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7. Nickel 1991

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CONTENTS

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INTRODUCTION

This survey of nickel coordination chemistry essentially covers the work published in 1991. It is based on a data search of the coordination complexes of nickel listed for 1991 in Chemical Abstracts, although the journals *Inorganic Chemistry, Inorganica Chimica Acta, Journal of the Chemical Society (Dalton Transactions and Chemical Communications), Journal of the American Chemical Society, Polyhedron, Journal of Coordination Chemistry* and *Acta Crystallographica (Section C)* have been searched independently for the period January to the end of December 1991.

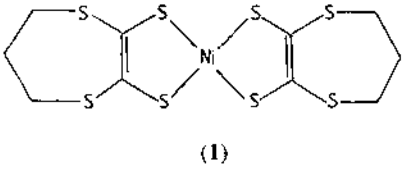
Generally, the review does not cover organometallic compounds of nickel such as organometallic cluster compounds, nickelaboranes, carboranes, carbonyl or allyl complexes, unless they contain a significant number of classical coordination chemistry ligands. Material has been arranged by oxidation state, with further subdivision in terms of ligand donor type. In addition, complexes with mixed ligands have been classified, wherever possible, according to the fundamental theme of the article in which they appeared.

By way of introduction, a general review of metal chelate monomers, including group VIII metals, has appeared. In this article the principle advances in and problems associated with the synthesis of the poly-, homo-, co- and graft polymers of these metal chelate monomers, as well as their properties, have been discussed. The metal chelate monomers have been classified in terms of type of metal bond with chelating ligands, including molecular metal chelates, intracomplex compounds, and macrocycles. Special attention has been paid to the effect of the metal on both the polymerisation and properties of the products formed [1].

7.1 NICKEL (IV)

7.1.1 Complexes with sulfur and selenium donor ligands

The crystal and molecular structure of the nickel(IV) complex, bis(2,3-dimercapto-6,7-dihydro-5*H*-1,4-dithiepin)nickel(IV) has been determined at 295 and 109K. The Ni-S bond lengths were in their expected range (2.13-2.15*A*), but the central NiS_4 moiety was noticeably non-planar, with one of the trans-S-N-S angles being 170°. The source of the non-planarity appears to be related to the unusual conformation of the seven-membered ring (1) [2].



(1)

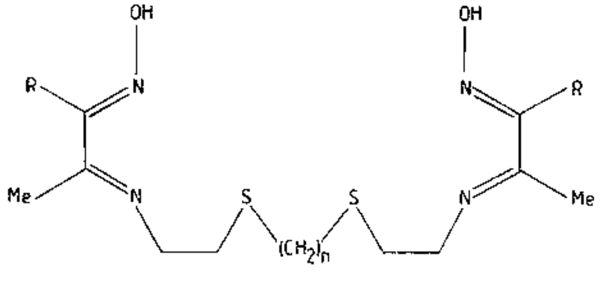
The synthesis and characterisation of the nickel(IV) anion, $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$, isolated as its tetraethylammonium salt, has been reported. This remarkable cubane Ni(IV) complex, which possesses a Ni_4Se_4 cubane core, results from a spontaneous assembly reaction in which the Ni(II) centres were oxidised to Ni(IV), with concomitant reduction of the Se species. Each Ni atom is located in a distorted octahedral environment, and is coordinated to three Se atoms in the cubane framework and by three Se atoms in the rings that bridge to the other three Ni atoms [3].

7.1.2 Complexes with arsenic donor ligands

1,2-Bis(dimethylarsino)tetrafluorobenzene (L) has been found to form high-spin tetragonal nickel(II) complexes of the type $[NiL_2X_2]$ (X = Cl or Br), and the planar diamagnetic complex $[NiL_2]I_2$. Upon oxidation these complexes were found to yield psuedo-octahedral nickel(III) and nickel(IV) complexes of composition $[NiL_2X_2]^{n+}$. In addition, the X-ray crystal structure of *trans*-$[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$ has been determined. Nickel is coordinated in a tetragonal fashion with bond lengths of 2.543(1)Å for Ni-Br, and 2.336(1) and 2.339(1)Å for Ni-As [4].

7.1.3 Complexes with nitrogen-sulfur donor ligands

The hexadentate thioether-imine-oxime binding ligands, H_2L (**2**), have been complexed with nickel perchlorate yielding paramagnetic Ni(II) complexes of the type $Ni(H_2L)(ClO_4)_2$. The complexes are tetragonally distorted octahedral in structure, with coordination occurring via the S_2N_4 donor set. The Ni(IV) complexes, $Ni(L)(ClO_4)_2$, were formed upon oxidation with cold nitric acid, and were found to decompose slowly in moist environments, regenerating the nickel(II) complexes via the nickel(III) complexes $NiHL^{2+}$ and/or NiL^+ [5].



(R = Me, Ph; n = 2, 3)

(**2**)

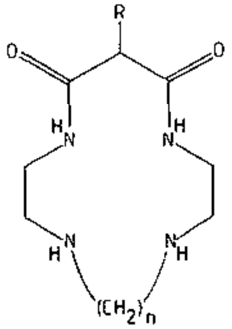
7.2 NICKEL (III)

Macrocyclic nitrogen-donor ligands continue to dominate nickel(III) coordination chemistry.

