which the tetraphosphaalkane functions as a tetradentate ligand. ^{31}P-n.m.r. indicates that the complexes exist as two, four, or more configurational isomers in solution, depending on the nature of R and R', while UV/visible spectra suggest square-based pyramidal coordination at the nickel atom. The X-ray analysis of a configurational isomer of $[Ni(CH_3HP$-$(CH_3)_2$-PCH_3-$(CH_2)_2$-PCH_3-$(CH_2)_2$-$PHCH_3)Br]Br$ (72) verifies the geometry [238].



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1.3.5 Mixed-donor ligands

1.3.5.1 N,O-donor ligands

These complexes have been the subject of much interest, and in particular, ligands derived from the condensation reactions of carbonyl compounds with primary amine derivatives, such as Schiff bases, hydrazones, semicarbazones, carbazones, oximes and azines, have been studied extensively.

The stereochemistry of four- and five-coordinate Schiff base complexes has been discussed in a recent review [239].

Solution studies of the complexation of various bidentate Schiff bases with Ni(II) have been undertaken. Complexation usually occurs via a deprotonated hydroxyl group and an azomethine nitrogen atom [240-244]. A noticeable exception is the Schiff base derived from vanillin and sulphanilic acid, which coordinates via a methoxy oxygen atom instead of the azomethine nitrogen atom [245]. The formation constants of Ni(II) with the potentially tridentate ligands, N-4-methylphenacylidene-anthranilic acid [246] and 2-[(1H-benzimidazol-2-ylmethylene)amino]phenol [247] have been determined. The former ligand forms 1:2 complexes, while the latter favours a less sterically hindered 1:1 complex. In addition, the intramolecular isomerization of bis[N-(2-piperidinoethyl)salicylaldimato]nickel(II) has been examined [248].

A substantial number of Ni(II)-Schiff base complexes have been isolated in the solid state. Some of these are listed in table 6. As a result of their mode of coordination, bidentate Schiff bases usually result in the formation of complexes of the type $[NiL_2]$ [249-253] and $[NiL_2(H_2O)_2]$ [254-256] (L= deprotonated Schiff base). The coordination geometry of the tetracoordinate complexes varies from planar to tetrahedral depending on the steric nature of the ligand, while the diaquo complexes are usually octahedral.

Tridentate Schiff bases containing N- and O-donor atoms may coordinate via an N_2O [258] or O_2N [259-264] donor set. Monobasic ligands usually yield octahedral complexes of the type $[NiL_2]$ [259], while dibasic ligands yield hexacoordinate complexes of the type $[NiL(H_2O)_3]$ [258,261], as well as tetrahedral [262] and square-planar [260] complexes of molecular formula $[NiL(H_2O)]$.

A variety of methods have been used in the synthesis of Ni(II) complexes of tetradentate Schiff bases. These include, preparation of the ligand prior to complexation, usually by the condensation of a suitable α-hydroxyaldehyde with a diamine [265-270], the use of template reactions [271], and by reaction in situ [272-273]. Although O_3N, O_2N_2 and ON_3 donor sets are possible, the most common tetradentate donor set is O_2N_2 [265-274]. The majority of ligands are dibasic and react with Ni(II) in their deprotonated form to yield square-planar complexes of the type [NiL] [265-269,274].

[2-[[[2-[[2-[[[-(1-azirindinyl)ethyl]imino]methyl]phenoxy]ethyl]amino]-ethyl]imino]methyl]phenolato]nickel(II) bromide dihydrate, an intermediate formed during the reaction of bis[N-[2-(1-aziridinyl)ethyl]saicylaldimino]-nickel(II) with HBr, has been isolated and characterized by X-ray crystallography. Effectively, a template synthesis has taken place, yielding a hexadentate ligand (73) which is coordinated to nickel via all its functional

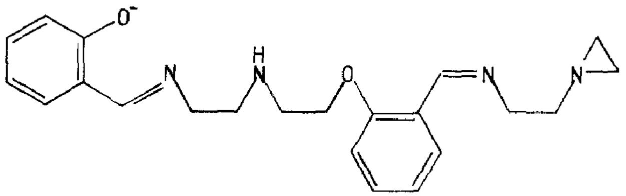
Table 6. Some Schiff base ligands and their Ni(II) complexes.

LIGAND	COMPLEX	COMMENTS	Ref.
2-Salicylideneamino-S-phenyl-1,3,4-oxadiazole (HL)	$[NiL_2]$	Tetrahedral	[249]
N-[1-(2,5-dihydroxyphenyl)ethylidene]aniline (HL)	$[NiL_2]$	Antifungacide	[250]
1-Methoxy-2,6-di-t-butylbenzene-4-salicylaldimine (HL)	$[NiL_2]$	Suare-planar or tetrahedral depending on substituent	[251]
N-cyclohexylsalicylideneamine (HL)	$[NiL_2]$	Square-planar; Crystal structure	[252]
N-methylsalicylaldimine (HL)	$[NiL_2]$	Phase transitions in solid state	[253]
2-Acetylacetonimino-5-(p-anisyl)-1,3,4-oxadiazole (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[254]
4'-Nitrobenzylidene-2-hydroxy-3,5-dinitroaniline (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[255]
Benzoiniminobenzene (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[256]
N-6-methylbenzothiazol-2-yl-salicylaldimine (HL)	$[NiL_2(L')_2]$	Octahedral;L'= 2-CH_3-benzimidazole	[257]
o-(N-α-pyrrolideneimino)benzenesulphonic acid (H_2L)	$[NiL(H_2O)_3]$	Octahedral	[258]
2-(N-α-pyrrolideneimino)ethanesulphonic acid (H_2L)	$[NiL(H_2O)_3]$	Octahedral	[258]
Furfural-R; (R= glycine, α-alanine, α-valine) (HL)	$[NiL_2]$	Octahedral	[259]
Salicylidene-o-aminophenol (H_2L)	$[NiL(H_2O)]$	Distorted planar	[260]
Salicylidene-2-hydroxynapthaldehyde (H_2L)	$[NiL(H_2O)_3]$	Octahedral	[261]
2-(2,4-Dihydroxyacetophenoneimino)ethanol (H_2L)	$[NiL(H_2O)]$	Tetrahedral	[262]
Salicylideneglycinato (H_2L)	$[NiL_2(H_2O)_2]$	Octahedral	[263]
	$[NiL(H_2O)_2]_2$	Octahedral dimer	[263]
Salicylidene-o-hydroxybenzene (H_2L)	$[NiL_2]$		[264]

Table 6. continued.

LIGAND	COMPLEX	COMMENTS	Ref.
N,N'-*isopropylene*-*bis*(2-OH,3-Br,5-CH_3-benzophenone-imine) (H_2L)	[NiL]	Square-planar	[265]
N,N'-butylenediamine-*bis*(2,5-dihydroxyacetophenone) (H_2L)	[NiL]	Square-planar	[266]
N,N'-(1,3-trimethylene)-*bis*(2-oxy-1-napthaldimine) (H_2L)	[NiL]	Tetrahedral	[267]
N,N'-ethylene-*bis*(salicylideneimine) (H_2L)	[NiL]	Square-planar; Crystal structure	[269]
N,N'-(1,3-trimethylene)-(β-hydroxy-α-napthaldehyde)-(pyrrole-2-carbaldehyde) (H_2L)	[NiL(py)]	Square-based pyramidal	[270]
N,N'-ethylene-*bis*(acetylacetoneimine) (H_2L)	[NiL]	Square-planar; Crystal structure	[274]
2-[[[2-[[2-[2-[[[2-(1-aziridinyl)ethyl] imino] methyl] -phenoxyl] ethyl] amino] ethyl] imino] methyl] phenol (HL)	[NiL]Br	Distorted octahedral	[275]

groups [275].

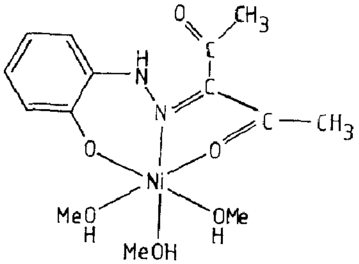


(73)

Hydrazone ligands are very similar to imines and as a result coordinate to Ni(II) in a similar fashion. Table 7 lists some hydrazone ligands and their Ni(II) complexes.

Bidentate hydrazone ligands [276-280], like their Schiff base counterparts, tend to coordinate via a deprotonated hydroxyl group and an azomethine nitrogen atom. 2-Aceto-1-napthol-N-benzoyl hydrazone is an interesting ligand that exhibits variable coordination. In its neutral form it coordinates via the azomethine nitrogen and carboxyl oxygen atoms to yield the octahedral complex $[Ni(HL)_2Cl_2]$, while in its deprotonated form it coordinates via the same two functional groups as well as the deprotonated hydroxyl group.

Tridentate hydrazone ligands containing an ON_2 donor set tend to be monobasic and yield complexes of the type $[NiLX]$ (X= halide ion), most of which are square-planar [281-283]. Those containing an O_2N donor set tend to be dibasic and yield octahedral complexes of the type $[NiL_2]$ [284-287]. 2-(2-hydroxyphenyl)hydrazonopentane-2,4-dione is of interest since it forms 1:1 and 1:2 (Ni:L) chelates. The *mono* chelate, $[NiL(MeOH)_3]NO_3$ has three coordinated methanol ligands (74), whereas the *bis* chelate is a more conventional octahedral *bis* chelate, $[NiL_2]$ (75) [285].



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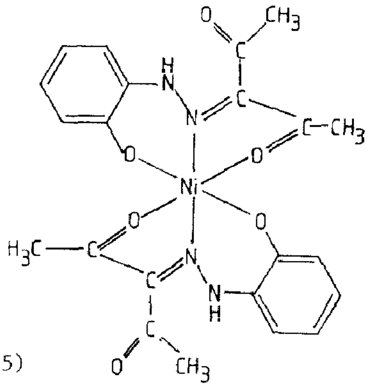


(75)

Reaction of the hexadentate dihydrazone ligands, *o*-$HO-C_6H_4CH:NNHC(CO)-(CH_2)_nC(O)NHN:CHC_6H_4-OH$-*o* (n=1,4) ($H_4L$) with Ni(II) may occur with two or four deprotonation steps. Double deprotonation yields the mononuclear complex $[Ni(H_2L)]$, whereas the binuclear complex $[Ni_2L(H_2O)_4]$ is formed when four

Table 7. Some hydrazone ligands and their Ni(II) complexes.

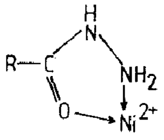
LIGAND	COMPLEX	COMMENTS	Ref.
2-Aceto-1-napthol-N-benzoyl hydrazone (HL)	$[Ni(HL)_2Cl_2]$	*Trans*-octahedral	[276]
	$[NiL_2]$	Octahedral	[276]
Resacetophenone phenylhydrazone (H_2L)	$[Ni(HL)_2]\cdot 2H_2O$	Square-planar	[277]
2-Picolyl-phenylketone benzoylhydrazone (HL)	$[NiL_2]$	Square-planar	[278]
Benzil-2,4-dinitrophenyl hydrazone (L)	$[NiLX_2]$	Square-planar; X= Cl^-,Br^-,NO_3^-	[279]
	$[NiL_2](ClO_4)_2$	Square-planar	[279]
	$[NiL_2(NCS)_2]$	Octahedral	[279]
Biacetylmonoxime-N,N-dimethylglycine hydrazone (L)	$[NiL_2(H_2O)_2]Cl_2$	*Trans*-octahedral	[280]
Isatin pyridylhydrazone (HL)	$[NiLCl]$	Tetrahedral	[281]
Isatin quinolylhydrazone (HL)	$[NiLBr]$	Square-planar	[281]
Salicylidene-2-hydrazinobenzoxazole (HL)	$[NiLCl]$	Square-planar	[282]
1,1,1-Trifluoro-4-(nitroguanylhydrazono)pent-2-one (H_2L)	$[NiLX]$	Square-planar; X= H_2O,pyridine	[283]
Methylpyruvate-N-benzoyl hydrazone (HL)	$[NiL_2]$	Octahedral	[284]
2-(2-Hydroxyphenyl)hydrazonopentane-2,4-dione (HL)	$[NiL(MeOH)_3]NO_3$	Octahedral	[285]
	$[NiL_2]$	Octahedral	[285]
Methyl-2-(N-acetylhydrazono)propionic acid (HL)	$[NiL_2]\cdot 2H_2O$	Distorted octahedral; Crystal structure	[286]
Biacetylmonoxime-salicoyl hydrazone (HL)	$[NiL_2]$	Octahedral	[287]
Diacetylmonoxime-benzoyl hydrazone (H_2L)	$[Ni(H_2L)(H_2O)Cl_2]$	Octahedral	[288]

protons are removed [289].

The nickel(II) complexes of benzil semicarbazone [290], benzalacetone semicarbazone and dibenzalacetone semicarbazone [291] have been prepared. Benzil and dibenzalacetone semicarbazone form the square-planar complexes [$NiLX_2$]($X= Cl^-$, NO_3^-, NCS^-), while benzalacetone semicarbazone yields both square-planar [$NiL(NCS)_2$] and [NiL_2]$(ClO_4)_2$, as well as the octahedral complexes [NiL_2X_2]($X= Cl^-$, NO_3^-). Dependence of stereochemistry on the variation of anion is further manifested in the complexes of acetone semicarbazone and ethylmethylketone semicarbazone. In this case the thiocyanato and nitrato complexes are octahedral, whereas the chloro and sulphato complexes are trigonal bipyramidal in structure [292]. In addition to the above, the complexation of variously substituted derivatives of diphenylcarbazone has been investigated in aqueous dioxane [293].

Thiosemicarbazone ligands and their complexes have also generated much interest. 1-Isovaleryl-4-phenyl-3-thiosemicarbazide [294] and 1-acetyl-trimethylammoniumchloride-4-phenyl-3-thiosemicarbazide [295] react with $NiCl_2$ yielding square-planar [NiL_2] and octahedral [NiL_2Cl_2] respectively. 1,4-Napthaquinone thiosemicarbazone complexes in a similar fashion with coordination occuring via the NH and enol O^- groups [296]. The tridentate ligand, benzoin thiosemicarbazone, however, coordinates via the thiocarbonyl sulphur as well as the NH and O^- groups [297].

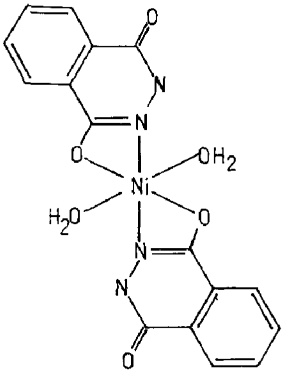
Octahedral tris complexes of Ni(II) with 3-nitrobenzoic acid hydrazide [298] and variously substituted halobenzoyl hydrazine ligands [299] are good examples of the mode of coordination favoured by hydrazine ligands in general. Coordination occurs via the amino and carbonyl groups thereby facilitating a stable five-bond chelate ring (76). This mode of coordination is also favoured by benzoyl hydrazine in its mixed ligand complex with ethylenediamine [300].



(76)

Formyl hydrazide, prepared by the reaction of ethylformate and hydrazine hydrate, has been reacted with various nickel salts yielding complexes of varying stoichiometry. The halo, sulphato, nitrato and perchlorate complexes are tris, whereas the thiocyanate complex is bis. Electronic and magnetic data reveal that the complexes are all octahedral [301].

Phthalic hydrazide (H_2L) reacts with Ni(II) yielding the complex $[Ni(HL)_2(H_2O)_2]\cdot 2H_2O$ (77). Reaction of (77) with acetylacetone and ethylenediamine gives the mononuclear adducts $[Ni(HL)(acac)_2(H_2O)]\cdot H_2O$ and $[Ni(HL)_2(en)_3(H_2O)]\cdot H_2O$ respectively [302]. In addition, it has been shown that the metal-ligand bonds in the bis-Ni(II) complexes of variously substituted phenylhydrazino propionic acid ligands, are considerably more covalent than in the corresponding mono complexes [303].



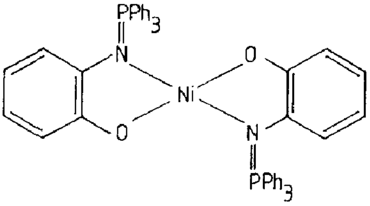
(77)

Dihydrazide ligands , such as malonic acid, succinic acid and phthalic acid hydrazide have been complexed with Ni(II). The resultant complexes have the general formula $[NiLX_2]$ (X= halide or pseudohalide), and are octahedral in structure [304]. The magnetic and spectral properties of a series of thiocarbohydrazone-Ni(II) complexes have been investigated. In all cases the ligands function as dibasic ONNO donors, forming square-planar complexes of the type [NiL] [305].

In a continuation of earlier work, the azine ligand 1-(2-quinolylazo)-2-phenanthrol has been reacted with various metal ions. Complexation with nickel yields the octahedral complex $[NiL_2]$ (HL= 1-(2-quinolylazo)-2-phenanthrol) [306]. The chemistry of the azo ligands, 2-carboxyphenyl azo-β-napthol and 4-carboxyphenyl azo-β-napthol has been studied [307], in addition to the kinetics and mechanism of chelation of Ni(II) by 2-(2-pyridylazo)-1-napthol [308].

3,5-Dinitroresacetophenone oxime [309], 3-bromo-2-hydroxy-5-methylacetophenone oxime [310]and α-benzilmonoxime [311]have been complexed with Ni(II) in the presence of base. Not unexpectedly, the resutant $[NiL_2]$ complexes are diamagnetic with square-planar geometry. A number of mixed-ligand complexes containing variously substituted benzoylacetanilide and α-oximinobenzoylacetanilide ligands have been prepared. Complexation occurs via the oxime and carbonyl groups resulting in square-planar geometry [312].

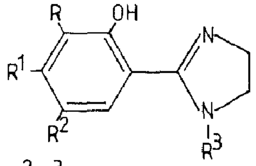
The complexation of 2-hydroxy-4-methyl-5'-methylchalkone oxime has been studied in solution [313]. Other oxime ligands that have been complexed with Ni(II) are isonitrosopropiophenone [314] and antifuran-2-carboxaldoxime [315], while the reaction of bis(1,2-benzoquinone monoxime)nickel(II) with triphenylphosphine yields the pseudotetrahedral triphenyl(2-hydroxyphenylimino)phosphorane complex (78) [316].



(78)

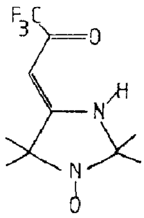
The stability constants of the Ni(II) complexes of 2-amino-3-hydroxypyridine [317]and pyridine-2,5-dicarboxylic acid [318] have been determined. In both cases 1:1 and 1:2 complexes are formed, with lower temperatures favouring coordination. Other substituted pyridine ligands that have been complexed with Ni(II) are 2-(2-pyridyl)ethanol [319], pyridine-2,6-dicarboxylic acid [320], 2-amino- and 2,6-diaminopyridine [321]. In addition, the crystal structure of (pyridine-2,6-dicarboxylato)(N,N,N',N'-tetramethyl-1,2-diaminoethane)nickel(II) dihydrate has been determined [320].