7.2.1 Complexes with nitrogen donor ligands

The coordination of 1,4,7,10-tetraazacyclotridecane ([13]aneN_4) to Ni(III) has been investigated. The crystal structure of [Ni([13]aneN_4)Br_2]Br, which has been determined by single-crystal X-ray diffraction, revealed a nickel centre which is octahedrally coordinated, with the four N atoms of the macrocycle in a square planar configuration (Ni-N = 1.869(12), 1.969(14)Å), and the bromide ions in the *trans* axial positions (Ni-Br = 2.664(1)Å). The correlation between the in-plane Ni-N and axial Ni-Br distances has also been discussed in terms of the size of the aperture in the cyclic ligand [6].

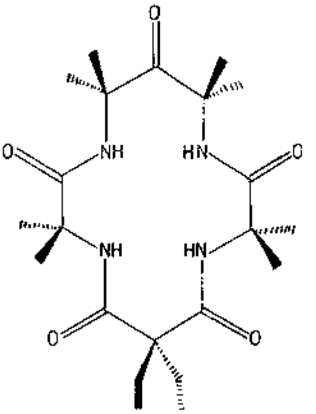
A number of oxotetraaza macrocyclic ligands have been used to stabilise nickel(III). The spectral characteristics of the nickel(II) and nickel(III) complexes of the unsubstituted and benzyl-substituted 13- and 14-membered dioxotetraaza macrocycle ligands H_2L (**3**) have been investigated. The interaction of the nickel(II) complexes with peroxodisulphate was shown to yield two products, depending on the ring size of the macrocycle. In the case of 14-membered ligands, the nickel(III) complexes [Ni(III)L]$^+$ were obtained, whereas in the case of 13-membered ligands the nickel(II) complexes with an oxidised macrocycle ligand NiL_{-2H} were obtained [7].



(n = 2, R = H, CH_2Ph; n = 3, R = H, CH_2Ph)

(**3**)

Similarly, the tetraamide macrocycle H_4L (**4**) has been found to stabilise nickel in the +3 oxidation state as the [NiL]$^-$ complex ion [8]. The crystal and molecular structure of this complex has been determined as its tetraethyl ammonium salt. The coordination sphere of the Ni atom is essentially distorted square-planar with the Ni atom sitting 0.09Å above the mean plane of the N donor atoms. The average Ni(III)-N distance of 1.84Å is considerably shorter than other reported Ni(III)-N distances [9].



(4)

The new open chain hexaaza ligand 6,6-bis(4-amino-2-azabutyl)-1,4-diazacycloheptane, L_1, and its corresponding macrocyclic analogue 2,5,9,12,16,19-hexaaza-7-spiro[6,13]eicosane, L_2, have been prepared and complexed with nickel(II) chloride. The resultant complexes had the compositions $[Ni(II)(HL_1)]Cl_3.1/2H_2O$, and $[Ni(II)(HL_2)]Cl_3.H_2O$ respectively. In the presence of perchlorate and iodide, the nickel(II) chloride complex of L_1 was converted to $[Ni(II)(HL_1)]I_5$, and subsequently $[Ni(II)(HL_1)]I_7$, while the nickel(II) chloride complex of L_2 was converted to the nickel (III) complex *trans*-$[Ni(III)Cl_2(H_2L_2)]Cl(ClO_4)_2.2H_2O$ in the presence of perchlorate and hydrochloric acid. The crystal structures of $[Ni(II)(HL_1)]I_7$ and *trans*-$[Ni(III)Cl_2(H_2L_2)]Cl(ClO_4)_2.2H_2O$ have been reported. The nickel atom in $[Ni(II)(HL_1)]I_7$ was found to adopt the stable trans III square planar configuration, while in *trans*-$[Ni(III)Cl_2(H_2L_2)]Cl(ClO_4)_2.2H_2O$, the nickel atom was found to adopt tetragonal octahedral geometry with the chloride ions occupying the *trans* axial positions [10].

The reactions of $[Ni(1,4,7\text{-triazacyclononane})_2]^{3+}$ with NO_2^- and NO have been studied in aqueous solution at 25°C. NO_2^- reacted to form $[Ni(1,4,7\text{-triazacyclononane})_2]^{2+}$ and NO_3^-, with electron transfer from NO_2^- to $[Ni(1,4,7\text{-triazacyclononane})_2]^{3+}$ proposed as the rate determining step. NO was found to react either via an outer-sphere-electron transfer reaction or via a pathway which leads to destruction of the complex [11].

The reactions of $Ni(1,4,8,11\text{-tetraazacyclotetradecane})^{2+}$ with alkyl radicals ($R^\cdot$) have been investigated. σ-Bonded organonickel(III) cations were obtained according to the reaction

$$NiL^{2+} + R^\cdot + H_2O \Leftrightarrow RNiL(H_2O)^{2+}$$

The rate constants for the forward and reverse reactions reveal that the forward reaction is most favourable for methyl radicals, and least favourable for secondary alkyls [12].