The coordinative behaviour of a number of N-substituted 2-(o-hydroxyphenyl)-Δ^2-imidazolines (79) and their use as metal extractants has been investigated. The imidazoline ligands coordinate in their deprotonated form yielding square-planar complexes of the type [NiL_2], in which the nitrogen atoms are mutually trans [322]. Distorted tetrahedral complexes, [NiL_2], have been obtained from the reaction of deprotonated 4-(3',3',3',-trifluoro-2'-oxopropylidene)-2,2,5,5-tetramethyl-3-imidazolidene-1-oxyl (80) with $NiSO_4 \cdot 7H_2O$ [323].



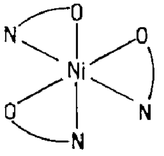
R,R¹,R²,R³=H,NO₂,butyl etc.

(79)



(80)

There have been two interesting reports on the synthesis of Ni(II) compounds containing 1-amino-2-propanol and 2-amino-1-propanol, both of which are optically active,as ligands. (R,S)-1-amino-2-propanol, (S)-1-amino-2-propanol, (R,S)-2-amino-1-propanol and (S)-2-amino-1-propanol react with nickel triflate yielding the *tris* complexes $[NiL_3]T_2$ (L= aminopropanol; T= $CF_3SO_3^-$). The 1-amino-2-propanol derivatives have a meridional configuration (81), while the 2-amino-1-propanol derivatives, with the exception of the (S)-derivative, have a facial configuration (82). Reaction with other nickel salts yields complexes of the type $[NiL_2X_2]$ and $[NiL_3]X_2$ (X= halide or pseudohalide). In this case the *tris* complexes are all facial, while the *bis* complexes have a *trans*-X, *cis*-L structure (83) [324,325].



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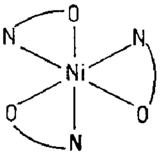

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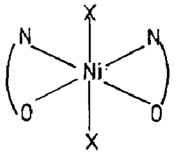
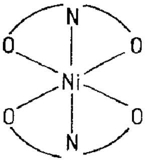


(83)

Carbamyldicyanomethanide ion is an interesting pseudohalide ion which possesses ampolydentate properties due to the donor capacity of the two nitrile and carbamyl groups. On the basis of its delocalisation, it has been proposed that coordination can take place via the carbonyl, nitrile and amide groups. $[NiX_2]\cdot 6H_2O$ (X= carbamyldicyanomethanide) is polymeric and octahedral in structure, with coordination occurring via the nitrile and amide nitrogen atoms, as well as the carbonyl oxygen atom [326]. Reaction with pyridine yields the octahedral complex $[NiL_4X_2]$ (L= pyridine), while reaction with the bidentate ligands, 2,2'-bipyridine, ethylenediamine and 1,10-phenanthroline, yields the octahedral complexes $[NiL_2X_2]$ [327]. In addition, the coordination properties of the carbamylcyanamide ion have been investigated [328].

8-Hydroxyquinoline has been used as a ligand in a series of Ni(II) complexes. Infrared spectroscopy has been used to study its mode of coordination in the complexes, $[NiL_2]$, $[NiL_2(H_2O)_2]$ and $[NiL_2(HL)]$ (HL= 8-hydroxyquinoline). The structure of the anhydrous chelate was found to be distorted planar, while the dihydrate and self-adduct exhibit square-planar and square-pyramidal geometry respectively [329]. Mixed-ligand complexes containing 8-hydroxyquinoline and various deprotonated β-diketones [330], as well as 2-aminobenzoate [331,332], have been prepared.

The mode of coordination of the iminodiacetate ligand has been investigated spectroscopically. The coordination polyhedron of $Li_2[NiL_2]\cdot 4H_2O$ (L= iminodiacetate) has the shape of an irregular octahedron, in which the ligand coordinates in a tridentate fashion having both nitrogen atoms in a *trans* configuration (84) [333]. This mode of coordination is supported by the X-ray structural determination of $Na_2[NiL_2]\cdot 4H_2O$ (L= bis-β-hydroxyethyliminodiacetate) [334].



(84)

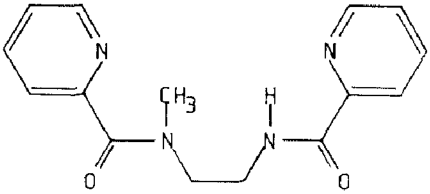
The interaction of the tetradentate ligand 3,3'-[ethane-1,2-diylbis-(imino)] bis(propanamide) (H_2L) with Ni(II) has been investigated potentiometrically. The complex formation equilibria may be represented as follows:

$$Ni^{2+} + H_2L \rightleftharpoons [Ni(H_2L)]^{2+}$$

$$[Ni(H_2L)]^{2+} \rightleftharpoons [NiL] + 2H^+$$

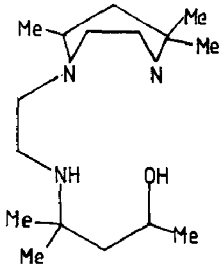
In addition, the above is an example of octahedral ⟷ square-planar equilibria for Ni(II), since it has been shown that $[Ni(H_2L)]^{2+}$ exists as an octahedral complex in solution, whereas [NiL], formed by the addition of base, exists as a square-planar complex [335].

N-methyl-N,N'-bis(2'-pyridine-carboxamide)-1,2-ethane (85) has been complexed with various nickel salts. Octahedral complexes of the type $[NiLX_2]$ are formed when X= Cl^-, Br^- and NO_3^-, whereas the binuclear complex $[Ni_2L_3]X_4$ is formed when X= ClO_4^-. Coordination is found to occur via the pyridyl nitrogen and carbonyl oxygen atoms [336].



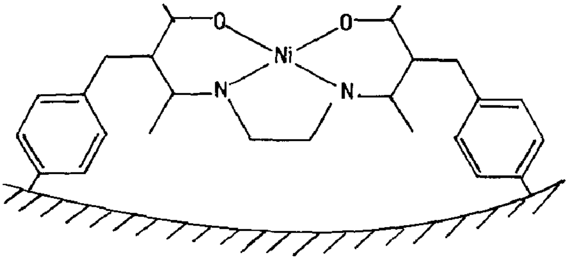
(85)

Reduction of 4,4,12,12-tetramethyl-5,8,11-triazapentadecane-2,14-dione diperchlorate with $NaBH_4$ yields predominantly one isomer of 4,4-dimethyl-7-(5,5,7-trimethyl-1,2-diazepan-1-yl)-5-azaheptan-2-ol (86). Reaction of (86) with $Ni(ClO_4)_2$ gives $[NiL](ClO_4)_2$, while reaction with $Ni(NCS)_2$ produces [NiL(NCS)] . The perchlorate compound has a planar structure, determined by X-ray crystallography, while the thiocyanate complex has been assigned a pentacoordinate structure [337].



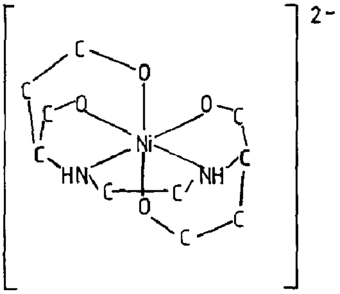
(86)

Anchoring of catalytically active transition-metal complexes to a polymer support has recently attracted considerable attention, since in certain cases polymer attachment has lead to stabilization of coordinatively unsaturated mononuclear reaction centres. In an ongoing series, $[Ni(en)_2]Cl_2$ has been reacted with a functionalized resin in a template synthesis to yield the polymer supported complex (87) [338].



(87)

The hexadentate ligand, ethylenediamine-N,N'-disuccinic acid, has been complexed with Ni(II) in the presence of base. The resultant octahedral complex, $Na_2[NiL]\cdot 3H_2O$, has been assigned structure (88) on the basis of X-ray diffraction data [339].

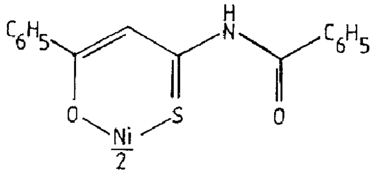


(88)

1.3.5.2 S,O-donor ligands

Monothio-β-diketonate complexes, like their β-diketonate counterparts, have enjoyed much interest [340-342]. Variously substituted monothio-β-diketone ligands have been complexed with Ni(II) in their deprotonated form to yield square-planar complexes of the type [NiL_2] (HL= monothio-β-diketone). Dipole moment data [340] and ^{19}F- and ^{13}C-n.m.r. spectroscopy [341] indicate that the complexes have a cis configuration.

The potentially tridentate ligand, N-α-dibezoylthioacetamide, has been found to coordinate in a bidentate fashion via the monothio-β-diketone part of the ligand, yielding a square-planar complex (89) in which the aza part of the ligand remains uncoordinated. The structurally related ligand, N-benzoyl-β-naptholinothiocinnamamide, however, is compelled to coordinate via the -C(O)-NH-C(S)- moiety and yields the corresponding square-planar complex (90) [343].



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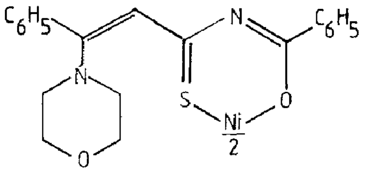
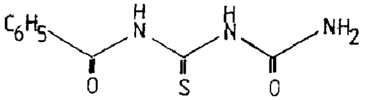


(90)

The complexation of 1-benzoyl-2-monothiobiuret (91) [344] and N-(2,3-dimethyl-1-phenyl-5-oxo-3-pyrazoline-4-yl)-N'-benzoylthiourea (92) [345] with Ni(II) has been investigated in solution. (91) forms a bis complex (log K= 8.16; -ΔG°= 10.93 kcal/mol), while (92) forms NiL^+ and NiL_2 , in which the ligand coordinates in a bidentate fashion via the benzoyl oxygen and sulphur atoms.



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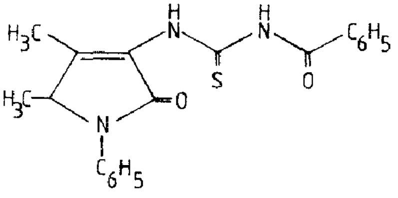
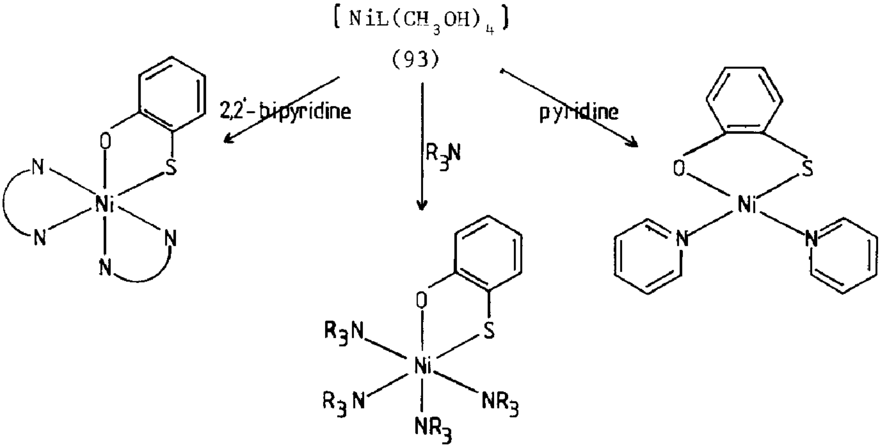


(92)

Variously substituted thiosalycylic acid derivatives, o-$RSC_6H_4CO_2H$ (R= allyl, $CH_2CH{:}CClCH_3$), have been reacted with $Ni(NO_3)_2 \cdot 6H_2O$, yielding the tetracoordinate complexes [NiL_2]$\cdot H_2O$ (HL= substituted thiosalicylic acid). Coordination occurs via the carboxyl oxygen and thioether groups [346].

o-Mercaptophenol reacts with $NiCl_2$, in the presence of a stoichiometric amount of trimethylamine, yielding the interesting methanol adduct

$[NiL(CH_3OH)_4]$ (93) (HL= o-mercaptophenol) [347]. This complex is useful as a synthon for various other adducts as shown below:



Compared to the large amount of interest that has centred on the coordination chemistry of dithiocarbamate complexes, very little attention has been given to the coordination properties of the monothiocarbamate ligands. The nickel complexes of indoline-N-carbothioate and indole-N-carbothioate have been prepared. Infrared spectroscopy suggests that both ligands function in a bidentate manner giving rise to complexes of the type $[NiL_2]$ [348].

Focusing on tetradentate ligands, the crystal structure of diaqua(2,5-dithiahexane-1,6-dicarboxylato)nickel(II) has been determined. The ligand coordinates via a OSSO donor set of atoms, with the other two coordination sites being occupied by water molecules [349].

1.3.5.3 N,S(Se)-donor ligands

Although these complexes have been studied to a lesser degree than their oxygen counterparts, it is evident that the chemistry does follow a similar pattern. As a result, ligands derived from the condensation reactions of carbonyl compounds with primary amine derivatives, such as Schiff bases [350], semicarbazides and hydrazides predominate.

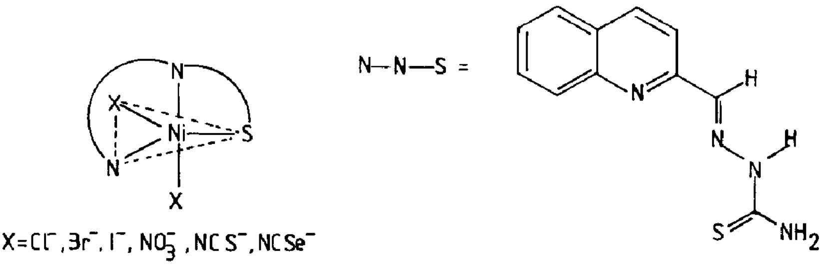
Thio- and selenosemicarbazide ligands and their nickel complexes have been studied widely, and some of these complexes are listed in table 8. Bidentate thiosemicarbazide ligands generally coordinate via the azomethine nitrogen atom and a deprotonated thiol group. As a result, square-planar complexes of the type $[NiL_2]$ are widely encountered [351-356].

The tridentate thio/selenosemicarbazide ligands listed in table 8 all coordinate via N_2S or N_2Se donor sets, and a broad range of coordination geometries have been generated. Of interest is the nickel complex of 1-formylquinoline thiosemicarbazone, $[NiLX_2]$, which has an unusual trigonal-

Table 8. Thio- and Selenosemicarbazone and carbazide ligands and their Ni(II) complexes.

LIGAND	COMPLEX	COMMENTS		Ref.
Bidentate				
Benzylmethylketone thiosemicarbazone (HL)	$[NiL_2]$	Square-planar		[351]
Methyl-n-hexylketone thiosemicarbazone (HL)	$[NiL_2]$	Square-planar		[351]
Thiophene-2-carboxaldehyde thiosemicarbazone (HL)	$[Ni(HL)_2]X_2$	Square-planar	$X = Cl^-$,	[352]
	$[Ni(HL)X_2]$	Square-planar	Br^-,	[352]
	$[NiLX]$	Square-planar	I^-,	[352]
	$[NiL_2]$	Square-planar	NO_3^-	[352]
	$[Ni(HL)_2(NCS)_2]$	Octahedral		[352]
	$[Ni(HL)(NCS)]$	Octahedral		[352]
1-Acetylpyridiniumchloride-4-phenyl-3-thiosemicarbazide (L)	$[NiLCl_2]Cl$	Tetrahedral		[353]
1-(2,4-dinitro)-4-phenyl-3-thiosemicarbazide (HL)	$[NiL_2]$	Square-planar		[354]
Furfural selenosemicarbazone (HL)	$[NiL_2]$	Square-planar		[355]
Acetone selenosemicarbazone (HL)	$[NiL_2]$	Square-planar		[356]
Tridentate				
1-Isobutyryl-4-phenyl-3-thiosemicarbazide (HL)	$[NiL_2]\cdot 2H_2O$	Octahedral		[354]
1-Formylisoquinoline thiosemicarbazone (L)	$[NiLX_2]$	Trigonal-bipyramidal	$X=Cl^-, Br^-, I^-$	[357]
2-Formylquinoline thiosemicarbazone (L)	$[NiLX_2]$	Trigonal-bipyramidal	NO_3^-, NCS^-	[357]
3-Azabicyclo 3,2,2 nonane-3-thiocarboxylic acid-2 (1-(2-pyridyl)ethylidene) (HL)	$[NiLX]$	Square-planar	$X=Cl^-, Br^-, I^-$, NO_3^-, OAc^-	[358]
3-Azabicyclo 3,2,2 nonane-3-selenocarboxyli acid-2 (1-(2-pyridyl)ethylidene) (HL)	$[NiLX]$	Square-planar		[358]
4-Benzamido-1-diacetylmonoxime-3-thiosemicarbazone (L)	$[NiLCl_2(H_2O)]\cdot H_2O$	Octahedral		[359]

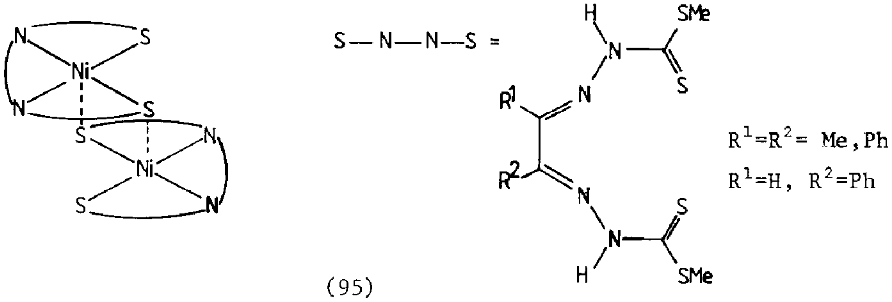
bipyramidal structure (94) [357].



(94)

Thiocarbohydrazones exhibit interesting coordination properties, due to the presence of the azomethine, hydrazine and thionic groups in the molecule. Salicylaldehyde thiocarbohydrazide [360], thiocarbohydrazone-2-aminobenzaldehyde [361] and 2-(hydrazinothioxomethyl)hydrazine [362], have been reacted with various nickel salts. In each case the ligand functions in a bidentate manner, with coordination occurring via the hydrazine and thionic groups.

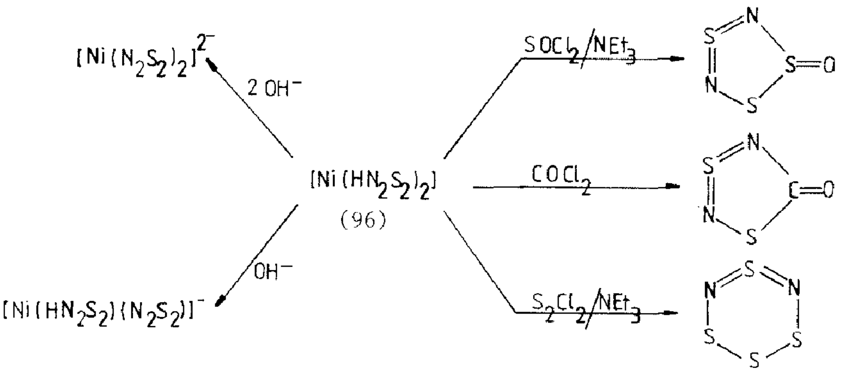
The coordination properties of the bis hydrazones, derived from the condensation of diacetyl, benzil and phenylglyoxal with hydrazine-S-methylcarbodithioate, have been investigated. The ligands are tetradentate and coordinate in their dibasic form to yield diamagnetic nickel chelates, which on the basis of spectral data have been assigned a dimeric pentacoordinate structure (95) [363].