Nickel complexes of mono-β-oxoporphyrin (NiMP), the five isomeric di-β-oxoporphyrins (NiDP), and two of the isomeric tri-β-oxoporphyrins (NiTP), have been prepared by hydrogen peroxide oxidation of octaethylporphyrin, followed by metallation. Cyclic Voltammetry was utilised to study the electrochemical characteristics in methylene chloride and acetonitrile solutions. It was suggested that the di- and tri-β-oxoporphyrin rings have a greater capacity to stabilise Ni(III) than the porphyrin ring, due to the greater tendency of the former compounds to bind axial ligands and thereby relieve the strain of ruffling [13].

Low temperature γ-radiation has been used to produce some interesting Ni(III) and Ni(I) complexes. ESR revealed that Ni(II) complexes of N-acetyltetraazamacrocyclic ligands in dichloromethane and thf undergo electron loss and gain, when exposed to low temperature γ-radiation, producing Ni(III) and Ni(I) centres [14].

7.2.2 Complexes with sulfur donor ligands

The crystal structure and electrical conductivity of N-methylquinolium bis(1,3-dithiole-2-thione-4,5-dithiolato)nickelate(III) has been reported. Two crystallographically independent $Ni(dmit)_2$ units were observed, both of which show considerable deviation from planarity. The Ni-S bond lengths were found to vary from 2.142(5) to 2.167(5)Å. Several short inter-unit S...S contacts were observed, resulting in a two-dimensional network and, in accordance with its structure and stoichiometry, the compound behaves as a semiconductor [15].

The related compound tris(N,N,N',N'-tetramethyl-*p*-phenylenediamine) bis(1,3-dithiole-2-thione-4,5-dithiolato)nickelate(III) has been studied in a similar fashion. Unlike the previous compound, it had an extremely low conductivity. A single crystal structure determination revealed the presence of fairly long S...S contacts between the complex units, which accounts for the high resistivity. The mean Ni-S bond length was approximately 2.193Å, which lies between bond lengths usually observed for Ni(II) and Ni(III) species, and indicates an effective mean charge of about 2.24 [16].

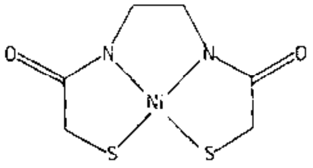
7.2.3 Complexes with phosphorus donor ligands

Nickel K-edge EXAFS data, supplemented by bromine K-edge data, have been used to obtain structural information relating to the complexes $[Ni(PR_3)_2X_3]$ (R = Et, Me_2Ph; X = Cl, Br). These studies confirmed the occurrence of rare trigonal-bipyramidal geometry for these Ni(III) complexes [17].

A catalytic application of $Ni(II)(dppe)Cl_2$ yielded some interesting variable oxidation state intermediates. In the presence of a catalytic amount of $Ni(II)(dppe)Cl_2$, electrolysis of bromobenzene in the presence of stoichiometric carbon dioxide, yielded a near quantitative amount of benzoic acid. The mechanism of the nickel-catalysed electrocarboxylation was shown to proceed through a chain reaction involving Ni(0), Ni(I), Ni(II) and Ni(III) intermediates [18].

7.2.4 *Complexes with nitrogen-sulfur donor ligands*

Ni(II) has been complexed with the tetraanions of the amide-thiol ligands N,N'-ethylenebis(2-mercaptoacetamide) (H_4ema), N,N'-1,2-phenylenebis(2-mercaptoacetamide) (H_4phma), and N,N'-1,2-ethylenebis(2-mercaptoisobutyramide) (H_4emi). The resultant anionic complexes $[Ni(ema)]^{2-}$ (**5**), $[Ni(phma)]^{2-}$ (**6**), and $[Ni(emi)]^{2-}$ (**7**), isolated as their Et_4N^+ salts, are diamagnetic. The tetradentate nature of the ligands was verified by the crystal structure determination of $[Et_4N]_2[Ni(ema)].2H_2O$. The complexes undergo reversible one electron oxidations in dmf solutions, the metal ion oxidation being verified by EPR spectra [19].



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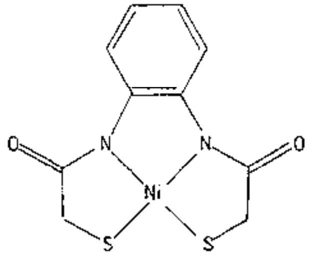

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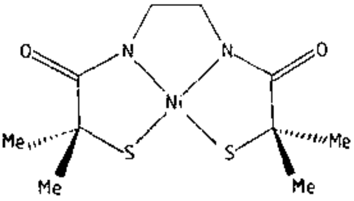


(7)

7.3 *NICKEL (II)*

7.3.1 *Complexes with nitrogen donor ligands*

An article, containing 147 references, which reviews the compounds of transition metals with MN_4 coordination mode, has been published. Ni complexes with amidines, triazines, azomethines, β-aminovinyl ketones, hydrazonimines, azo compounds, formazans and N-containing heterocycles have been included [20].