(95)

p-Hydroxyphenylthiohydrazide is a potential nitrogen,sulphur and oxygen donor ligand, and can coordinate in its neutral, basic or dibasic forms. In acidic or neutral medium it has been shown to coordinate as a simple thiohydrazide, yielding square-planar complexes of the type $[Ni(HL)_2]X_2$ (X= halide or pseudohalide) and $[NiL_2]$ (HL= p-hydroxyphenylthiohydrazide) [364]. Not surprisingly, the mode of coordination of 2-furanthiocarboxyhydrazide is similar, exhibiting neutral and monobasic bidentate behaviour. Both square-planar $[NiL_2]$ and octahedral $[Ni(HL)_3]Cl_2$ (HL= 2-furanthiocarboxyhydrazide) have been isolated [365]. A series of related ligands, N,N'-substituted formamidino-N''-substituted thiocarbamides, have been reacted with $NiCl_2$. The resultant complexes are tetracoordinate with general formula $[NiL_2]Cl_2$ [366].

The complex $[Ni(HN_2S_2)_2]$ (96) has generated interest both in its own complex chemistry [367] and as a synthetic route to cyclic sulphur-nitrogen compounds [368]. Depending on the base used, (96) may be deprotonated, yielding $[Ni(HN_2S_2)(N_2S_2)]^-$, or double-deprotonated to give $[Ni(N_2S_2)_2]^{2-}$. The crystal structure of $[Ph_4As][Ni(HN_2S_2)(N_2S_2)]$ has been determined, while the use of $[Ni(HN_2S_2)_2]$ as a synthon for cyclic sulphur-nitrogen compounds has been investigated.



1-Amidino-2-thiourea ligands have the ability to coordinate as SN or NN donors depending on the pH of the reaction medium. Reaction with Ni(II) has shown that NN-bonded complexes are formed under alkaline conditions, while SN-bonded complexes are obtained under neutral or slightly acidic conditions [369]. Other thiourea complexes that have been studied are a series of octahedral complexes $[NiL_2(NCS)_2]$ (L= variously substituted phenylthiourea)[370].

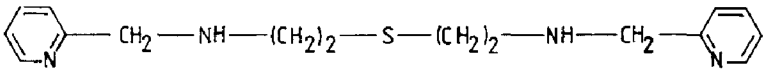
Square-planar complexes of Ni(II) with Quinazoline-2-thione-4-one and its 3-phenyl derivative have been prepared. Complexation occurs with deprotonation and coordination is effected via the sulphur atom and the nitrogen atom at position one [371]. The crystal structure of the related 2-isopropylquinoline-8-thiolate complex, in which the nickel atom is surrounded by a distorted tetrahedral environment, has been determined [372]. In addition, a solution study of the complexation of 2-thiocarbamyl-thiazoline reveals that the octahedral complex $[NiL(H_2O)_4]^+$ is favoured over the square-planar complex $[NiL_2]$ (HL= 2-thiocarbamyl-thiazoline) [373].

The thermal decomposition of $[Ni(NCS)_2(NH_3)_4]$ under nitrogen atmosphere has been investigated. Key intermediates $[Ni(NCS)_2(NH_3)_2]$ and $[Ni(NCS)_2]$ have been characterized using single-crystal X-ray methods [374].

Turning to multidentate ligand complexes, the crystal structure of bis-

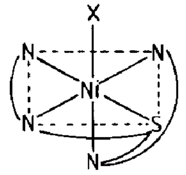
(1,7-diaza-4-thiapheptane)nickel(II) perchlorate has been determined. The ligand coordinates in a tridentate fashion with the sulphur atoms occupying cis positions. Data obtained were, a mean Ni-S bond length of 2.459 Å, a mean Ni-N bond length of 2.11 Å, and a 10Dq value of 11180 cm^{-1} [375].

The potentially pentadentate ligands 1,9-bis(2-pyridyl)-2,8-diaza-5-thianonane (97) and 1,4,10,13-tetraaza-7-thiatridecane (98) have been reacted with NiX_2 ($X= Cl^-, NCS^-, ClO_4^-$). The resultant complexes have the general formula [NiLX]X (L= 97, 98), and are octahedral in structure, with (97) and (98) coordinating in a pentadentate fashion as shown below [376]:



(97)

$H_2N—(CH_2)_2—NH—(CH_2)_2—S—(CH_2)_2—NH—(CH_2)_2—NH_2$ (98)



1.3.5.4 P,N-donor ligands

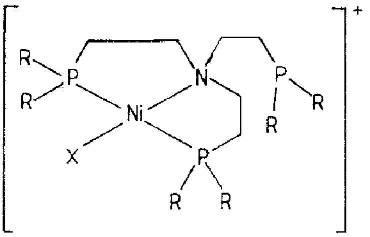
Bis(o-amidophenyl)diphenylphosphine, when deprotonated, chelates with Ni(II) in a bidentate fashion to form the neutral complex cis(bis{o-amidophenyl}diphenylphosphine)nickel(II) acetone solvate. The molecular structure of this complex has been determined and shows coordination occurring via the phosphine and deprotonated amido moeities. ^{31}P-n.m.r. evidence indicates that the cis species remains the preferred form in solution, with the trans isomer present only in slight abundance [377].

$HN(SiMe_2CH_2PPh_2)_2$ reacts with $NiCl_2$ yielding the distorted tetrahedral complex $[NiCl_2NH(SiMe_2CH_2PPh_2)_2]$, in which the ligand coordinates in a bidentate fashion via donation through the phosphine atoms. However, when deprotonated, the ligand has the ability to coordinate in a tridentate fashion and gives rise to the distorted square-planar complex $[NiClN(SiMe_2CH_2PPh_2)_2]$, in which coordination occurs via the deprotonated amido and phosphine donors

[378].

2,6-Bis(diphenylphosphinomethyl)pyridine, apart from its ability to function as a tridentate ligand, also generates various coordination geometries depending on the nickel salt and reaction conditions employed. Various spectroscopic methods [379], including X-ray photoelectron spectroscopy [380], have been used to determine the stuctures of these complexes. Of particular interest are the XPS spectral patterns for [NiL(NCS)$_2$] which reveal the presence of [NiL(NCS)] as well as more ionic NCS$^-$ ligands, possibly contained in pseudo-octahedral [NiL(NCS)$_3$]$^-$ environments. Evidence is also presented for the occurrence of two inequivalent 2,6-bis(diphenylpnosphinomethyl)pyridine ligands in [NiL$_2$]$^{2+}$, one of which is tridentate, while the other is bidentate with an uncoordinated pyridine nitrogen atom [380].

The tripod ligand, tris(2-dicyclohexylphosphinoethyl)amine, has the ability to coordinate via various donor sets. Reaction with a variety of nickel salts yields complexes of the type [NiLX]BPh$_4$ (X=Cl, Br, I, NCS). These complexes are tetracoordinate with square-planar geometry and have the unusual feature that the ligand functions as a tridentate NP$_2$ donor with one pendant arm "free" (99) [381].



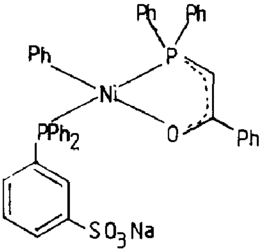
R= cyclohexyl

(99)

The pentacoordinate complex [NiClL]PF$_6$ (L= CH$_2$[CH$_2$P(Ph)CH$_2$CH$_2$CH$_2$NH$_2$]$_2$) has been isolated as its meso isomer. The crystal structure confirms a low spin complex with square-pyramidal geometry in which the chlorine atom occupies the axial site. All the chelate rings are in the chair conformation and the bond lengths are Ni-Cl (2.699(7)), Ni-N (2.006(10) and 2.036(11)) and Ni-P (2.178(4) and 2.168(4)) respectively [382].

1.3.5.5 P,O-donor ligands

A series of nickel ylides containing sulphonated group-V ligands have been synthesized. Of particular interest is (100), which was found to be a useful catalyst for the oligomerization of ethylene [383].

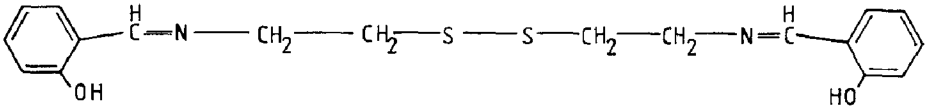


(100)

1.3.5.6 N,O,S-donor ligands

Schiff bases and in particular thiosemicarbazones form the bulk of ligands, containing NOS donor atoms, which have been studied. The tridentate Schiff bases, 2-acetylthiopheneglyoxaldimino-bis(p-aminophenyl)sulphide [384] and o-(thiophene-2-aldimino)benzoic acid [385] have been complexed with $NiCl_2$ to yield $[NiLCl_2(H_2O)]$ (L= 2-acetylthiopheneglyoxaldimino-bis(p-aminophenyl)-sulphide) and $[NiL_2]$ (HL= o-(thiophene-2-aldimino)benzoic acid) respectively. In addition, the crystal structure of $[NiL_2]$ (L= $CH_3C(O)CCH_3NNC(S)SCH_3^-$), prepared from nickel(II)acetate and the Schiff base of hydrazine-carbodi-tioic acid methyl ester with diacetyl, has been determined. The coordination geometry is distorted octahedral with the two essentially planar tridentate ligands perpendicular to each other [386].

The condensation of salicylaldehyde and bis(2-aminoethyl)disulphide yields an interesting quinquedentate Schiff base ligand (101). Reaction of (101) with Ni(II) gives rise to two complexes both with stoichiometry [NiL] (H_2L= 101) One complex is tetracoordinate, with coordination taking place via two imino nitrogen and two phenolic oxygen atoms, while the second complex is penta-coordinate, with coordination occurring via one of the sulphur atoms as well as the imino and phenolic groups [387].



(101)

All of the tridentate thiosemicarbazone ligands that have been investigated coordinate via a ONS donor group. Octahedral complexes of the type $[NiL_2]$ (HL= thiosemicarbazone ligand) have been isolated from the reaction of

$NiCl_2$ with 1-salicyl-4-benzylamidothiosemicarbazone [388], 4-phenyl-isatin-β-thiosemicarbazone [389] and 9,10-phenanthroline monothiosemicarbazone [390] respectively. In contrast, α-hydroxy-β-napthaldehyde thiosemicarbazone reacts with $NiCl_2$ yielding the square-planar complex [NiLCl] , probably due to the steric effect of the napthaldehyde group [391]. In addition, the base adducts of a series of Ni(II) chelates of thiosemicarbazones, derived from 2-hydroxy-5-chloro-acetophenone/propiophenone and 2-hydroxy-5-methyl-acetophenone/propiophenone, have been prepared and isolated. Square-planar complexes of the type [NiLB] (H_2L= thiosemicarbazone) are obtained for monodentate bases (B) such as α,β,γ-picolines, piperidene and morpholine [392].

Finally, two new hexadentate ligands, 1,2-*bis*(*o*-1-methyltriazine-1-oxido-3-phenoxy)ethane and its ethyl analogue (H_2L) have been reacted with $NiCl_2$. The resultant complexes [NiL] are hexacoordinate, as manifested by the magnetic moments (μ= 3.11 and 3.22 BM) [393].

1.3.5.7 Miscellaneous

The synthesis and single-crystal X-ray structure of chloro(triphenylphosphine) diphenyl(methylene)phosphoranylthio-S,C nickel(II) has been reported. The coordination environment of the nickel atom is essentially planar and the metal-ligand bond lengths are Ni-C (1.999{8}), Ni-S (2.284{2}), Ni-P (2.197{2}), Ni-Cl (2.216{2}) respectively [394].

1.3.6 Macrocyclic ligands

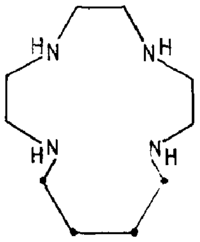
1.3.6.1 Nitrogen-donor ligands

This constitutes by far the largest group of Ni(II) macrocyclic compounds studied. In this discussion, complexes are dealt with in order of increasing ring size.

1,4,7,10-Tetramethyl-1,4,7,10 tetraazacyclododecane, when complexing with Ni(II), can give rise to four isomeric forms of $[NiL]^{2+}$, as a result of the four possible orientations of the methyl groups. The crystal structure of the isomer in which all four methyl groups are on the same side of the tetraaza plane has been determined. Of note is the fact that the complex does not possess internal symmetry due to different skew of the four cyclic rings [395].

Template reactions involving substitution at the 12-methine position of 13-membered macrocyclic ligands, bound to Ni(II), have been investigated by various workers [396-398]. In addition, the crystal structure of 11,13-dimethyl-12-(*p*-methylbenzoyl)-1,4,7,10-tatraza-10,12-cyclotridecadienato - nickel(II) hexafluorophosphate has been reported. The coordination environment is essentially square-planar, with a slight tetrahedral distortion 399 .

Sugimoto et al have synthesized the following three macrocyclic ligands (102-104), in which one of the potential chelate rings has been increased by the successive addition of a methylene group [400]. The perchlorate complexes $[NiL](ClO_4)_2$ (L= 102-104) are tetracoordinate and diamagnetic in the solid state, as shown by the single-crystal X-ray analysis of $[NiL](ClO_4)_2$ (L= 103) [401]. The chloro complexes $[NiLCl_2]$ (L= 102-104) are hexacoordinate and trans with the macrocycle in an open conformation. However, when (102) is reacted with $Ni(NCS)_2$ it yields the complex $[NiL(NCS)_2]$ in which the geometry is cis and the macrocycle adopts a folded conformation [402].



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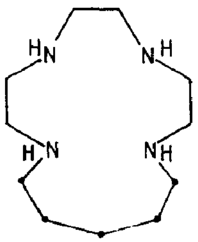

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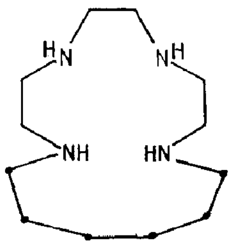
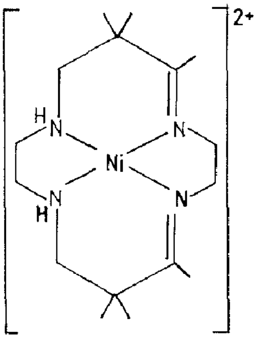


(104)

A new base initiated template reaction for the synthesis of substituted complexes of dihydro-dibenzo[b,i][5,9,14,18]tetraaza[14]annulene has been developed [403]. In a related area of research, a method of acylating 5,7,12,14-tetramethyldibenzo[b,i]-1,4,8,11-tetraazacyclotetradecahexaenato nickel(II) has been reported. Acylation is achieved using the appropriate acyl chloride, with both mono- and diacylated species being obtained [404]. In addition, the crystal and molecular structure of 5,7,12,14-tetramethyl-dibenzo[b,i]-1,4,8,11-tetraazacyclotetradecahexaenatonickel(II) has been determined. The complex has a pronounced saddle shape conformation, with the Ni atom at the saddle point, coordinated to the four nitrogen atoms (average Ni-N bond length= 1.866 Å) [405].

The position of the double bonds in variously substituted 1,4,8,11-tetra-azacyclotetradecadienatonickel(II) complexes may be varied, and depending on the position of the substituent, isomers may exist. Field desorption mass spectrometry has been used to characterize 6,6,7,12,13,13-hexamethyl-1,4,8,11-tetraazacyclotetradeca-7,11-dienatonickel(II), in which the double bonds occupy cis positions (105). [406]. 2,5,9,12-tetramethyl-1,4,8,11-tetraaza-cyclotetradeca-4,11-diene has been complexed with Ni(II). The resultant complex $[NiL]^{2+}$ exists as two forms in the solid state, the α-form which is diamagnetic and square-planar (106), and the β-form which is the hexacoordinate diaquo species (107) [407].



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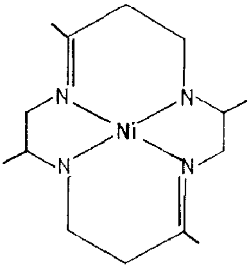

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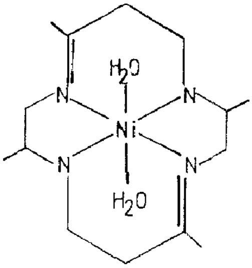
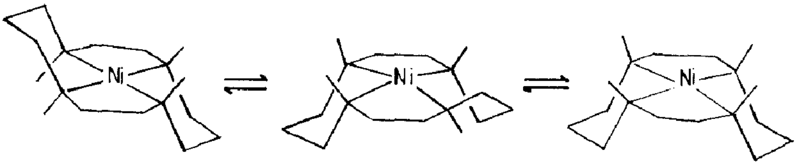


(107)

Isomeric tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,11-dienato nickel-(II) diperchlorate complexes have been prepared by the condensation of methyl vinyl ketone with R,S- and R-(-)-1,2-propylenediamine monohydrogen perchlorate, followed by reaction with nickel(II)acetate. The C- and N-diastereoisomeric forms of the complexes were isolated and characterized on the basis of resolution, racemization and mutarotation of the complexes, dehydrogenation of the complexed ligand, and spectroscopic results [408].

Ligands of the cyclam family continue to be of significant interest. A single-crystal X-ray analysis of [Ni(cyclam)I]I·H_2O has been undertaken. The structure is interesting in that the Ni atom occupies a pseudooctahedral environment, with a long contact (3.34 Å) between Ni and a bridging iodide centre situated in the axial position. The second iodide is situated in the lattice and is not associated with the Ni centre [409].

N,N',N'',N'''-tetra-substituted cyclam has elicited much interest, particularly the facile isomerization in solution. The solution equilibria of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane nickel(II) has been studied in various strongly coordinating solvents. Contrary to expectations, there is a substantial conversion of the thermodynamically predicted R,S,S,R conformation (108) into the R,S,R,S conformation (109). A R,S,R,R intermediate (110) is proposed in the exchange mechanism [410]. In addition, the formation constants of some cyclam complexes have been determined potentiometrically [411].



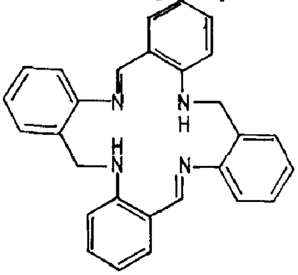
(108) (110) (109)

N,N',N'',N'''-tetra(2-cyanoethyl)-1,4,8,11-tetraazacyclotetradecane has been reduced, yielding the octa-amine ligand N,N',N'',N'''-tetra(3-aminopropyl)-1,4,8,11-tetraazacyclotetradecane. Complexation of this ligand with Ni(II), under neutral conditions, gives a high-spin pentacoordinate species in which coordination occurs via the four tertiary amine nitrogen atoms and one of the pendant primary amine nitrogen atoms. Selective protonation of the pendant amino-groups, thereby preventing them from coordinating to the metal ion, was also carried out. This gave rise to either a diamagnetic species, in the case of a weakly coordinating counterion, or a paramagnetic species in the case of a strongly coordinating counterion [412]. However, Barefield and co-workers emphasize that care should be taken when working with these ligands and that elevated temperatures and acidic or basic conditions should be avoided in order to maintain the integrity of the kinetic products derived from metal complexation. They have observed that both dealkylation and isomerization reactions can occur, particularly for ligands containing β-substituted N-alkyl groups [413].

The postulate that 1,4,7,11-tetraazacyclotetradecane (isocyclam) functions as a tridentate, rather than a tetradentate ligand, thereby accounting for its appreciably higher enthalpy of complex formation, has been found to be incorrect in the case of [Ni(isocyclam)] $(ClO_4)_2$. The single-crystal X-ray structure, solved using a force-field calculation, shows that the ligand functions in a tetradentate manner [414].

Two synthetic pathways for the introduction of a single, functionalized pendant side chain into a tetraazamacrocycle, in this case isocyclam, have been reported. Variously substituted isocyclam ligands were reacted with Ni(II). The unsubstituted ligand forms a square-planar complex, whereas when a pendant side chain containing a tertiary amino group is present, it appears that the amino group coordinates with an apical position of the metal ion [415].

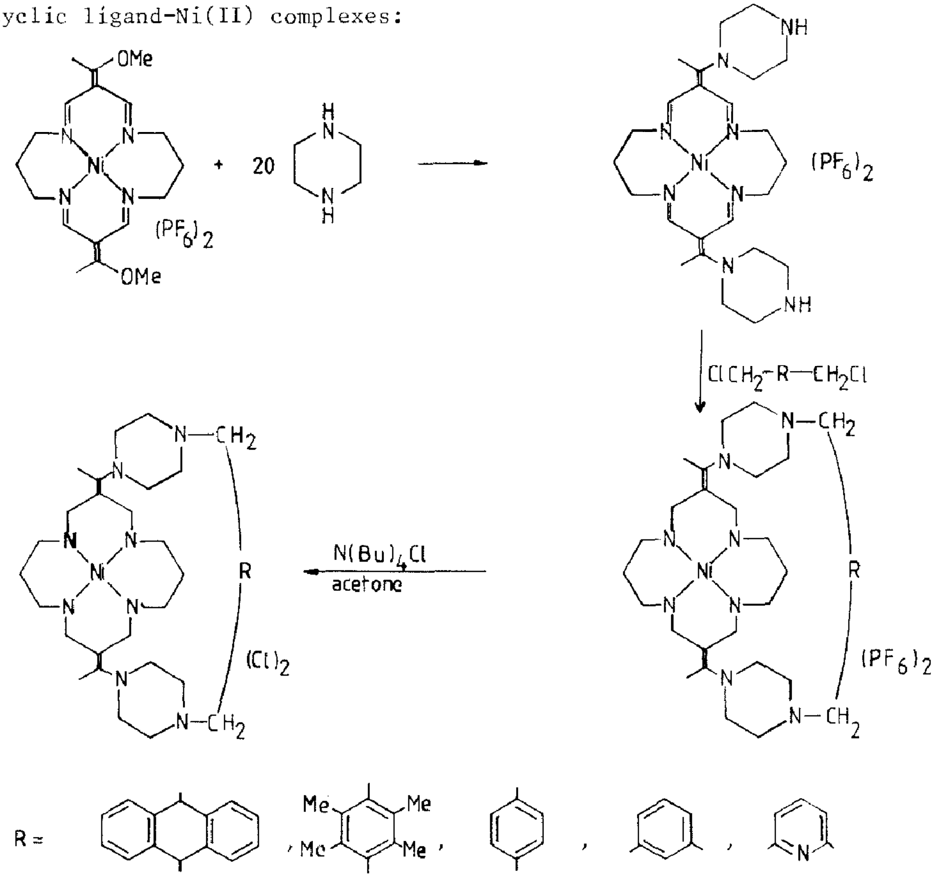
Turning to the sixteen membered macrocycles, complexes of Ni(II) with Bz [16]dienN_4 (111) and a series of axial ligands have been synthesized. The complexes were analysed spectroscopically and were found to be hexacoordinate in all cases, with the axial ligands being water molecules or anions, depending on the relative ligand field strengths [416].



(111)

The stability constants of the Ni(II) complexes of 1,4,7,10-tetraazacyclotetradecane, 1,4,8,12-tetraazacyclopentadecane and 1,5,9,13-tetraazacyclohexadecane have been determined potentiometrically for the first time. The stabilities of the 1:1 complexes $\{NiL\}^{2+}$ have been compared with the analagous open-chain ligand complexes. As expected, the macrocyclic complexes are more stable due to a favourable entropy contribution [417].

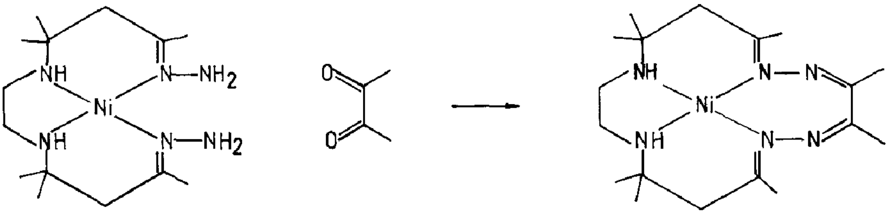
Busch et al have designed a method for the preparation of vaulted macrobicyclic ligand-Ni(II) complexes:



The single-crystal X-ray structure of the 9,10-anthracene analogue(systematic name: {2,17,19,25-tetramethyl-3,6,13,16,20,24,27,31-octaazaheptacyclo-[16.7.-7.$4^{9\ 10}$.$4^{33\ 34}$.$2^{3\ 6}$.$2^{8\ 11}$.$2^{13\ 6}$]hexatetraconta-1,8,10,17,19,24,26,31,33,35,-37,39,41-tridecaeneN_4}nickel(II) hexafluorophosphate) has been determined, from which it can be seen that the macrocycle retains the basic characteristics of the lacunar family of macrocycles [418].

The rate of reaction of (1,2,8,9-tetraphenyl-3,4,6,7-tetraaza-5,5-dimethylnona-1,3,6,8-tetraene-1,9-dioxy)nickel(II) with 1,3-propanediamine has been studied in tetrahydrofuran-ethanol solution. The suggested mechanism involves two steps,corresponding to the successive reaction of the two coordinated CO groups with a molecule propanediamine [419].

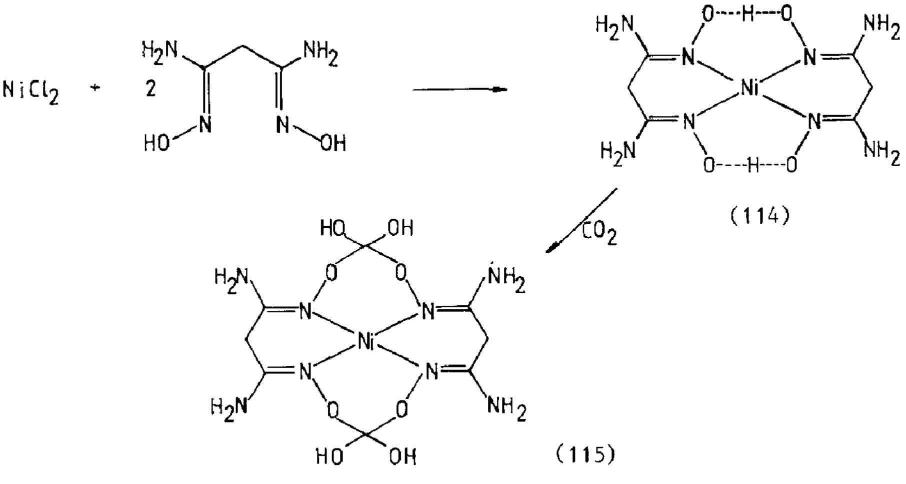
A similar Schiff base-type condensation can occur when using dihydrazine and dihydrazone ligands as shown below:



(112) (113)

The structure of (112) has been determined as the bis thiocyanato complex [NiL(NCS)$_2$] and as the nitrito complex [NiL(NO$_2$)]ClO$_4$. The flexibility of the ligand is effectively demonstrated, since it is planar in the thiocyanato complex and folded in the nitrito complex [420]. The single-crystal X-ray structure of (113), isolated as the bis perchlorate complex, has been reported in a subsequent article. As expected the complex is tetracoordinate, with the macrocycle in a N-rac configuration [421].

Oximes and dioximes have been used as synthetic precursors for some interesting Ni(II) macrocyclic complexes. Malonenamide oxime has been used to synthesize the tetraaza macrocyclic complex (115). The reaction scheme proceeds via the bis chelate complex (114), which when reacted with CO$_2$ yields the final macrocyclic complex (115). Single-crystal X-ray structures of both complexes are reported [422].



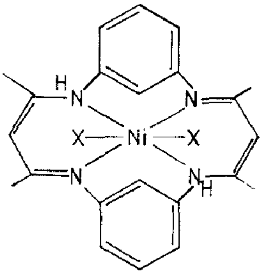
(114)

(115)

The structure of the 1:1 adduct of benzylamine with *bis*(difluoroborondimethylglyoximato)nickel(II) has been determined. The complex is dimeric, with a Ni···Ni interaction of 3.873 Å. Each nickel atom occupies a square-based pyramidal environment, formed by four nitrogen atoms of the essentially planar macrocycle, and the benzylamino nitrogen atom [423].

Macrocyclic complexes derived from the metal template condensation of aromatic diamines with dicarbonyl compounds, have been synthesized by various groups. Reaction of metaphenylenediamine, acetylacetone and the appropriate nickel salt yields (116) [424], while use of 1,3-diphenyl-1,3-propanedione as the dicarbonyl gives (117) [425]. In addition, reaction of 2,6-diaminopyridine and 2,3-butanedione in the presence of a nickel salt yields the tetragonal macrocyclic complexes (118), in which the pyridyl nitrogen atoms remain uncoordinated [426].

X = Cl, Br, NO_3, NCS



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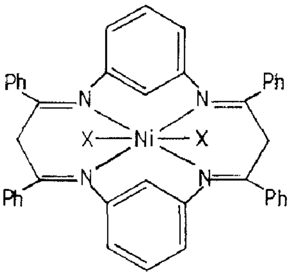

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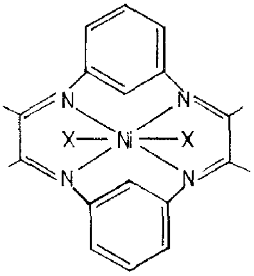

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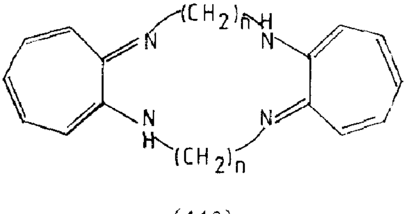
The ability of 2-alkoxytroponeimines to undergo nucleophilic substitution reactions at the 2-position has been used in the synthesis of macrocyclic ligands containing conjugated enamine imine moeities. Macrocycles with linker chains of variable length (119) have been synthesized and complexed with Ni(II). The crystal structures of five of these complexes have been determined, revealing that the metal coordination geometry is strongly affected by the length of the linker chain, changing from square-planar to pseudo-tetrahedral with increasing length [427].



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Although the crystal structure of the Ni(II) complex of hemiporphyrazine has been known for some time, very few adducts of the complex have been reported. The water adducts and complexes of the type [Ni(L)$(HX)_n$] (L= hemiporphyrazine; HX= HCl, HBr; n= 1,2) have been synthesized and characterized spectroscopically. The structure changes from square-planar, in the case of the parent complex, to tetragonally distorted in the case of the adducts[428].

Resonance Raman spectroscopy has been used to study metalloporphyrins in which a ligand has been inserted between the metal and a pyrrole nitrogen atom. In particular, the insertion of a carbenic ligand into a Ni-N bond can be easily detected by a noticeable lowering of the two highest Raman frequencies of the porphyrin ring [429].

Evidence that petroporphyrins are derived from chlorophyll has been provided by Fookes. Nuclear Overhauser effect difference spectroscopy was used to determine the structure of two porphyrins isolated from Julia Creek oil shale as nickel(II) 3,4-didehydro-3,9,14-triethyl-4,8,13,18-tetramethylphorbine and its 9-desethyl homologue [430].In addition, a homologous series of nickel(II) 15,17-butanoporphyrins, containing a seven-membered exocyclic ring, were isolated [430].

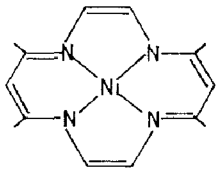
In a continuation of the work on the structural investigation of porphyrin complexes, the valence distribution in (5,10,15,20-tetramethylporphyrinato)nickel(II) has been investigated. It is suggested that the observed difference of 0.020(11) Å in the Ni-N bond lengths is caused by intermolecular stack interactions [431]. Raman difference spectroscopy has been used to study the molecular complexes formed by Ni(II) uroporphyrin and a variety of aromatic heterocycles in aqueous alkaline solution [432].

Corphin derivatives have been used to prepare tetrahydro- and hexahydrocorphinoid nickel(II) complexes which contain novel chromophore systems. The complexes have been characterized using UV/visible, ^{1}H- and ^{13}C-n.m.r. spectroscopy. In addition, the single-crystal X-ray structure of nickel(II)-cis-4,18,19,20-tetrahydrocorphinate has been reported [433].

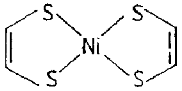
Two significantly different macrocyclic complexes of Ni(II) have been obtained from the reaction $NiCl_2 \cdot 6H_2O$, benzil and carbohydrazide. The resultant complexes, which have been characterized spectroscopically, are assigned square-planar and pseudooctahedral geometries respectively. The former complex contains a tetradentate N-donor macrocycle, while the latter contains a hexadentate N-donor macrocycle [434].

The planar macrocyclic metal complex nickel-1,4,8,11-tetraaza-5,7,12,14-tetramethyl[14]annulene, [Ni(TATMA)], has been used to form new Π-D·A compounds of the type $[Ni(TATMA)]_2A$ (A= TCNQ, $NiS_4C_4H_4$)(120). Magnetic susceptibility and conductivity measurements for both compounds, as well as the

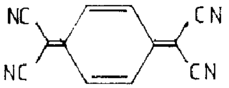
X-ray structure of the $NiS_4C_4H_4$ derivative have been obtained [435].



Ni (TATMA)



$NiS_4C_4H_4$
(120)

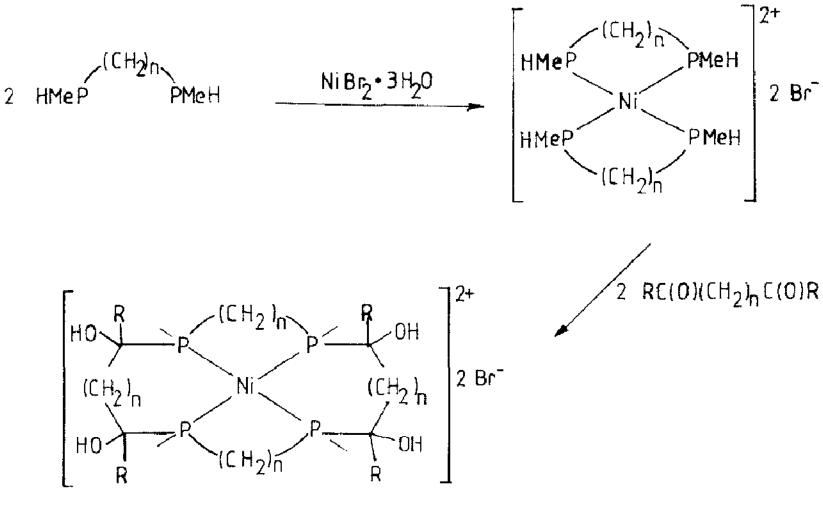


(TCNQ)

The physical and structural properties of a similar system involving the Ni(II) complex of tetramethylporphyrin (TMP) have been investigated. The first compound [Ni(TMP)]TCNQ consists of stacks of alternating, parallel [Ni(TMP)] and TCNQ molecules, and is diamagnetic. The second compound studied, [Ni(TMP)]I , obtained by the iodine oxidation of [Ni(TMP)] , consists of S_4-ruffled [Ni(TMP)] molecules, stacked metal over metal, with a Ni···Ni spacing along the stack of 3.466(3) Å, and exhibits a high magnetic susceptibility [436].

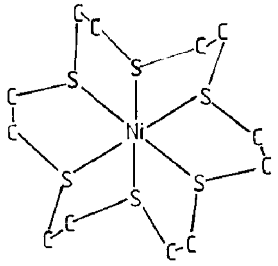
1.3.6.2 Phosphorous-donor ligands

A general synthetic route to square-planar Ni(II) complexes that contain 14-membered macrocyclic tetradentate phosphine ligands has been developed. The reaction involves a single-stage template-moderated ring closure between the complexes $[Ni(HMeP(CH_2)_nPMeH)_2]X_2$ (n= 2,3; X= Cl, Br) and dialdehydes or diketones $RC(O)(CH_2)_nC(O)R$ (n= 0,1; R= H, Me), and proceeds with high yield [437].



1.3.6.3 Sulphur-donor ligands

The single-crystal X-ray structure of the Ni(II) complex of 1,4,7,10,13,16-hexathiacyclooctadecane, the hexathia analogue of 18-Crown-6, isolated as the dipicrate, has been reported. The NiS_6 coordination sphere is essentially octahedral, with the Ni-S bond lengths varying from 2.376(1) to 2.397(1) respectively (121) [438].



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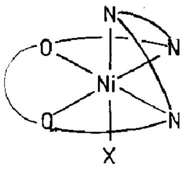
1.3.6.4 Mixed-donor ligands

A range of 17-19-membered macrocycles incorporating O_2N_3 and O_3N_2 donor sets have been synthesized and their interaction with Ni(II) studied. The complexes were investigated in the solid state and in solution, and in all cases either octahedral or pseudooctahedral geometries were observed. In solution the unsubstituted 17- and 18-membered rings adopt a configuration about the nickel atom in which two oxygen and two nitrogen atoms occupy equatorial positions, while the remaining nitrogen atom occupies an axial position. A halide ion occupies the remaining axial site (122). In contrast the 19-membered ring complexes and substituted 17- membered ring complexes were found to adopt a different structural geometry [439]. The effect of introducing methyl substituents in the 1,4,7-triazaheptane fragment of the O_2N_3 macrocycle has been further emphasized in the crystal stuctures of three complexes [NiL(NCS)$_2$] (L= methyl-substituted O_2N_3 macrocycle) [440].



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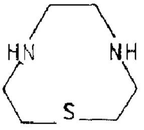
1-Thia-4,7-diazacyclononane (123) and its open chain analogue 3-thiapentane-1,5-diamine (124) have been prepared and reacted with Ni(II). The complex formation constants have been determined and compared to those of the corresponding nitrogen (125) and oxygen (126) analogues. In addition, the crystal structure of $[NiL_2]$(L= 123) is also reported. Unlike the structure of $[NiL_2]$ (L= 124) , the sulphur atoms are situated in the trans axial positions [441].