A review of metal complexes with aniline and substituted anilines, and their infrared and Raman spectra, covering the years 1965 to 1987, has been published. In particular, the review refers to isotopic labelling and metal ion substitution as assignment techniques, and to the structural and bonding information which can be derived from the spectra. A number of classes of nickel(II) complexes containing aniline or substituted anilines have been included [21].

The electronic spectra of the tetragonal nickel(II) complexes of pyridine $[Ni(py)_4L_2]$ (L = NCS, Cl, Br or I) have been measured in methanol solutions at room temperature. The ligand field parameters have been examined and discussed in terms of their chemical utility and their relation to ligand field strengths. It was found that the stereochemistry of the complexes varied depending on the nature of the solution or if they were in the solid state [22].

The crystal and molecular structure of the substituted pyridine complex tris(2,4-dimethylpyridine)bis(isothiocyanato)nickel(II) has been reported. The coordination sphere about Ni was found to be intermediate between trigonal bipyramidal and tetragonal pyramidal. Ni-N bond lengths were 1.995(9)*A* (Ni-NCS), 2.085(3) and 2.159(7)*A* (Ni-py) [23].

The relationship between thermochemical parameters such as quasi-equilibrium decomposition temperature, activation energy and frequency factor, and the degree of tetragonal distortion in the complexes $NiL_4(NCS)_2$ (L = pyridine, 3-ethylpyridine, or piperidine), has been investigated. It was shown that as the degree of tetragonal distortion of the coordination sphere increases, the activation energy increases, while the decomposition temperature decreases [24].

Turning to imidazole ligands, the crystal and molecular structure of tetrakis(imidazole)bis(isothiocyanto)nickel(II) has been determined. The structure consists of isolated molecules of $[Ni(imH)_4(NCS)_2]$ in which Ni is in a distorted octahedral environment. The NCS ligands occupy *trans* positions, and the imidazole ligands define an equatorial plane. The mean Ni-N(imidazole) distance was 2.113(4)*A*, while the mean Ni-N(NCS) distance was found to be 2.080(3)*A* [25].

N-methylimidazole has been complexed with nickel metal in the presence of sulfur to form the most interesting polysulphide salt, $[Ni(N\text{-methylimidazole})_6]S_8$. The crystal structure of this complex revealed isolated $[Ni(N\text{-methylimidazole})_6]^{2+}$ and S_8^{2-} units. The coordination about Ni is essentially octahedral, with the Ni-N distances varying from 2.117(5) to 2.125(5)*A*, which is typical for this type of cation. Detailed discussion of the S_8^{2-} anion was limited by a disorder problem [26].

Bis(hydrazinium)tetra(thiocyanato-N)nickel(II) dihydrate has been prepared and characterised. Based on the crystal structure of the isostructural Co(II) complex, the coordination sphere about Ni was assumed to be octahedral with the hydrazinium ligands occupying *cis* positions [27]. In addition, the structurally analogous chloride complex $(N_2H_5)_2NiCl_4$ has been prepared and reported by the same authors. Based on the crystal structure of the isostructural Fe(II) complex, the coordination sphere about Ni was assumed to be octahedral with the hydrazinium ligands occupying *trans* positions in this instance [28].

Titration calorimetry has been used to determine the thermal effects of the complexation reactions of Ni(II) with NH_3 and ethylenediamine in H_2O/dmso mixtures. It was found that at low concentrations of dmso, step-wise heats of complexation differed little, but at higher concentrations of dmso, the heats increased in the order $[Ni(en)]^{2+} < [Ni(en)_2]^{2+} < [Ni(en)_3]^{2+}$ [29,30].

Continuing with ethylenediamine and related ligands, the kinetic parameters for dissociation and formation of $[Ni(en)]^{2+}$ have been determined in aqueous/methanol solutions. The $[Ni(en)]^{2+}$ dissociation rate was found to decrease as the methanol concentration increased, while the formation rate constant was found to increase [31].

The complex formation of Ni(II) with N,N,N',N'-tetramethylethylenediamine has been studied in aqueous medium, using potentiometric and calorimetric methods. Successive as well as overall stability constants of the system were determined [32].

Thermochemical changes in the coordination sphere of the complexes $[Ni(H_2O)_2L_2]X_2.nH_2O$ (L = N,N- or N,N'-dimethylethylenediamine, N,N- or N,N'-diethylethylenediamine; X = Cl^-, Br^-, I^-, or NO_3^-; n = 0, 1, 2, 3) have been investigated using TGA-DTA and electronic spectroscopy. All of the complexes exhibited a *trans* configuration, with the exception of $[Ni(H_2O)_2L_2]I_2$ (L = N,N-dimethylethylenediamine) which exhibited a *cis* configuration. Upon heating the complexes were found to lose water and coordination of the anions occurred. In the case of the complexes containing symmetrical diamine ligands, the *trans* configuration was retained, whereas conversion to the *cis* configuration occurred for the complexes containing asymmetric diamine ligands [33]. In addition, the X-ray crystal structures of *trans*-$[Ni(H_2O)_2L_2]Cl_2.2H_2O$ (L = N,N-dimethylethylenediamine) and *trans*-$[Ni(H_2O)_2L_2]Cl_2$ (L = N,N-diethylethylenediamine) have been determined. Both complexes exhibit a *trans* configuration, and the Ni-NMe_2 and Ni-NEt_2 bond distances (2.183 and 2.271Å respectively) were found to be much longer than the corresponding Ni-NH_2 distances (2.078 and 2.064Å respectively). This resulted in distorted octahedral geometry for both complexes, apparently originating from the steric requirements of the N-substituted groups [34].

The crystal structure of the related complex diaquabis(1,2-propanediamine)nickel(II) dibromide dihydrate has been reported. A *trans* pseudo-octahedral coordination configuration was obtained, with Ni-N distances of 2.106(6) and 2.099(6)Å, which are typical for this mode of coordination. The slight difference in Ni-N bond length was ascribed to the effect of asymmetric C-substitution [35]. As part of their on-going study of nickel(II) compounds with C-substituted ethylenediamine ligands, the same authors have reported the structure of bis(*cis*-1,2-

cyclohexanediamine)nickel(II) dichloride. This complex is essentially square-planar, involving two cis-1,2-cyclohexanediamine ligands, with an average Ni-N bond length of 1.912(2)Å, and an average N-Ni-N bond angle of 86.6(1)° [36].

Single-crystal X-ray diffraction techniques have been used to determine the structures of the diastereomeric salt pair, Λ-*lel*$_3$-[Ni(S,S,-chxn)$_3$](*d*-tart).3H$_2$O and Δ-*lel*$_3$-[Ni(R,R-chxn)$_3$]-(*d*-tart)·5H$_2$O. Both complexes are octahedral, but the interaction of the tartarate anion with the complexes varied considerably. In the Λ-complex, the tartarate ion makes the familiar face-to-face contact, in which two alcoholic and one carboxylic O atoms of tartrate are involved in hydrogen bonding with the three NH groups on the triangular face of the complex. However, in the Δ-complex no such interaction was observed [37]. This type of "molecular recognition" has been observed with the related nickel(II) complexes of optically active N,N'-diethylcyclohexane-1,2-diamine ligands. The chirality of the bound ligand was shown to have a considerable effect of the complex to epimerise aldoses [38].

The electrochemical reduction of a series of high-spin octahedral complexes of nickel(II) with a variety of Schiff base ligands of the type R-N=CH-py (R = CH_3; C_6H_5; *o*-, *m*-, *p*-CH_3-C_6H_4; *o*-, *m*-, *p*-Cl-C_6H_4; *o*-, *m*-, *p*-CH_3O-C_6H_4) has been investigated in acetonitrile. All of the complexes underwent a fairly reversible two-electron reduction process in which the parent hexacoordinate nickel(0) species was initially formed, followed rapidly by decomposition of this species leading to the release of free ligand [39].

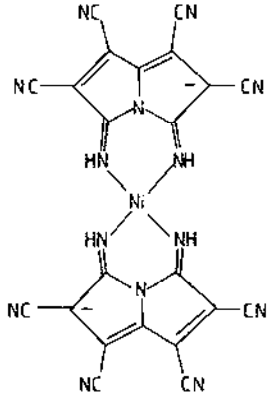
A series of complexes of the type [Me$_4$][Ni(AA)Cl$_2$] (Me$_4$ = tetramethylammonium ion; AA = pyridyl-2-aldoxime (pyao), acetylacetonate (acac), and 2-mercaptobenzothiazole (mbt)), [n-cepy][NiCl$_3$L] (n-cepy = n-cetylpyridinium ion; L = γ-picoline (γ-pic), pyridine-N-oxide (pyNO) and 4-cyanopyridine-N-oxide (4-CNpyNO)), [Me$_4$][Ni(et$_2$dtc)$_2$Cl] (et$_2$dtc = diethyldithiocarbamate), and [Me$_4$][Ni(OX)$_3$] (OX = 8-hydroxyquinoline) has been prepared and characterised using a variety of analytical techniques. All of the complexes are 1:1 electrolytes and have been assigned tetrahedral coordination, with the exception of [Me$_4$][Ni(et$_2$dtc)$_2$Cl] and [Me$_4$][Ni(OX)$_3$] which are trigonal bipyramidal and octahedral respectively [40].

The complex NiL$_2$(imH)$_2$ (HL = 2-picolyl-*p*-toluene sulphonamide) has been prepared by reaction of nickel(II)nitrate hexahydrate in the presence of HL and imidazole in methanol. Tributylamine was used as the base in the generation of L [41].

The coordination behaviour of 1-(1-phenyl-3-*p*-chlorophenyl)pyrazolcarboxaldehyde thiosemicarbazone (L) with Ni(II) has been investigated. NiL$_2$Cl$_2$ was prepared and characterised using a variety of analytical techniques [42].