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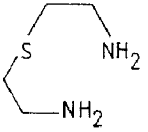

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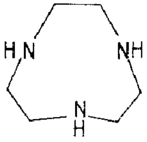

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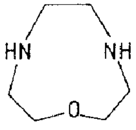

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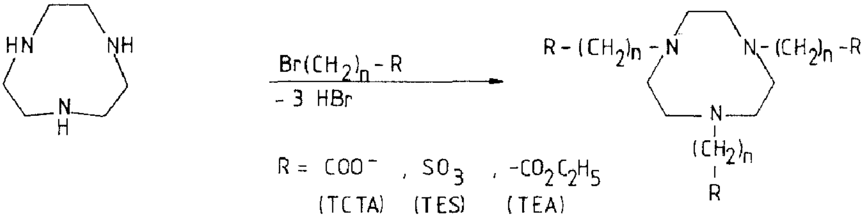
1,4,7-Triazacyclononane has been further functionalized by the attachment of pendant arms to the nitrogen atoms as shown below:



Complexation of the potentially hexadentate ligands with Ni(II) results in a hexacoordinate structure with five coordination sites being occupied by the ligand (N_3O_2-donor) and the sixth being occupied by H_2O. The single-crystal X-ray structure of $[Ni(TES)(H_2O)]^-$ has been determined, and provides evidence of the above mode of coordination[442].

The macrocyclic polyphosphanes 1,10-dipropyl-4,7,13,16-tetraphenyl-1,10-diaza-4,7,13,16-tetraphosphacyclooctadecane [443] and 4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane [444] have been synthesized and complexed with Ni(II). The ligands are potentially hexadentate and occur as five interconvertible diastereoisomers at ambient temperature. Complexation of the five diastereoisomers gives rise to various coordination modes. The crystal and molecular structures of (4RS,7SR,13SR,16RS)-4,7,13,16-tetraphenyl-1,10-dioxa-4,7,13,16-tetraphosphacyclooctadecane nickel(II) [445] and 1,10-dipropyl-(4RS,7SR,13RS,16SR)-4,7,13,16-tetraphenyl1,10-diaza-4,7,-

13,16-tetraphosphacyclooctadecane nickel(II) [443] have been determined.

1.3.7 Biological ligands

A large number of ligands with NO and NS donor atoms are of biological interest. The nickel(II) complexes of some of these ligands have been listed in table 9. The bulk of these ligands fall into two broad catagories, viz. substituted polyheterocycles [446-466] and amino acids or peptides [467-483].

The polyheterocyclic ligands consist of variously sustituted azoles [446-453], pyrimidines [454,455], barbituric acids [458-460],azines [461-462] and thiazoles [463-466]. Most of the complexes are of the type [NiL_2X_2] (L= polyheterocyclic; X= halide ion or H_2O), and exhibit octahedral or pseudooctahedral geometry.

The nickel metalloenzyme, jack bean urease, has been investigated by various workers. Preliminary EXAFS and XANES spectral results indicate that the local environment of the Ni(II) ions in urease most closely resembles that of the nickel ions in the model compound [$Ni(HL)_2(L)$]ClO_4 , where HL is 1-n-propyl-2-α-hydroxybenzylbenzimidazole and L is the deprotonated form [467]. In addition, light scattering experiments indicate that the coordination sphere of the nickel ion in urease is consistent with Ni(II) in an octahedral complex [468].

Turning to amino acids, the bulk of complexation with Ni(II) has been studied in solution using potentiometry [469-483]. Of interest is the reaction of N-phenylglycine and N-napthylglycine with Ni(II). N-phenylglycine reacts in the presence of base forming the monomeric octahedral complex [$NiL_2(H_2O)_2$] (HL= phenylglycine), as well as the polymeric octahedral complex [NiL_2]$_n$, in which both bidentate and bridging carboxylate groups are present. N-α-napthylglycine reacts yielding only the polymeric complex [470].

Soluble models have been used to mimic the separation mechanism of α-amino acid enantiomers by ligand exchange chromatography on chiral, metal complexed stationary phases. In the study, structures were assigned to the coordination complexes involved in the stereoselection [472].

Calorimetry has been used to study the thermodynamics of the complexation of Ni(II) with L-aspartic acid in aqueous solution. Both $NiL(H_2O)_3$ (127) and $NiL_2(H_2O)_2^{2-}$(128) (H_2L= aspartic acid) were formed. The change in the mode of coordination proceeding from the <u>mono</u> to the <u>bis</u> complex is manifested by an enthalpy change on coordination of the second ligand, which is more than double the enthalpy of attachment of the first ligand [475].

Table 9. Biological ligands and their Ni(II) complexes.

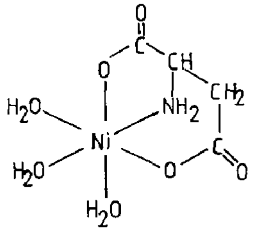
LIGAND	COMPLEX	COMMENTS	Ref.
α-(3,5-dimethyl-1-pyrazolyl)acetamide (L)	$[NiL_2X_2]$	Pseudooctahedral; $X=Cl^-, Br^-, I^-, NCS^-, ClO_4^-, NO_3^-, BF_4^-$.	[446]
1-Hydroxymethyl-3,5-dimethylpyrazole (HL)	$[Ni(HL)_2X_2]$	Octahedral; $X=Cl^-, Br^-, I^-, NCS^-, ClO_4^-, NO_3^-, \frac{1}{2}SO_4^{2-}$	[447]
	$[NiL_2(H_2O)_2]$	Octahedral	[447]
1,5-Dimethylpyrazole-3-carboxylic acid (HL)	$[NiL_2B]$	Octahedral; B= 2,2'-bipy, 1,10-phen.	[448]
Bis(methylaminoantipyryl)-ethane (L)	$[NiL(NCS)_2]$	Tetrahedral	[449]
1-Phenyl-2,3-dimethyl-5-pyrazolone-4-methylamino-methane sulphonate (L^-)	$[NiL_2]$	Octahedral	[450]
5-Benzylthio-1,2,4-triazole (HL)	$[NiL_2]$	Tetrahedral	[451]
3-Mercapto-4-ethyl-5- 4'-(4''X-phenylsulphonyl)-phenyl -1,2,4-triazole (HL; X=H,Cl,Br)	$[NiL_2]$	Complexes in the thionic form	[452]
3-Aryloxymethyl-4-aryl-5-mercapto-1,2,4-triazole(L)	$[NiL_2X_2(H_2O)_2]$	Octahedral; $X= NO_3^-$.	[453]
2-Ureido-4,6-dimethylpyrimidine (L)	$[NiL_2Cl_2]$	Octahedral	[454]
4-Amino-6-hydroxy-2-mercapto-5-nitroso-pyrimidine (HL)	$NiL_2 \cdot 2H_2O$		[455]
Isocyanuric acid (HL)	$[NiL_2]$		[456]
Barbituric acid (HL)	$NiL_2 \cdot 2H_2O$		[458]
	NiL_3Cl	Distorted octahedral	[459]
5,5-Diethylbarbituric acid (HL)	$NiL_2 \cdot 2H_2O$		[460]
5,5-Dihydroxybarbituric acid (HL)	$NiL_2 \cdot 11H_2O$		[460]

Table 9. continued.

LIGAND	COMPLEX	COMMENTS	Ref.
Pyrazine-2-amide (HL)	$[NiL_2]$	Square-planar	[461]
Pyrazine-2,3-diamide (L)	$[NiL_2X_2]$	Distorted octahedral; $X=Cl^-,Br^-,NO_3^-$.	[461]
2,4-*Bis*(isopropylamino)-6-methoxy-1,3,5-triazine (L)	$[NiL_2Cl_2]$	Distorted octahedral;Crystal structure	[462]
N-benzothiazolyl-N'-alkyl thiourea (HL)	$[NiL_2]$		[463]
2-Substituted Thiazolidine-4-carboxylic acids		Potentiometric study	[464]
Benzothiazole sulphonamide morpholide (L)	$[NiL_2X_2]$	Octahedral; $X=Cl^-,NO_3^-,OAc^-$.	[465]
N-cyclohexylbenzothiazole sulphonamide (L)	$[NiL_2X_2]$	Octahedral; $X=Cl^-,NO_3^-,OAc^-$.	[466]
4-Hydroxy-L-proline (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[469]
N-R-glycine (HL; R=phenyl,α-naptha)	$[NiL_2(H_2O)_2]$	Distorted *trans*-octahedral	[470]
	$[NiL_2]$	Bridging and bidentate COO^- groups	[470]
Dihydro-1H,3H,5H-*oxazolo* 3,4-e *oxazole-7a-carboxylic* acid (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[471]
Tyrosine	$[NiLX]^{n-}$	X= ATP, ADP, AMP; n= 3,2,1.	[473]
Tryptophan		Potentiometric study	[474]
L-aspartic acid (H_2L)	$[NiL(H_2O)_3]$	Calorimetric study	[475]
Glycyl-L-histidine (HL)		Potentiometric study	[476]
L-histidineglycine (HL)		Potentiometric study	[476]
L-carnosine (HL)		Potentiometric study	[476]
o-Phospho-D,L-serine (HL)	$[NiL_2]$	Potentiometric study	[477]
L-alanine (HL)		Ni(II) catalysed racemization	[478]

Table 9. continued.

LIGAND	COMPLEX	COMMENTS	Ref.
Cysteine-cysteine (L)	$[NiL_2]$	Bonded through sulphur only	[480]
Glycinehydroxamic acid (HL)	$[NiL_2]$	Square-planar	[482]
Serinehydroxamic acid (HL)	$[NiL_2]$	Square-planar	[482]
Oxamic acid (H_2L)	$K_2[NiL_2]\cdot 2H_2O$	Octahedral	[483]
	$K_4[NiL_3]$	Octahedral	[483]
1-[(3-aminopropyl)-amino]-1,6-dideoxy-L-mannose(L)	$[NiL_2]Br_2\cdot 2H_2O$	Octahedral; Crystal structure	[484]
2-[(2-aminoethyl)-amino]-2-deoxy-L-sorbose (L)	$[NiLB]Cl_2$	Octahedral; B= ethylenediamine Crystal structure	[485]
3-Amino-2-benzoylbenzofuran (L)	$[NiLCl_2]\cdot H_2O$	Octahedral; Polymeric with bridging chloride groups	[486]
Brucine (L)	$[NiL_2Cl_2]$	Square-planar	[487]
1-Oxidopyridinium-2-thiol (HL)	$[NiL_2(PPh_3)]$		[488]



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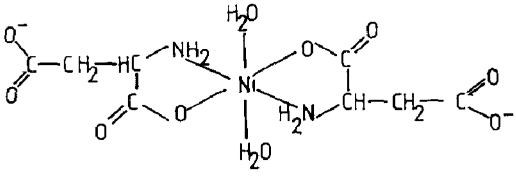

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Ni(II) reacts with the peptide antibiotic, Bacitracin A, yielding a Ni-bacitracin complex which contains a group having a pK_a near pH 5.5. Deprotonation of this group results in the aggregation and precipitation of the metal-bacitracin complex. It has been shown that the group, which is the N-terminal amino of isoleucine, is protected by the metal from reacting with 2,4,6-trinitrobenzene sulphonate [479].

Carbon dioxide dehydrogenase from Clostridium thermoaceticum has been isolated and purified. The enzyme dissociates to form a dimer with an αβ structure, which apparently contains per mol 2 nickel. Under acidic conditions a low molecular weight nickel factor separates from the enzyme [481].

Finally, the interaction of carbohydrates with Ni(II) has been examined. The single-crystal X-ray structures of bis{1-[(3-aminopropyl)amino]-1,6-dideoxy-L-mannose}nickel(II) dibromide [484] and (ethylenediamine)(2-[(2-aminoethyl)amino]-2-deoxy-L-sorbose)nickel(II) dichloride [485] have been determined.

1.4 NICKEL (I)

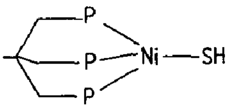
Synthetic methods that have been used in the preparation of nickel(I) complexes involve both chemical and electrochemical techniques applied to the oxidation of Ni(0) complexes, or the reduction of Ni(II) complexes. These techniques have been used with great success, as shown by the new Ni(I) complexes which are listed in table 10.

The reduction of nickel(II) halides with $Na[BH_4]$, in the presence of various ligands still appears to be a popular and effective method for preparing nickel(I) complexes [489-491]. This method has been used to synthesize a range of distorted tetrahedral complexes of the type $[NiL_4]^+$, $[NiL_3X]$, $[NiL_2X_2]^-$, $[NiLX_3]^{2-}$, $[NiL_2X]_2$ and $[NiLX]_n$ (L= ligand containing group-V donor atom; X= halide) [489,490].

Table 10. Ni(I) complexes.

COMPLEX	μ_{eff}/μ_B (BM)	COMMENTS	Ref.
$[NiL_4]BPh_4$ (L= PPh_3, $AsPh_3$, $SbPh_3$)	2.10-2.38	Distorted tetrahedral	[489]
$PR_4[NiX_2L_2]$ (X= Cl^-, Br^-, I^-)	2.16-2.31	Distorted tetrahedral	[489]
$[PR_4]_2[NiX_3L]$ (R= Ph, $PhCH_2$)	2.25	Distorted tetrahedral	[489]
$[NiXL_3]$ (L= $SbPh_3$; X= Cl^-, Br^-, I^-)	1.71-2.06	Distorted tetrahedral	[490]
$[NiXL_2]_2$ (L= $SbPh_3$, PPh_3, $AsPh_3$; X= Cl^-, Br^-, I^-)	1.71-2.06	Distorted tetrahedral	[490]
$[NiXL]_n$ (L= PPh_3; X= Cl^-)	1.64-1.72	Distorted tetrahedral	[490]
$[NiL(SH)]$ (L= 1,1,1-tris(diphenylphosphino)methylethane)		Distorted tetrahedral	[491]
$[NiLX]$ (L= tris(2-diphenylphosphinoethyl)amine; X= Cl^-, Br^-, I^-)		Trigonal bipyramidal	[492]
$[Ni\{P(CH_2CH_2PPh_2)_3\}]ClO_4$	2.10	Trigonal pyramidal; Crystal structure	[493]
$[Ni\{N(CH_2CH_2AsPh_2)_3\}(PPh_3)]ClO_4$	2.01	Distorted trigonal bipyramidal	[493]
$[Ni(\mu\text{-}t\text{-}Bu_2P)(PMe_3)]_2$		Ni-Ni interaction (2.375(3) Å)	[494]
$[Ni(SiMe_3)_2(PMe_3)]_2$		Ni-Ni interaction (2.38 Å)	[495]
$[(NiL)_2(\mu\text{-}S_2)]$ (L= 1,1,1-tris(diphenylphosphino)methylethane)	2.04	Dimer bridged by two sulphur atoms	[496]

Reduction of the dithiocarbamate complex [Ni(triphos)(S_2CNEt_2)]BPh_4 (triphos= 1,1,1-tris{(diphenylphosphino)methyl}ethane) with Na[BH_4] yields [Ni(triphos)(SH)] (129), which has a distorted tetrahedral structure and a room-temperature magnetic moment of 2.11 μ_B corresponding to a doublet ground state [492]. In addition, the related compound [(triphos)Ni(μ-S_2)-Ni(triphos)]ClO_4 is a novel nickel dimer bridged by two sulphur atoms (130). The Ni_2S_2 bridging framework is planar, with a Ni-Ni distance of 3.865(1) Å, while a formal oxidation of I/II has been assigned [492].



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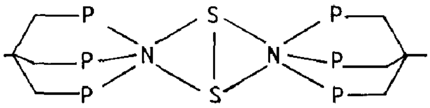
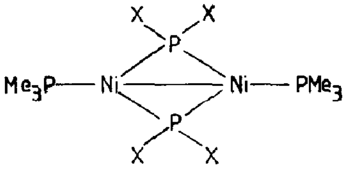


(130)

Two relatively rare nickel(I) phosphido-bridged compounds have been synthesized recently. Reaction of di-tert-butylphosphido lithium with [$NiCl_2(PMe_3)_2$] yields the dinuclear complex [Ni(μ-t-Bu_2P)(PMe_3)$_2$]$_2$ (131), the structure of which has been determined crystallographically. The phosphorous and nickel atoms are coplanar and the Me_3P-Ni-Ni-PMe_3 moeity is linear, giving the molecule D_{2h} symmetry. The Ni-Ni separation of 2.375(3) Å is in accordance with a single metal-metal bond [493]. The crystal stucture of a similar phosphido-bridged dinuclear complex, [$Me_3PNiP(SiMe_3)_2$]$_2$ (132), has also been determined. Each nickel atom is trigonally-planar coordinated, and the Ni-Ni separation is 2.38 Å, corresponding to a single Ni-Ni bond [494].



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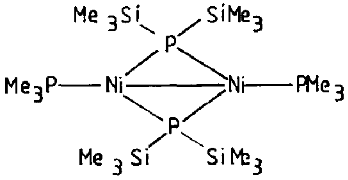


(132)

While on the subject of binuclear bridged nickel(I) complexes, much work has been done on dicyclopentadienyl dinuclear nickel complexes which contain various bridging moeities. Spectroscopic techniques, including infrared [495] and photoelectron spectroscopy [496], have been used to study the electronic stucture of $[Ni(\eta^5-C_5H_5)(\mu-CO)]_2$. An interesting result emanating from this study is the occurence of two back-bonding interactions between four metal-based d-electrons and the Π^* molecular orbitals of the bridging carbonyl groups. Irradiation of $[Ni(\eta^5-C_5H_5)(\mu-CO)]_2$ in the presence of a suitable alkyne leads to the photochemical formation of the corresponding alkyne-bridged dinuclear complex $[\{Ni(\eta^5-C_5H_5)\}_2(RC{\equiv}CR')]$ (R,R'= H, CH_3, C_6H_5) [497]. In addition, the gas phase UV photoelectron spectra of some of the alkyne-bridged complexes have been reported. Spectral features related to ionizations from molecular orbitals involved in metal-alkyne back-donation have been detected for the first time [498].

Tripod-like polytertiary phosphines or closely related ligands such as tris(2-diphenylphosphinoethyl)amine (133), tris(2-diphenylphosphinoethyl)-phosphine (134) and tris(2-diphenylarsenoethyl)amine (135), have been shown to be suitable for the stabilization of nickel(I) [499,500]. The Ni(I) complex is usually obtained by oxidation of a suitable nickel(0) complex:

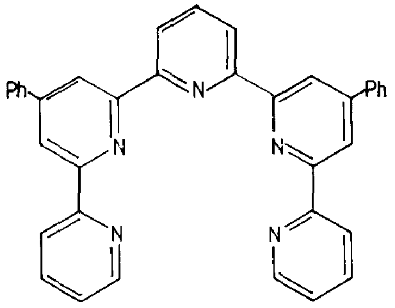
$$\underset{(L=\ 133)}{NiL} \quad + \quad \underset{(RX=\ \text{organic halide})}{RX} \longrightarrow \underset{(136)}{NiLX}$$

$$\begin{tikzcd}
Ni(C_2H_4)(PPh_3)_2 & + & L \arrow[r, "C_3Ph_3\ ClO_4"] \arrow[d, dash] & NiL\ (ClO_4)\ (137) & (L=\ 134) \\
& & {} \arrow[r] & NiL(PPh_3)\ (ClO_4)\ (138) & (L=\ 135)
\end{tikzcd}$$

Complex (136) has been assigned trigonal-bipyramidal geometry, in which the three phosphorous atoms occupy the equatorial positions, while the nitrogen atom and halide ion occupy the axial positions. The crystal structure of (138) reveals a similar configuration with the arsenic atoms occupying the equatorial positions, while the nitrogen atom and PPh_3 group occupy the axial positions. Compound (137) exhibits an unusual trigonal-bipyramidal goemetry in which the nickel atom is coordinated to the four phosphorous atoms of the ligand.