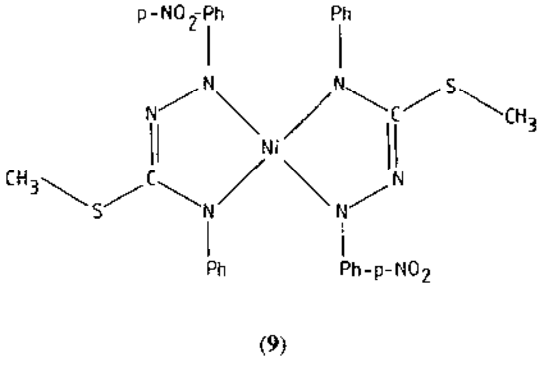
2-Cyanopyridine has been reacted with a variety of Ni(II) salts in the presence of 2-amino-2-hydroxymethyl-1,3-propanediol. Different complexes were formed depending on the nickel salt used. Complexes of the type [NiL$_2$X$_2$] (L = 2-(2'-pyridyl)-4,4-di(hydroxymethyl)-2-oxazoline) were formed when NiX$_2$ (X = Cl, Br, SCN) is used, whereas use of nickel(II) perchlorate yielded the complex [NiL$_2$(H$_2$O)$_2$](ClO$_4$)$_2$.2H$_2$O [43].

The synthesis, characterisation, and electrochemical behaviour of the nickel complex bis(1,2,6,7-tetracyano-3,5-diimino-3,5-dihydropyrrolizinido)nickel(II), Ni(β-dtpy)$_2$, have been reported. In solution, the complex was square-planar (**8**) and exhibited a metal-phthalocyanine type electronic structure. A single crystal X-ray structure determination of [Ni(β-dtpy)$_2$(H$_2$O)$_2$].3diox (diox = 1,4-dioxane) reveals that, in the solid state, it is hexacoordinated, with two water molecules occupying *trans* apical positions (Ni-N = 2.068(4) and 2.081(4)Å, Ni-O = 2.132(4)Å). The crystal structure of the TTF (tetrathiafulvalene) and thf adduct, Ni(β-dtpy)$_2$.TTF.2thf, has also been determined. This complex was essentially square-planar (Ni-N = 1.902(3) and 1.893(3)Å) [44].



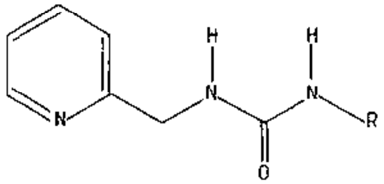
(**8**)

p-Nitrophenylazothiomethyl-N-phenylcarboximide anion radical (L) has been complexed with nickel(II) and the crystal structure of the resultant complex, NiL$_2$ (**9**), has been determined. The molecular structure of NiL$_2$ revealed a tetrahedral coordination sphere for Ni. This is thought to be the first example of an S-methylisothiosemicarbazide complex series, in which tetrahedral coordination was observed. The Ni-N distances of 1.892(2), 1.899(2), 1.920(2), and 1.905(2)Å are longer than those found in the corresponding square planar complexes [45].



(**9**)

The substituted urea ligands (**10**) have the potential to coordinate via a number of donor sets. Complexation with nickel(II)chloride yielded compounds of the type [NiL_2] (HL = (**10**)) in which coordination was found to occur via the pyridine and amido N atoms, leaving the O donor site uncoordinated. The coordination sphere about Ni was assigned a distorted square-planar configuration on the basis of a comparison with its Cu analogue [46].



(R = H, Ph, 4-$NO_2C_6H_4$)

(**10**)

3,3'-Bipyrazidine (L) has been complexed with nickel(II)perchlorate. The resultant complex ion [NiL_3]$^{2+}$ was found to contain a strong ligand field, while the complex [NiL_3][ClO_4]$_2$ exhibited an unusually short Ni-N bond length of 2.060(7)*Å*. These phenomena were explained in terms of the absence of *ortho*-hydrogen atoms in the ligand molecules relative to the 2,2'-bipyridine [47].

The complex [Ni(phen)$_3$]$^{2+}$ has been used as a cation in the heterobimetallic complexes [Ni(phen)$_3$][M(DED)$_3$] (M = Mn(IV), Fe(IV); DED = 1,1-dicarboethoxy-2,2-ethylenedithiolate). Electronic spectra indicated octahedral geometry for Ni in [Ni(phen)$_3$]$^{2+}$ [48].

The structure of aqua{N,N-bis[2-(2-pyridyl)ethyl]benzylamine} bis(trifluoromethanesulfanato)nickel(II), [Ni(bpeb)(CF_3SO_3)$_2$(H_2O)], has been determined. The complex exhibits pseudooctahedral coordination geometry with Ni-N bond lengths of 2.073(8)*Å* (pyridine N), 2.103(7)*Å* (pyridine N), and 2.134(7)*Å* (amine N). The three Ni-O distances were 2.129(6)*Å* (CF_3SO_3), 2.149(7)*Å* (H_2O), and 2.185(5)*Å* (CF_3SO_3) [49].

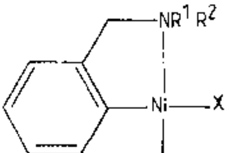
Ni(II) complexes with the tridentate terimine ligands 2,2'-bipyridine-6-carbaldehyde phenylhydrazone (bph) and 2,2'-bipyridine-6-carbaldehyde 2-pyridylhydrazone (bpyh) have been prepared and characterised. The crystal structure of [Ni(bph)$_2$][ClO_4]$_2$ revealed meridional coordination of the tridentate units, with the azomethine N atom of the hydrazone moiety being coordinated to the Ni atom. The Ni-N bond lengths were 1.945(11), 2.096(12), and 2.225(12)*Å* respectively [50].