Electrochemical reduction has been used to generate various nickel(I) complexes in solution. The reductive electrochemistry of the complexes $[Ni(\eta^5-C_5H_5)(PR_3)_2]^+$ (R= C_2H_5, C_3H_7, C_4H_9, C_6H_5), $[Ni(\eta^5-C_5H_5)(Ph_2PCH_2CH_2PPh_2)]^+$ and $[Ni(\eta^5-C_5H_5)(Ph_2AsCH_2CH_2AsPh_2)]^+$ has been investigated in acetonitrile. In each case, with the exception of the triphenylphosphine complex, a single reduction process was observed, corresponding to a fast single electron transfer leading to a stable Ni(I) species. The triphenylphosphine complex $[Ni(\eta^5-C_5H_5)(PPh_3)_2]$ appears to undergo a chemical reaction, the reason for which is not yet clear [501]. Similar behaviour has been observed in the redox chemistry of phosphine-dithiolate and phosphine-catecholate complexes of nickel. The complexes $[Ni(PPh_3)_2L]^{n+}$ (L= dithiolate {n=0} or dithiocarbamate {n=1}) and [NiLL'] (L= dithiolate or catecholate, L'= *bis*(diphenylphosphine)) all exhibit a reversible or quasi-reversible one-electron reduction process, with the reduction potentials for the PPh_3 complexes being approximately 0.5V higher than those of the corresponding *bis*(diphenylphosphine) complexes. In the case of triphenylphosphine complexes such as $[Ni(PPh_3)_3(\{CN\}_2C_2S_2)]$, the voltammetry shows evidence of a dissociation equilibrium involving loss of PPh_3 from the nickel species after the electron process has occurred [502]. Similarly, the complex $[Ni\{(NC)_2C_2S_2\}\text{-}\{(CH_3)_2C_2N_2Ph_2\}]$ undergoes a one-electron reduction yielding a species containing nickel in the +1 oxidation state. This species is unstable and disproportionates yielding $[Ni\{(NC)_2C_2S_2\}_2]^{2-}$ and $[Ni\{(CH_3)_2C_2N_2Ph_2\}_2]$. However, a similar one-electron reduction of $[Ni(Ph_2C_2S_2)(1,10\text{-phen})]$ has been found to give a stable Ni(I) species with greater delocalization of the unpaired electron over the ligand [503].

The preparation and electrochemistry of the nickel (II) complexes of 4,4'''-diphenyl-2,2':6'2'':6'',2''':6''',2''''quinquepyridine (139) and the ligand derived from the template condensation of 6,6''-*bis*(methylhydrazino)-4'-phenyl-2,2':6',2''-terpyridine with glyoxal (140), have been reported [504,505]. Of interest are the Ni(I) complexes which have been generated electrochemically, since relatively few examples of nickel in the +1 oxidation state with nitrogen donor ligands are known.



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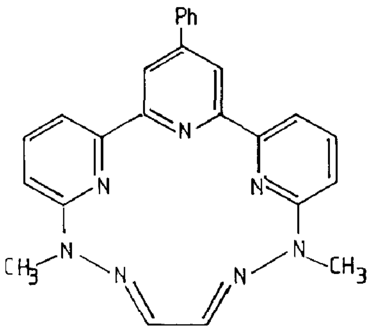
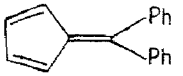


(140)

1.5 NICKEL (0)

Ni(0) complexes containing good leaving groups such as 1,5-cyclooctadiene (cod) and ethylene have been used extensively as synthons in the preparation of new Ni(0) complexes [506-515]:

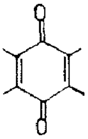
$[Ni(cod)_2] + L \longrightarrow [Ni(cod)L]$ (L= ) [506]

$[Ni(cod)_2] + 2PR_3 + 2CS_2 \longrightarrow [Ni(PR_3)_2(CS_2)_2]$ (R= Me, Et) [507]

$2[Ni(cod)_2] + 2PR_3 + 2CS_2 \longrightarrow [Ni(PR_3)(CS_2)]_2$ (R= Ph) [507]

$[Ni(cod)_2] + PPh_3 + HCOOC_2H_5 \longrightarrow [Ni(CO)(PPh_3)_3] + C_2H_5OH$ [508]

$[Ni(bipy)(cod)] + SCO \longrightarrow [Ni(bipy)(SCO)]$ [509]

$[Ni(bipy)(cod)] + L \longrightarrow [Ni(bipy)(\eta^4\text{-}L)]$ (L= ) [510]

$[NiL(cod)] + H_2C{:}CHCH{:}CHCO_2Me \longrightarrow [NiL(H_2C{:}CHCH{:}CHCO_2Me)]$ [511]
(L= $Ph_2PCH_2CH_2PPh_2$)

$[Ni(PPh_3)_2(C_2H_4)] + MeC{\equiv}CMe \longrightarrow [Ni(PPh_3)_2(MeC{\equiv}CMe)]$ [512]

$[Ni(PPh_3)(C_2H_4)] + H_2C{:}CHSiR_3 \longrightarrow [Ni(PPh_3)_2(H_2C{:}CHSiR_3)]$ [513]
(R= Me, OMe)

$[Ni(\eta^3\text{-}C_3H_5)_2] + L \longrightarrow [NiL_2]$ (L= bis{diphenylphosphino}-N-methylmaleimide) [514]

Many of the complexes have been isolated as solids, and structural data obtained from X-ray crystallographic studies are listed in table 11. Of particular interest is the structure of [Ni(bipy)(cod)], in which the nickel atom is tetrahedrally coordinated, while the cod ligand maintains a twisted boat conformation [516].

The reactions of carbon dichalcogenides with Ni(0) complexes have generated much interest of late [507,509,517-520]. The decisive factor for reaction to occur has been shown to be the HOMO-energy of the complex, relative to the LUMO-energy of the potential ligand. For example, [Ni(bipy)(cod)] reacts with SeCS, CS_2 and SCO, whereas $[Ni(PPh_3)_2(C_2H_4)]$ only reacts with CS_2, and not SCO. Generally the carbon dichalcogenides are bonded side-on (η^2), and it is always the most electronegative heteroatom of the asymmetric ligands SeCS and SCO which does not interact with the central metal atom [509].

Table 11. Crystallographic data of some Ni(0) complexes.

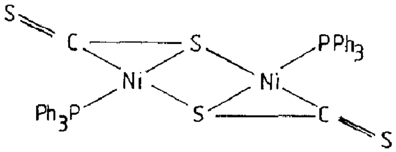
COMPLEX	CONFIGURATION	STRUCTURAL DATA (Å)	Ref.
[Ni(bipy)(cod)]	Tetrahedral	Ni-C 2.052 Ni-N 1.940(4); 1.936(4)	[516]
[Ni(6,6-diphenylfulvene)(cod)]	Tetrahedral	Ni-C(cod) 1.36(1) Ni-C(fulvene) 2.20(1); 2.07(1)	[506]
[Ni(PPh$_3$)(μ-CS$_2$)$_2$]	Distorted square-planar	Ni-P 2.232(4) Ni-C 1.81(1) Ni-S 2.157(4); 2.150(4)	[518]
[Ni(SC(S)SC(PMe$_3$)S)(PMe$_3$)]	Severely distorted square-planar	Ni-P(average) 2.165(7) Ni-S(average) 2.156(5) Ni-C(average) 1.92(1)	[519]
[Ni(PEt$_3$)$_2$(PSiMe$_3$)$_2$]	Square-planar	Ni-PEt$_3$ 2.236(2) Ni-PSiMe$_3$ 2.258(2) P-P 2.149(2)	[524]
[Ni(benzaldehyde)(PCy$_3$)$_2$]	Square-planar	Ni-P 2.244(2); 2.171(2) Ni-O 1.867(3) Ni-C 1.983(5)	[528]
[Ni(Ph$_2$PCH$_2$CH$_2$PPh$_2$)L] (L= penta-2,4-dienoic acid methyl ester)	Tetrahedral	Ni-P 2.146(1); 2.178(1) Ni-C(average) 2.139(4)	[511]

The reactions of CS_2, CO_2 and COS with Ni(0) complexes have been reviewed [507]. Compounds of varying stoichiometry have been obtained, depending on the phosphine used:

$$2[Ni(cod)_2] + 2PR_3 + 2CS_2 \longrightarrow [Ni(PR_3)(CS_2)]_2 \quad \text{(R=Ph, } \underline{p}\text{-toluene, cyclohexyl)}$$

$$[Ni(cod)_2] + 2PR_3 + 2CS_2 \longrightarrow [Ni(PR_3)_2(CS_2)_2] \quad \text{(R=Me, Et)}$$

$[Ni(PR_3)(CS_2)]_2$ was originally assigned the binuclear structure (141), on the basis of spectroscopic evidence [507,517]. However, a subsequent single-crystal X-ray analysis of the triphenylphosphine complex has revealed that the complex has the binuclear structure (142) [518].



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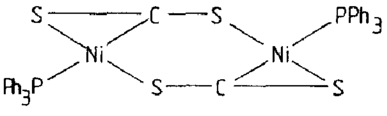
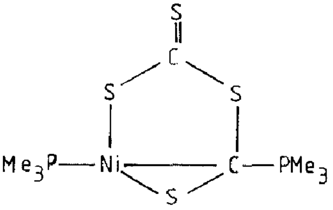


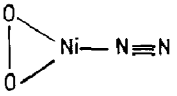
(142)

The single-crystal X-ray structure of $[Ni(PMe_3)_2(CS_2)_2]$ has been determined. The complex displays NiPSCS coordination (143), and is severely distorted from square-planar. Of interest is the fact that the SC(S)SC(PMe_3)S linkage can be formally described as a condensation product of two molecules of CS_2 with one molecule of PMe_3 [519].



(143)

Another route used in the synthesis of Ni(0) complexes utilizes the rather volatile and unstable carbonyl complex $Ni(CO)_4$. The unstable metal carbonyl species $[Ni(CO)_3N_2]$ has been generated by photolysis of $Ni(CO)_4$ in liquid krypton, doped with nitrogen at 114 K [520]. Infrared spectroscopy has been used to monitor the decay kinetics of $Ni(CO)_3N_2$ in the presence of dissolved CO. The reaction rate exhibits a first order dependence on the concentration of $Ni(CO)_3N_2$ and a more complex dependence on the concentrations of CO and N_2. The reaction pathway has been assigned a simultaneous dissociative/associative mechanism, and the Ni-N_2 bond dissociation energy has been estimated at 10 kcal per mole [521]. In addition, ab initio MO calculations have been used to predict the bonding between Ni and N_2 in the related complex $[Ni(O_2)(N_2)]$. Of the three geometrical isomers with a C_{2v} symmetry considered (144,145,146), it was shown that end-on coordination of N_2 (144) is preferred to the side-on structure [522].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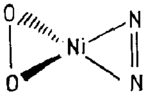
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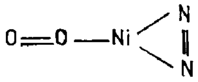
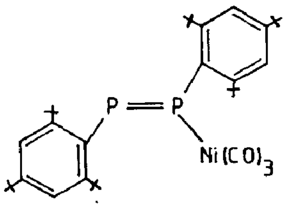

(146)

The diphosphene (2,4,6-t-$Bu_3C_6H_2)_2P_2$ reacts with $Ni(CO)_4$ yielding the complex $[Ni(CO)_3L]$ (L= diphosphene) (147). The complex is noteworthy, since not only is it the first indication that compounds with P=P bonds will react with organometallic reagents, but a new mode of coordination for diphosphene ligands is also exhibited [523]. Bis(triethylphosphine) η^2-bis(trimethylsilyl)diphosphene nickel, the crystal structure of which has been determined [524], shows the diphosphene ligand coordinated in the more common η^2-mode. The complex is of interest since it is the first example of a molecule showing a bond between a Ni atom and a tricoordinated P atom (148).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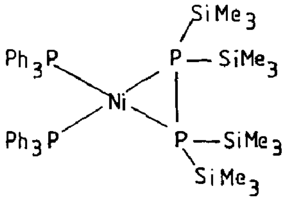

(148)

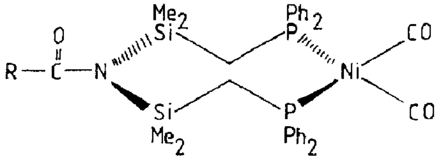
The behaviour of the chelating donor ligand o-lithiobenzyldiphenylphosphine (149) with a series of nickel(0) complexes has been investigated. The resultant complexes vary according to the donor properties of the ligands in the Ni(0) complexes [525]:

$$[Ni(cod)_2] \quad + \quad 2(149) \longrightarrow (Li\cdot THF)_2[\overline{Ni(\underline{o}\text{-}C_6H_4CH_2PPh_2}{)}_2]$$

$$[Ni(CO)_4] \quad + \quad 2(149) \longrightarrow Li(Et_2O)_3[\overline{Ni(\underline{o}\text{-}C_6H_4CH_2PPh_2}{)}(CO)_2]$$

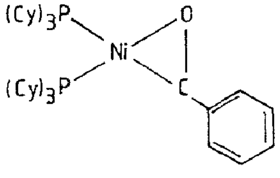
$$[Ni(PPh_3)(C_2H_4)] \quad + \quad 2(149) \longrightarrow Li(Et_2O)[\overline{Ni(\underline{o}\text{-}C_6H_4CH_2PPh_2}{)}(PPh_3)_2]$$

A novel nickel(0) dicarbonyl complex has been synthesized from the Ni(II) complex $[Ni(R)N(SiMe_2CH_2PPh_2)_2]$ (R= CH_3, η^3-C_3H_5, $HC{=}CH_2$, Ph). The mechanism involves migratory insertion of CO into the Ni(II) carbon bonds of $[Ni(R)N(SiMe_2CH_2PPh_2)_2]$, which promotes rearrangement of the amidophosphine hybrid ligand to generate the nickel(0) carbonyl derivative $[Ni(CO)_2\{RCON(SiMe_2CH_2PPh_2)_2\}]$ (150) [526].



(150)

The stereochemistry of $[Ni(PH_3)_2(H_2CO)]$ and $[Ni(PH_3)_2(CO_2)]$ has been studied using the ab initio MO method. Energy decomposition analysis indicates that, due to stronger back-donation, the planar side-on mode of coordination is favoured for $[Ni(PH_3)_2(CO_2)]$ [527]. Support for this mode of coordination is given by the crystal structure of the related complex $Ni(PCy_3)_2(PhCHO)$ (151). The benzaldehyde ligand is Π-coordinated, with strong back-donation from the Ni atom to the C=O group, while the coordination environment of the nickel atom is essentially planar [528].



(151)

$[Ni\{(+)-(diop)\}_2]$ $\{(+)-(diop)=$ (+)-(2S,3S)-(2,3-isopropylidenedioxybutane-1,4-diyl)bis(diphenylphosphine)$\}$ has been prepared and used as a catalyst for the asymmetric addition of HCN to alkenes. The zerovalent complex was prepared by borohydride reduction of $NiCl_2$ in the presence of the diphosphine ligand [529]. Other catalytic uses for nickel(0) complexes have been the electrochemical synthesis of arylcarboxylates [530] and the oligomerization of alkynes [531].

1.6 POLYNUCLEAR COMPLEXES

Polynuclear complexes may be divided into two broad catagories viz. those that contain nickel-nickel or nickel-metal interactions (clusters), and those that do not (miscellaneous). In addition, it should be noted that some polynuclear complexes have been described in earlier sections.

1.6.1 Clusters

The field of cluster chemistry has recieved much attention recently. Table 12 lists some relevant data concerning homonuclear [532-536] and heteronuclear [539-550] nickel-containing cluster complexes. In most cases, characterization of the complexes has been achieved by single-crystal X-ray methods.

Homonuclear nickel clusters range from those containing three Ni atoms to those containing twelve, with the average Ni-Ni interaction varying from 2.410 to 2.818 Å. The complex anions $[Ni_3(\eta^5-C_5H_5)(\mu_3-CO)_2]^-$ and $[Ni_3(\eta^5-C_5Me_5)-(\mu_3-CO)_2]^-$ exhibit the steric effects of introducing the bulky pentamethylcyclopentadienyl ligand, with the average Ni-Ni distance changing from 2.410 Å to 2.530 Å [532].

$[Ni_6(CO)_{12}]^{2-}$ has been used as a synthon for the preparation of a variety of large nickel-carbonyl-phosphinidene and arsinidene clusters [537]. In addition, when hydrolysed under buffered conditions, it yields the carbonylnickelate complexes $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n= 2,3,4) [538].

As can be seen from table 12, a large variety of heteronuclear nickel-containing cluster complexes have been prepared. Chiral organotransition-metal tetrahedral clusters of the type $[(RC{\equiv}CR')Ni(\eta^5-C_5H_5)M]$ $\{M=(\eta^5-C_5H_5)-Mo(CO)_2$; $Co(CO)_3$; $(\eta^5-C_5H_5)Ni$ $\}$ react with $Fe_2(CO)_9$, yielding square-pyramidal chiral clusters of the general formula $[(RC{\equiv}CR')Ni(\eta^5-C_5H_5)MFe(CO)_3]$. In this general synthetic route, the alkyne is used as a bridging ligand for the metal centres [551].

Di-t-butoxytin(II) and bis(trimethylsiloxy)tin(II) react with $Ni(CO)_4$, yielding the disubstituted complex $[Ni(CO)_3Sn(OCMe_3)_2]_2$ and monosubstituted complex $Ni(CO)_3[Sn(OSiMe_3)_2]_2$ respectively [552].

Table 12. Crystallographic data of some homonuclear and heteronuclear nickel containing clusters.