In a continuation of previous work on tridentate ligands, which incorporate two five-membered heterocycles flanking a pyridine nucleus, 2,6-di(thiazol-2-yl)pyridine, 2,6-di(4-methylthiazol-2-yl)pyridine, and 2,6-di(2-imidazolin-2-yl)pyridine have been prepared and complexed with nickel(II). The resultant bis(ligand) complexes were isolated as their bis perchlorate salts. The coordination sphere about nickel is essentially octahedral in each of the complexes, as verified by their electronic spectra [51].

The terdentate ligand 4'-phenyl-2,2':6,2"-terpyridine (L) has been synthesized and complexed with nickel(II). A range of 1:1 and 1:2 complexes have been isolated, consisting of $[NiLCl_2]$, $[NiL_2][BF_4]_2$, $[NiL_2][PF_6]_2$, and $[NiL_2]Cl_2.10H_2O$. In addition, the crystal structure of the last complex has been determined. It was found to possesses a distorted octahedral structure with two approximately planar terdentate L ligands, with the phenyl groups adopting angles of about 17° with respect to the central pyridine rings. The Ni-N bond lengths varied from 1.986(3) to 2.118(2)Å [52].

The structure of the octahedral pyrazolylboratonickel complex, Ni[HB(3-isopropyl-4-bromopyrazole)$_3$][HB(3,5-dimethylpyrazole)$_3$], has been reported. The molecule exhibits octahedral coordination geometry with the Ni-N distances involving the sterically more demanding HB(3-isopropyl-4-bromopyrazole)$_3$ ligand (2.13-2.16(1)Å) being longer than those involving the HB(3,5-dimethylpyrazole)$_3$ ligand (2.05-2.08(1)Å) [53]. Reaction of HB(pyrazole)$_3$ with $[\eta^3C_3H_5NiCl]_2$ produced the structurally related complex Ni[$\eta^3C_3H_5$][HB(pyrazole)$_3$]. The crystal structure of this complex yielded Ni-N bond lengths of 1.978(2) and 2.153(3)Å [54].

Two series of square-planar Ni(II) complexes that contain the potentially terdentate ligands $[2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3]^-$ (R^1 and R^2 = Et; R^1 = isopropyl, R^2 = Me) have been synthesized. In one series, $[NiX(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)]$ (X = Br, I), the ligand coordinated to nickel(II) in a terdentate fashion via C(ipso) and two N donor atoms (**11**), while in the second series, $[NiX(2,6\text{-}\{R^1R^2NCH_2\}_2C_6H_3)(PR_3)_2]$ (X = Cl, Br, I), the nickel(II) centre was bonded to a halide anion, two phosphorus ligands, and only the C(ipso) of the potentially terdentate ligand (**12**) [55].



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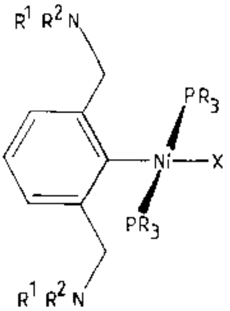


(12)

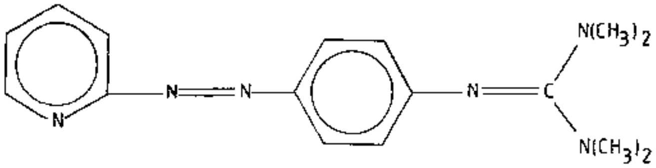
The tetrapodal ligand tetrakis(1-pyrazolylmethyl)ethene (L) has been prepared and complexed with nickel(II). The resultant complex $[NiL(H_2O)](ClO_4)_2$ was assigned pseudooctahedral coordination geometry, based on the crystal structure of the analogous Co(II) complex [56].

Several coordination compounds of the two potentially tetradentate ligands 3,6-dimethyl-1,8-(3,5-dimethyl-1-pyrazolyl)-3,6-diazaoctane (ddad), and 1,4-bis(2-ethyl-(3,5-dimethyl-1-pyrazolyl)-piperazine (bedp), have been prepared and characterised. Coordination by the ligands was generally found to be square-planar, while $Ni(ddad)(NCS)_2$ contained additional *trans* N-coordinated thiocyanate ligands [57].

Two new C-phenyl bis-picolinamide tetradentates, N,N'-bis(2-pyridinecarboxamide)-1,2-diphenylethane (S,S-bpstienH_2) and N,N'-bis(2-pyridinecarboxamide)phenylethane (S-bpstyenH_2), have been prepared and complexed with Ni(II). Deprotonation occurred during complexation resulting in complexes of the type [NiL] (H_2L = S,S-bpstienH_2 or S-bpstyenH_2). NMR spectra indicated that the molecules have C_2 or *pseudo* C_2 symmetry [58].

Pyridine-2-azo-p-phenyltetramethylguanidine (PAPT, L = (**13**)), has been synthesized and its coordination properties with Ni^{2+} investigated in aqueous and acetonitrile solutions.