COMPLEX	STRUCTURAL DATA (Å)	COMMENTS	Ref.
Homonuclear			
$[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_2]^-$	Ni-Ni(av.)= 2.410	Comparison shows the steric influence of	[532]
$[Ni_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}CO)_2]^-$	Ni-Ni(av.)= 2.530	Me groups on Ni·Ni interaction.	[532]
$[Ni_3(\mu_3\text{-}S)(\underline{o}\text{-}\{SCH_2\}_2\text{-}C_6H_4)_3]^{2-}$	Ni-Ni(av.)= 2.818	Each Ni atom is square-planar.	[533]
$[Ni_3(\mu_3\text{-}Se)(PEt_3)_6]^{2+}$	Ni-Ni(av.)= 3.16(1)	Not a significant Ni-Ni interaction.	[534-5]
$[Ni_8C(CO)_{16}]^{2-}$	Ni-Ni(av.)= 2.55		[536]
$[Ni_9C(CO)_{17}]^{2-}$	Ni-Ni(av.)= 2.55		[536]
Heteronuclear			
$[(\mu\text{-}H)_3NiOs_3(CO)_9(\eta^5\text{-}C_5H_5)]$	Ni-Os(av.)= 2.567	Two distinct molecules differing in the	[539]
	Os-Os(av.)= 2.871	orientation of $\eta^5\text{-}C_5H_5$.	[540]
$[(\eta^5\text{-}C_5H_5)_3Ni_3Os_3(CO)_9]$	Ni-Ni = 2.54	High yield pyrolitic synthesis.	[541]
	Ni-Os(av.)= 2.61		
	Os-Os(av.)= 2.769		
$[(\eta^5\text{-}C_5H_5)_2Ni_2Ru(CO)_3(C_2Ph_2)]$	Ni-Ni = 2.418	Triangular cluster.	[542]
	Ni-Ru(av.)= 2.495		
$[(\eta^5\text{-}C_5H_5)_2Ni_2Ru_2(CO)_6\{C_2(H)C(=CH_2)CH_3\}]$	Ni-Ni = 2.368	Ni_2Ru triangle with pendant Ru.	[543]
	Ni-Ru(av)= 2.505		
	Ru-Ru = 2.960		
$[(\eta^5\text{-}C_5H_5)_2Ni_2Fe(CO)_3(C_2Ph_2)]$	Ni-Ni = 2.404	Triangular cluster.	[542]
	Ni-Fe(av.)= 2.385		

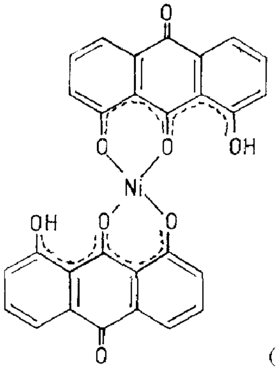
Table 12 continued.

COMPLEX	STRUCTURAL DATA (Å)	COMMENTS	Ref.
$[Fe_2Ni(\mu_3\text{-}C_2Ph_2)(CO)_6(\eta^5\text{-}C_5H_5)]^-$	Ni-Fe(av.)= 2.463 Fe-Fe = 2.506	$[Ni(PMe_3)_2(\eta^5\text{-}C_5H_5)]^+$ as cation.	[544]
$[(\eta^5\text{-}C_5H_5)NiCoFe(CO)_5(PPh_3)(C_2Ph_2)]$	Ni-Fe = 2.486 Ni-Co = 2.390 Fe-Co = 2.467	Asymmetric CO bridge on the Fe-Co bond.	[545]
$[(CH_3C)CoMoNi(\eta^5\text{-}C_5H_5)_2(CO)_5]$	Ni-Co = 2.336 Ni-Mo = 2.557 Co-Mo = 2.651	Novel synthesis; Capped triangle.	[546]
$[(PhC)MoNi_2(\eta^5\text{-}C_5H_5)_3(CO)_2]$	Ni-Ni = 2.373 Ni-Mo = 2.622	Novel synthesis; Capped triangle.	[546]
$[(\eta^5\text{-}C_5H_5)_2Mo_2(\mu_3\text{-}S)_4Ni_2(CO)_2]$	Ni-Ni = 2.962 Ni-Mo(av.)= 2.722 Mo-Mo = 2.829	Weak Ni-Ni interaction.	[547]
$[(\eta^5\text{-}C_5H_5)_4Cr_2Ni_2(\mu_3\text{-}S)_2(\mu_4\text{-}S)]$	Cr-Cr = 2.62 Cr-Ni(av.)= 2.75	Butterfly structure; Ni···Ni=4.34 Å.	[548]
$[(\eta^5\text{-}C_5H_5)_2Nb(CO)(\mu\text{-}H)Ni(CO)_3]$	Ni-Nb = 3.218	Weak Ni-Nb interaction; H-bridge.	[549]
$[\{(\eta^5\text{-}C_5H_5)(CO)_2Fe\}\{(\eta^5\text{-}C_5H_5)(CO)Ni\}\text{-}\{(CO)_4Co\}SnCl]$	Ni-Sn = 2.493 Co-Sn = 2.651 Fe-Sn = 2.544	Sn(IV) is tetrahedrally coordinated by Ni, Co, Fe and Cl.	[550]

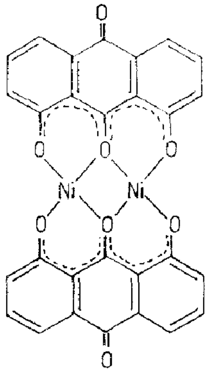
Finally, new polynuclear organometallic compounds containing Ge, Hg, Cd and Ni have been prepared by the reaction of the germyl derivatives of Cd and Hg with $Ni(PPh_3)_4$ [553], while the reaction between $[Ni(cod)_2]$ and $[Rh_2(\mu\text{-}CO)_2(\eta^5\text{-}C_5Me_5)]$ affords the thermally unstable and air-sensitive complex $[NiRh_2(\mu\text{-}CO)_2(cod)(\eta^5\text{-}C_5Me_5)]$ [554].

1.6.2 Miscellaneous

The chelating ability of 1,8-dihydroxyanthraquinone with Ni(II) has been studied, with both mononuclear (152) and binuclear (153) chelates being isolated, depending on whether the ligand is in its monoanionic or dianionic form [555]. Similar binuclear complexes have been prepared using 2,4,6-heptatrione, o-acetoacetylphenol and 2-benzoylacetophenol in their dianionic forms. In addition, by using LiOH as base, it was possible to isolate the mononuclear complex as well [556].



(152)



(153)

Triionized citrate has been complexed with Ni(II), yielding the binuclear complex $K_2[NiL_2(H_2O)_2]_2\cdot 4H_2O$ (H_3L= citric acid). The crystal structure reveals that each triionized citrate ion is bound as a tridentate ligand, through two carboxylate oxygen atoms and a hydroxyl group, to one Ni atom, while a bridging bond to the second Ni atom is provided by a third carboxylate oxygen. Octahedral coordination is completed by water molecules [557].

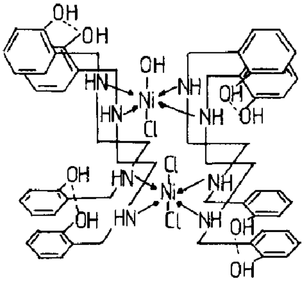
Naptharazin has the ability to form binuclear complexes if it functions as a tetradentate ligand. The binuclear complex $[Ni_2(L)(bipy)_2](PF_6)_2$ (H_2L= naptharazin) has been prepared, in which the naptharazinato ligand functions as a bridging unit between the two metal centres. Spectroscopic and magnetic data indicate that each metal ion is surrounded by two oxygen and two nitrogen atoms in a nearly tetrahedral configuration [558].

18-Crown-6 reacts with $NiCl_2\cdot 6H_2O$, yielding two products viz. $Ni_2Cl_2(H_2O)_8Cl_2\cdot$18-crown-6 and $2NiCl_2\cdot 2H_2O\cdot$18-crown-6. Both complexes have been characterized spectroscopically. In addition, the single-crystal X-ray structure of $Ni_2Cl_2(H_2O)_8Cl_2\cdot$18-crown-6 reveals an unusual conformation of the 18-crown-6 polyether and a $NiCl_2(H_2O)_8$ unit, containing the nickel atoms in the form of a bridged dinuclear unit. The cohesion of the structure is given by hydrogen bonds between the crown ether and the water molecules surrounding the dinickel unit [559].

A binuclear complex of nickel with bridging hydroxyl groups has been prepared by the reaction of 1-hydroxyethylidenediphosphonic acid and nickel(II) acetate in aqueous medium. The complex, $Ni_2L\cdot 6H_2O$ (L=1-hydroxyethylidenediphosphonic acid) is distorted octahedral in structure [560].

Circular dichroism has been used to study the binuclear nickel(II) complex of quinine . The complex has the general formula $Ni_2LCl_4(H_2O)_8$ with each nickel atom situated in an octahedral environment. The absence of Cotton effects indicates that the hydroxyl group of the quinine ligand does not participate in coordination [561].

α,α'-(ethylenediimino)bis-o-cresol reacts with Ni(II) giving rise to the binuclear complex $[Ni_2L_4(OH)Cl_3]$. The nickel atoms are octahedrally coordinated, while the ligand is in its gauche form (154) [562].



(154)

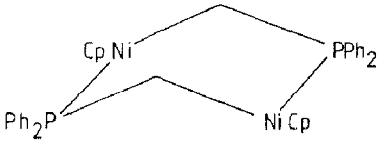
Binuclear complexes containing di-2-pyridylamine have been prepared. The complexes have the general formula $[Ni_2LX(NO_3)_2]$ (L= di-2-pyridylamine; X= bridging group) and are bridged by μ-oxamido, μ-oxamato and μ-oxalato groups respectively. Magnetic measurements reveal that the magnetic moments are slightly less than those found for mononuclear Ni(II) high spin complexes [563].

Reaction of the "1,2-dithiolene-like" ligand C_2S_4 with the dimeric complex $[Ni_2(\eta^5\text{-}C_5R_5)_2(\mu\text{-}CO)_2]$ (R= H, Me) yields two remarkably different products, depending on the cyclopentadienyl substituent. The hexanickel complex $[\{(Ni_3(\eta^5\text{-}C_5H_5)_3(\mu\text{-}S)\}_2(C_2S_4)]$ is formed when R=H, while the dinuclear complex $[Ni_2(\eta^5\text{-}C_5H_5)_2(C_2S_4)]$ is formed when R=Me. This effect is assigned to the bulky nature of the substituted cyclopentadienyl groups which preclude the formation of the hexanickel complex in the latter case [564].

The structure of $[(\eta^5\text{-}C_5H_5)_2Ni_2(C_{10}Cl_4S_4)]$,obtained by the reaction of $[(\eta^5\text{-}C_5H_5)_2Ni_2(CO)_2]$ with the tetrathiolate ligand, $C_{10}Cl_4S_4$, has been determined. The potentially tetradentate ligand functions in a bidentate fashion forming two sulphur bridges between the Ni atoms, which are eached capped by a cyclopentadienyl moeity [565].

While on the subject of sulphur bridging atoms, thiophenol and p-toluene thiol have been reacted with Ni(II) in isopropanol, yielding the sulphur bridged complexes $[Ni(HL)(L)(isopropanol)]_2$ (HL= thiophenol or p-toluene thiol). The complexes are square-planar with the deprotonated ligand functioning as the bridging group [566].

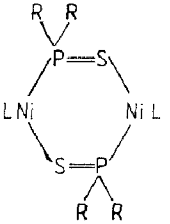
Various binuclear complexes containing monodentate phosphine ligands have been prepared [567-569]. Chloride bridging moeities have been found in the complexes $[Ni(PPh_3)_2XCl]_2$ ($X= Cl^-$, Br^-, NCS^-, NO_3^-) and $[Ni(CCF_3{=}CCF_3CH_2C_6H_4{-}NMe_2)(PEt_3)(\mu{-}Cl)]_2$. The complexes differ in coordination geometry with the former being distorted tetrahedral and the latter square-planar. In addition, the single-crystal X-ray structure of the phosphino methanide complex $[Ni(\eta^5{-}C_5H_5)P(C_6H_5)_2CH_2]_2$ (155) has been determined. The complex has a boat conformation with an average Ni-P bond distance of 2.134 Å [569].



(155)

The crystal structure of dibromobis{μ-[2-(diphenylphosphino)ethanethiolato]-P,μ-S}-dinickel(II) has been determined. The 2-(diphenylphosphino)ethanethiolate ion functions as a bidentate ligand, with coordination occurring via the P and S donor atoms, forming a five-membered non-planar ring. The coordination sphere of each Ni atom is square-planar, and the Ni-Ni distance is 2.695(2) Å [570].

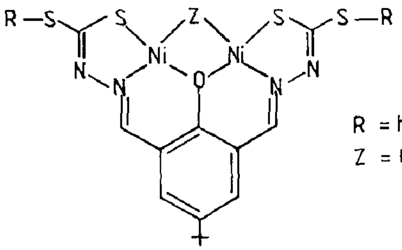
The unstable three-membered ring systems $[(\eta^5{-}C_5H_5)NiS{=}PR_2]$, obtained by the reaction of $[(\eta^5{-}C_5H_5)_2Ni]$ with *diorganylphosphane sulphides* R_2HPS (R= Me, Ph), dimerize at room temperature giving the binuclear complex $[(\eta^5{-}C_5H_5)Ni{-}S{=}PR_2]_2$ (156) [571].



(156)

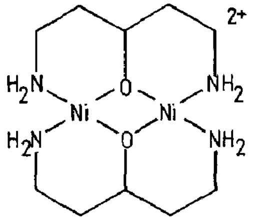
Ni-Ni bimetallomers of 4-*tert*-butyl-2,6-*bis* N-[[(heptylthio)thiocarbonyl amino]formimdoyl]phenol with a variety of bridging ligands ($Z= CH_3CH_2O^-$, OH^-, N_3^-, Br^-, CN^-), have been prepared. The ligand functions in a pentadentate manner, with each Ni atom in a square-planar environment (157) [572].

(157)



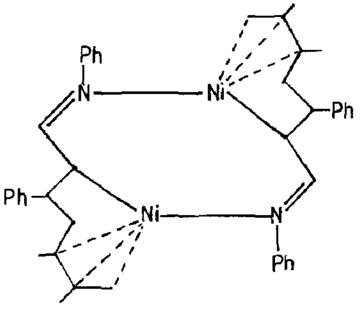
R = heptyl
$Z = CH_3CH_2O^-, OH^-, N_3^-, Br^-, CN^-$

A stable alkoxo-oxygen bridged planar Ni(II) complex has been reported, in which the ligand 1,5-diamino-3-pentanol coordinates in a tridentate manner, yielding $[Ni_2L_2](BPh_4)_2 \cdot 2CH_3OH$ (158) [573].



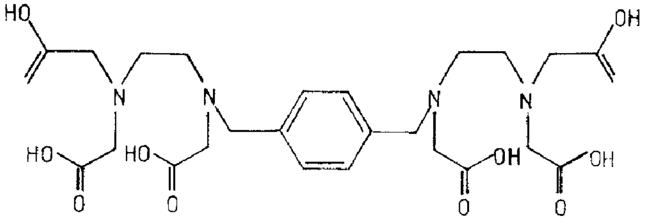
(158)

Reaction of cinnamaldehydaniline and 2,3-dimethylbutadiene with $Ni(cod)_2$ yields the binuclear complex *bis*[(μ-1,2,3,6-η)-2,3-dimethyl-5,8-diphenyl-8-aza-2,7-octadiendiyl]dinickel(II) (159). The nickel atoms are bonded to the Π-allyl and σ-azallyl groups, with the coordination number of both nickel atoms being four [574].



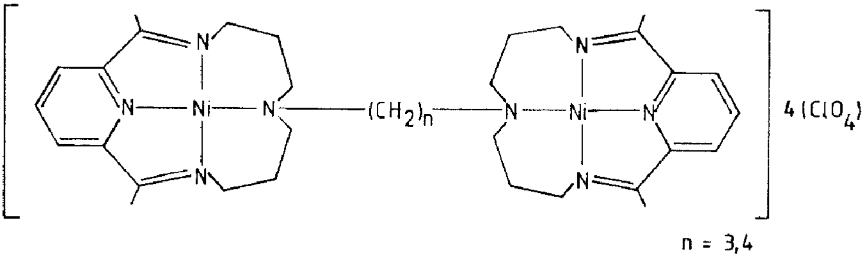
(159)

Ethylenediaminetetraacetic acid (H_4L= EDTA) reacts in its deprotonated form, yielding isomorphic complexes of the type $NiML \cdot 6H_2O$ (M= Ni, Zn, Co, Mn, Mg). X-ray and spectroscopic methods indicate that $EDTA^{4-}$ functions as a bridging ligand, and that both bridging and monodentate carboxylate groups are present [575]. The related ligand, 1,2-cyclohexanediaminetetraacetic acid, complexes with Ni(II) and Ca(II) in its deprotonated form, yielding $Ni_2L \cdot 6H_2O$ and $Ca_2L \cdot 7H_2O$ respectively. Mixing of these two complexes in aqueous solution results in the bimetallic complex $CaNiL \cdot 6H_2O$ [576]. In addition, the synthesis of a new decadentate binucleating ligand, 1,4-bis(2,5,5-tris(carboxymethyl)-2,5-diazapentyl)benzene (H_6L) (160) and its aqueous equilibria with Ni(II) has been described. The mode of coordination is found to be strongly dependent on pH [577].



(160)

Interest in binuclear macrocyclic complexes of Ni(II) has been sustained, with quite a few examples being reported. The single-crystal X-ray structure of meso,meso'-ethylenebis[octaethylporphyrinatonickel(II)] has been determined. The molecule has an interesting symmetry, containing parallel porphyrin rings linked by the ethylene bridge [578]. Similar complexes, containing two tetraaza macrocyclic rings connected by an alkyl chain of varying length (161) have been prepared (Systematic name: 7,7'-alkanebis{2,12-dimethyl-3,7,11,17-tetraazabicyclo[11,3,1]-heptadeca-1(17),2,11,13,15-pentaene}) [579].

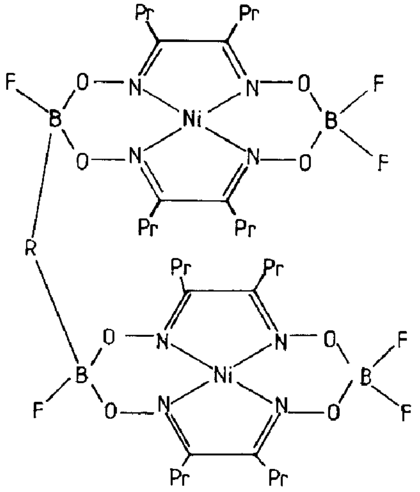


(161)

A new series of binuclear Ni(II) macrocyclic complexes with a terephthaloyl or isophthaloyl bridge have been prepared by the electrophilic substitution reaction of (11,13-dimethyl-1,4,7,10-tetraaza-10,12-cyclotridecandienato)-nickel(II) or (12,14-dimethyl-1,4,8,11-tetraaza-11,13-cyclotetradecandienato)nickel(II) with terephthaloyl chloride or isophthaloyl chloride. Substitution occurs at the γ-carbon atom of the macrocycle [580].

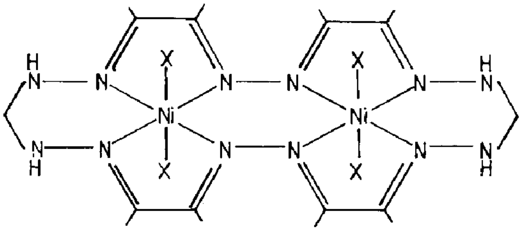
The use of oximes and dioximes in the synthesis of mononuclear macrocyclic complexes has been extended to the synthesis of binuclear macrocyclic complexes. *Bis*(α-dioximato)nickel(II) has been utilized as a synthetic precursor in the preparation of the binuclear complexes (162). The complexes may be synthesized via two routes, both of which utilize an organo*bis*(difluoroborane) as a linking reagent. The complexes were characterized using ^{1}H-, ^{13}C- and ^{19}F-n.m.r. [581].

(162)



$R = 1,4\text{-}C_6H_4,\ \text{-}(CH_2)_4\text{-}$

A novel binuclear macrocyclic complex of Ni(II) (163) has been prepared by the action of formaldehyde on tetrathiocyanato*bis*(3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone)dinickel(II). The complex has been characterized by spectroscopic, magnetic and polarographic methods, and is tetragonally distorted [582].

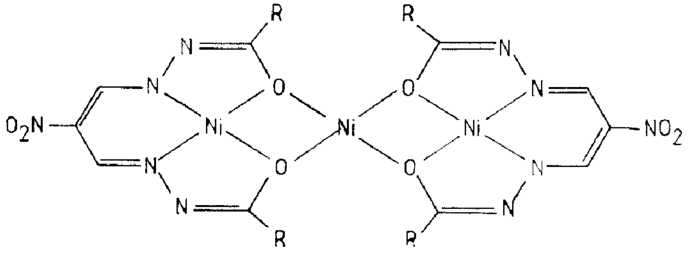


$X = {}^{-}NCS$

(163)

While on the subject of dihydrazone ligands, 3,6-dimethyl-2,7-dioxo-4,5-diazaocta-3,5-diene-2,7-dihydrazone has been reacted with various nickel salts. Octahedral binuclear complexes $[Ni_2L_3]X_4$ are obtained when X= Cl^-, Br^-, I^-, NO_3^- and ClO_4^-, while the tetragonally distorted binuclear complex $[Ni_2L_2X_4]$ is obtained when X= NCS^- [583].

A series of tetradentate bis(aroylhydrazones) of various β-dialdehydes have been synthesized. These ligands coordinate to Ni(II), yielding trinuclear complexes with molecular formula $[Ni_3L_2]$ (164), in which each Ni ion is in a square-planar environment. (164) reacts with pyridine giving the complex $[Ni_3L_2(pyridine)_6]$ in which all the Ni ions are octahedrally coordinated. Reaction with dimethylformamide (DMF) affords the complex $[Ni_3L_2(DMF)_4]$ in which two of the Ni ions are octahedrally coordinated, while the remaining Ni ion is in a square-planar environment [584]. Similar trinuclear complexes are obtained from the reaction of 2-HO-5-$RC_6H_3C(OH)$:CHCH:NC_6H_3R'-5-OH-2 (R= Me, Cl; R'= H, NO_2) (H_3L) with Ni(II). The resultant complexes $[Ni_3L_2]$ are paramagnetic and exhibit ferromagnetic exchange between the Ni ions [585].

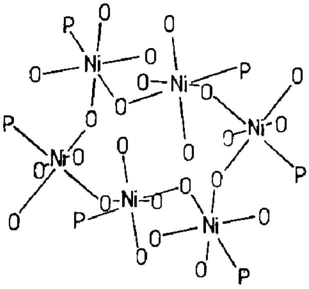


R = Ph, 4-NO_2-C_6H_4, 3-NO_2-C_6H_4

(164)

Tetranuclear hexaketonato nickel(II) complexes with m-bis(1,3,5-trioxohexyl)benzene and m-bis(1,3,5-trioxo-5-phenyl)benzene have been prepared. The complexes have the general formula $[Ni_4L_2(H_2O)_8]$ and each Ni atom is hexacoordinate, with the H_2O ligands occupying the trans axial positions. Reaction of the above complexes with o-phenylenediamine yields the corresponding macrocyclic Schiff base complexes $[Ni_4L'(H_2O)_4]$. These complexes are unusual in that the two central Ni ions are assigned octahedral coordination, whereas the terminal Ni ions are spin-paired and in a square-planar environment [586].

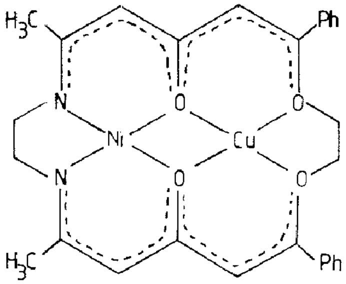
The hexanuclear complex $[Ni_6(Ph_2PCH_2CH_2CO_2)_{12}]$ has been prepared by the interfacial reaction of solutions of $Ph_2PCH_2CH_2CO_2H$ in CH_2Cl_2 and $Ni(NO_3)_2$ in aqueous $NaHCO_3$. The single-crystal X-ray analysis reveals a structure based on a Ni_6O_6 ring with a nearly octahedral field of five oxygen atoms about each Ni atom (165). Of interest is the mode of coordination of the ligands $Ph_2PCH_2CH_2CO_2^-$, half of which are coordinated through the carboxylate oxygen groups to two Ni sites, while the other half are coordinated through P and O in a normal bidentate fashion. The Ni-Ni distances of 3.510(1) Å preclude any type of metal-metal bonding [587].



(165)

The thiocyanato ligand has been used widely as a bridging moiety in the synthesis of polynuclear nickel complexes. Most of the complexes consist of Ni(II) in an octahedral or pseudooctahedral environment bonded to the nitrogen atom of the bridging thiocyanate groups. The other metal in the complex, which bonds to to the sulphur atom, is usually a "softer" metal such as Hg(II) or Cd(II) [588-590]. The complex $[NiLAg(SCN)_3]$ (L= p-methoxybenzamide) is of interest, since it contains both terminal and bridging NCS groups [591]. In addition, the complex $[Ni(NCS)_2(PPh_3)_2Cu_2(SCN)_2]$ has been synthesized and reacted with a number of Lewis bases, yielding complexes of the type $[NiL_2(NCS)_2Cu_2(SCN)_2(PPh_3)_2]$ (L= dimethylformamide, urea) [592]. While on the subject of Ni-Hg and Ni-Cd complexes, the new bimetallic tetrakis dithiocarbamate complex $[NiHgL_4]$ (L= diethyldithiocarbamate) [593] and bis-triethanolamine complex $[NiCdL_2Cl1]\cdot 2H_2O$ (HL= triethanolamine) [594] have been prepared, while an infrared and Raman spectroscopic study of the Hofmann-type complexes $[M(NH_3)LNi(CN)_4]$ (L= 4-chloropyridine or 4-methylpyridine) and $[ML_2Ni(CN)_4]$ (L= 3-methyl- or 4-methylpyridine) (M= Ni or Cd), has been undertaken [595].

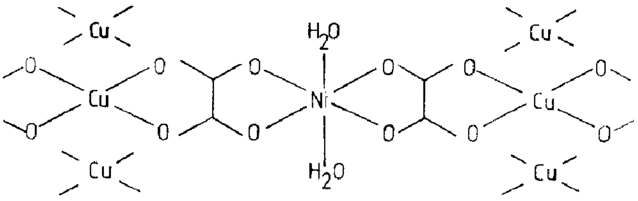
Heterobinuclear complexes containing nickel and copper have attracted much attention. The electrochemical properties of the complex [5,5'-(1,2-ethanediyldinitrilo)bis(1-phenyl-1,3-hexanedionato)(4-)] nickelcopper (166) have been investigated. Magnetic results and a single-crystal X-ray analysis reveal that Ni(II) exists in a square-planar, diamagnetic form, while Cu(II) is in its normal paramagnetic state. Comparison of the electrochemical properties with those of the mononuclear complex reveals that the introduction of a second metal ion has a profound effect on the redox properties [596].



(166)

The effect of introducing a second metal ion has also been investigated in the strati-bis complexes [NiCuL] {H_4L= 1,2,3,4-tetrakis(R-salicylideneamino)-2,3-dimethylbutane} and [NiCuL'] {H_4L'= 1,2-bis(R-salicylideneamino)-1,2-bis-(R-salicylideneaminomethyl)cyclohexane} (R= H,5-Me, 5-Br). Based on cyclic voltammetry and differential pulse polarography, it was shown that the Cu(II)-Cu(I) reduction occurs at a higher potential than that of the mononuclear reference complex [597]

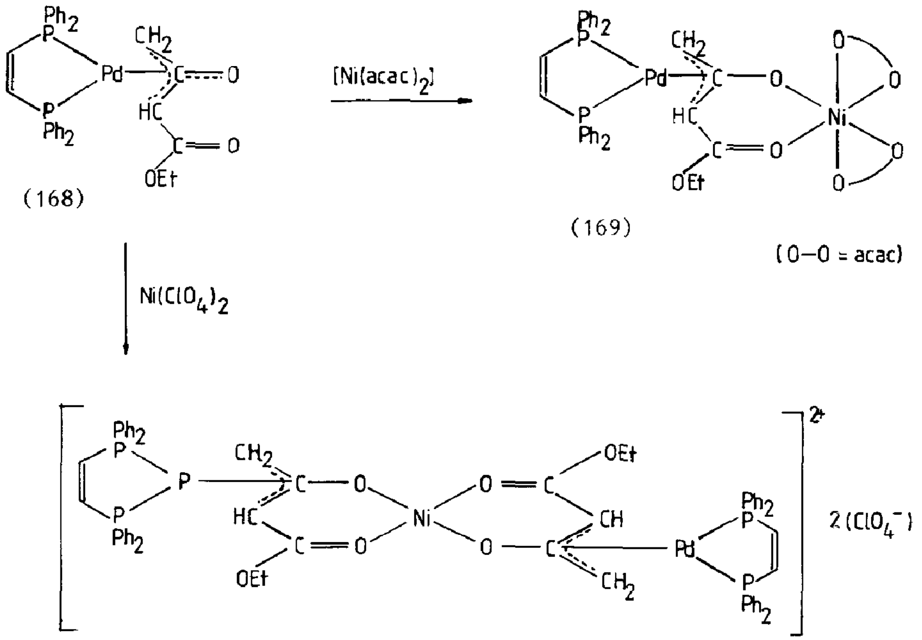
The EXAFS structure and magnetic properties of $[NiCu(C_2O_4)]\cdot 4H_2O$ have been investigated, and the data are consistent with an ordered bimetallic chain structure (167). Each Cu(II) has four oxygen atoms (Cu-O= 1.69 Å), and each Ni(II) has six oxygen atoms (Ni-O= 2.04 Å), as their nearest neighbours, while in addition to the atoms of the equatorial oxalato bridges, each Cu(II) sees two other Cu(II) ions, belonging to other chains located at approximately 4 Å [598].



(167)

A series of Ni(II)-Zn(II) hydrazine complexes have been prepared and their magnetic and electronic properties reported. The diffuse reflectance electronic spectra and magnetic moments of the complexes $[NiZn(N_2H_4)_6](SO_4)_2$, $[NiZn(N_2H_4)_6](NO_3)_4$ and $[NiZn(N_2H_4)_4Cl_2]Cl_2$ indicate that the coordination geometry of Ni within these complexes is octahedral in each case [599].

η^3-3-ethoxycarbonyl-2-oxidoallyl{*cis*-1,2-*bis*(diphenylphosphino)ethylene}-palladium(II) (168) reacts with Ni(acac)$_2$, yielding the β-diketonate bridged binuclear complex (169) in which the nickel ion is octahedrally coordinated. Reaction of the trihapto complex (168) with Ni(ClO$_4$)$_2$ yields the β-diketonate bridged complex (170) in which the nickel ion appears to be tetrahedrally coordinated [600].



(168)

(169)

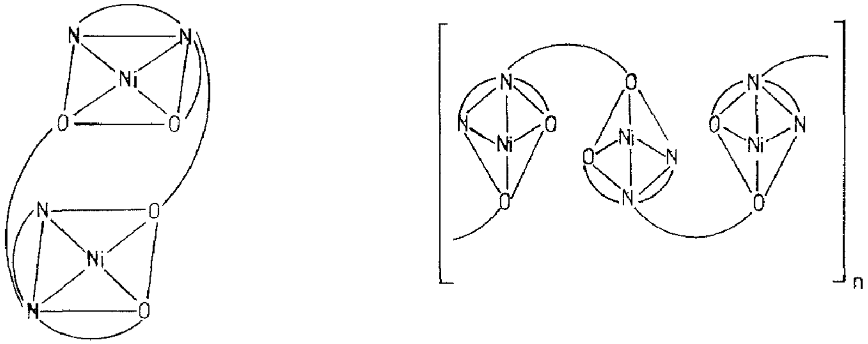
(O—O = acac)

(170)

Reaction of the dicationic *tris*(trialkylphosphite) complexes,$[(\eta^5\text{-}C_5H_5)\text{-}M\{P(OMe)_3\}_3]^{2+}$ (R= H, Me; M= Co, Rh) , with iodide or cyanide proceeds in a sequence of three Michaelis-Arbusov reactions giving the anionic complexes, $[(\eta^5\text{-}C_5H_5)M\{P(O)(OMe_3)_3\}]^-$. Reaction of these complexes with Ni(II) yields the *bis* complexes $[Ni(\{\eta^5\text{-}C_5H_5\}M\{P(O)(OMe_3)_3\})_2]$, in which the nickel ion is octahedrally coordinated by six P=O oxygen atoms of the two anionic ligands, which function as two tripods [601].

Continuing with metal complexes that behave as complex ligands, the Schiff base complex, nickel(II)-N,N'-disalicylidene ethylenediamine, has been used as a bidentate complexing agent, coordinating through two phenolic oxygen atoms to various alkali metal salts , ML (ML= Li, Na or K salts of 1-nitroso-2-napthol, 8-hydroxyquinoline, anthranilic acid, as well as the alkali metal salts KSCN, LiCl, NaBr and NaI) [602].

A variety of Schiff base [603-607] and related ligands such as carbohydrazides [608] and dihydrazides [609] have been used in the synthesis of binuclear Ni(II) complexes. The bulk of these ligands function in a tetradentate fashion, with coordination occurring via NO donor groups. Of particular interest is a study that has been undertaken to examine the influence on coordination, of a lengthening of the hydrocarbon bridge, from two to three methylene groups, in the Schiff base formed by the reactin of 2,2'-hydroxychalkone with ethylenediamine and 1,3-diaminopropane, respectively. Both ligands react with Ni(II), yielding complexes having a 1:1 stoichiometry. However, magnetic and spectroscopic data suggest a dimeric structure[NiL]$_2$(171), in which the coordination geometry is square-planar, for the ethylenediamine derivative, and a polymeric structure [NiL]$_n$, in which the coordination geometry is tetrahedral, for the 1,3-diaminopropane derivative [607].



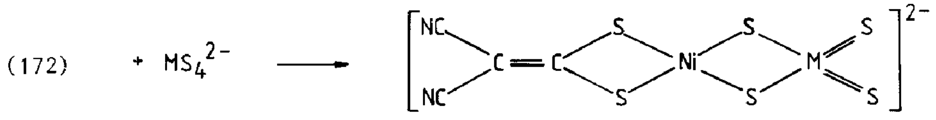
(171)

While on the subject of coordination polymers, poly-Schiff base [610-612] and semicarbazone [613,614] ligands have been utilized in the preparation of Ni(II) coordination polymers. The coordination geometry of the nickel ion in these polymeric complexes is usually octahedral, with the polymer coordinating in a tetradentate fashion, and water molecules occupying the remaining two coordination sites.

Coordination polymers of Ni(II) with monoaryl thioureas [615], dithiooxamides [616], homo- and copolymers of *p*-vinylbenzoylacetone [617], and various phthalocyanine polymers [618,619], have been prepared. Coordination polymers have also been reported from the reaction of *p*,*p*-*bis*(benzoylthiourea)-

biphenyl[620] and 1-isonicotinyl-4-allyl-3-thiosemicarbazide[621] and Ni(II).

Bridging sulphur groups have been used in the synthesis of mixed nickel-molybdenum and nickel-tungsten complexes. The dithiolate ligand $(NC)_2CCS_2^{2-}$ reacts with Ni(II) forming the dianionic complex $[Ni\{(NC)_2CCS_2\}_2]^{2-}$ (172), which may then be reacted with MS_4^{2-} to give the resultant mixed-metal complexes (173) [622].

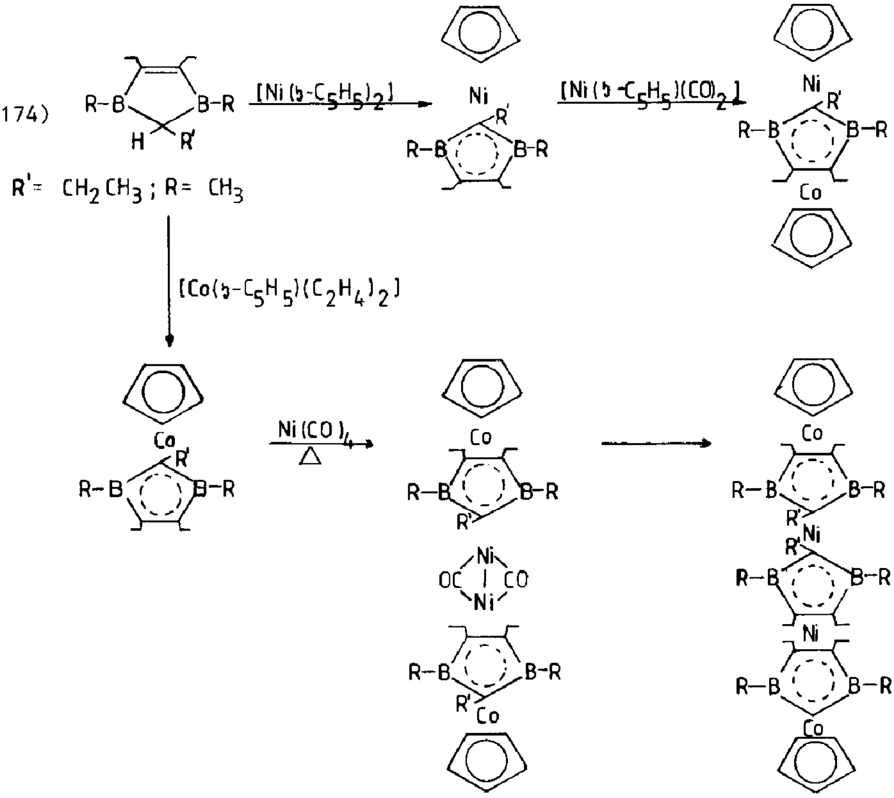


(173)

The Lewis base character of the N atom of the μ-CNMe ligand in the complex $[Fe_2(\eta^5\text{-}C_5H_5)(CO)(L)(CNMe)]$ has been utilized in the formation of the adduct $[Fe_2(\eta^5\text{-}C_5H_5)(CO)(L)(\mu\text{-}CO)\{\mu\text{-}CN(Me)E\}]$, where E is the Lewis acid $NiCl_2 \cdot 6H_2O$. The adduct has been characterized using infrared spectroscopy [623].

Δ^4-1,3-diborolenes (174) have proved useful as synthons in the preparation of sandwich and polynuclear complexes [624-626]. In addition, the synthesis and structure of the supersandwich complex $[U\{Ni[P(O)(OCH_3)_2]_2(\eta^5\text{-}C_5H_5)\}_4]$ has been reported [627].

(174)



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