Stability constants for the formation of LNi^{2+} and $L(Ni^{2+})_2$ have been determined. Formation of LNi^{2+} was found to occur much faster than formation of $L(Ni^{2+})_2$ [59].



(**13**)

The related quadridentate ligand, ethylenebisbiguanide, has been complexed with Ni^{2+} in aqueous acetate buffer media. The kinetics of complexation and formation of the square-planar complexes have been followed spectrophotometrically. The observed rate constants were independent of pH and acetate concentration, but were first order with respect to ligand concentration [60].

The structure of diperchlorato[(2SR,5RS,8RS,11SR)-2,5,8,11-tetraazadodecane]nickel(II) has been determined. The coordination about Ni was found to be distorted square pyramidal, with the tetraamine ligand equatorial and the two O atoms of the perchlorate ions axial. The four Ni-N distances range from 1.895(7) to 1.908(9)*A*, while the Ni-O bond length is 2.840(11)*A*. The configuration of the four chiral N centres was found to be 2SR, 5RS, 8RS and 11SR [61].

Electrophilic substitution of an acetyl group onto the quasi-aromatic ring in position 6 of (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene) nickel(II) has been reported. The position of substitution was confirmed by the single crystal X-ray structure. Other crystallographic data of interest are a square planar configuration about Ni, and Ni-N bond lengths which range from 1.836(4) to 1.861(4)*A* [62].

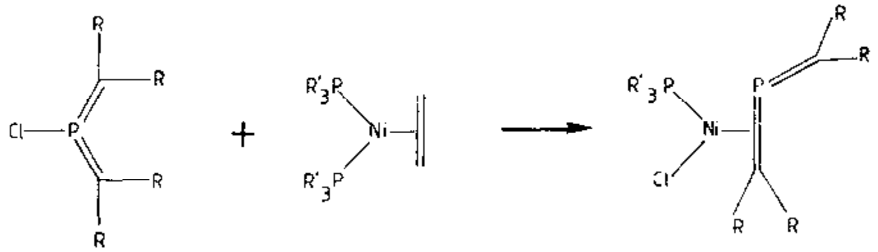
3,10-dimethyl-4,9-diaza-3,9-dodecadiene-2,11-dione dioxime (H_2L) has been complexed with nickel(II)perchlorate. A crystal structure determination of the resultant complex, [NiL], revealed the Ni atom in a distorted square planar coordination sphere. During complexation, an oxime proton was lost, and as is commonly found, the remaining oxime proton formed an intramolecular hydrogen bond between the two oxime oxygens. Important crystallographic data are Ni-N(oxime) = 1.869(3) and 1.873(4)*A*, Ni-N(amine) = 1.887(3) and 1.927(3)*A*, while the O...O distance for the intramolecular hydrogen bond is 2.442*A* [63].

7.3.2 Complexes with phosphorus donor ligands

The complex *trans*-$NiHCl(PBz_3)_2$ ($Bz = CH_2C_6H_5$) has been prepared in good yield by the reduction of $NiCl_2(PBz_3)_2$ with Super-Hydride. The related complexes *trans*-$NiHCl(PR_3)_2$ (R = isopropyl, cyclohexyl) have been reacted with NaOPh to give the corresponding hydrido phenoxo complexes *trans*-$NiH(OPh)(PR_3)_2$, while reaction of *trans*-$NiHCl(PBz_3)_2$ with NaOPh yielded the complex *trans*-$NiH(OPh)(PBz_3)_2$.HOPh. The crystal structure of the latter complex confirmed that Ni was coordinated in a distorted *trans* square-planar fashion with the following relevant crystallographic data: Ni-P = 2.163(3) and 2.171(3)*A*, Ni-O = 1.949(7)*A* [64].

Ni K-edge studies have been carried out on the propene dimerisation catalysts formed by the interaction of solutions of $NiCl_2(PEt_3)_2$ with $Al_2Me_3Cl_3$ and $AlEt_3$ at -40°C. These studies confirmed a first coordination sphere of P and C atoms, and Ni...Al shells at *ca.* 2.97*A*, which suggests that Ni-C-Al interactions may stabilise the nickel centre [65].

The reaction of chlorobis(methylene)phosphorane (**14**) with $(R_3P)_2Ni(olefin)$ (**15**) (R = Et, olefin = cod; R = Ph, olefin = ethylene) afforded the 2-phosphonioallene complexes (**16**). The structure of this new class of three-electron donor ligand, involving a low-coordinated phosphorus cation, has been clarified by NMR and a single crystal X-ray determination of the triethylphosphine analogue [66].



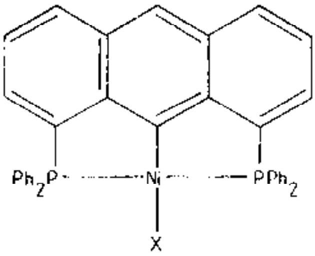
(14) **(15)** **(16)**

The molecular structures of *trans*-$[Ni(ClC{=}CCl_2)(C_6H_4Me\text{-}4)(PMe_3)_2]$, its thermal isomerisation product *trans*-$[NiCl\{C(C_6H_4Me\text{-}4){=}CCl_2\}(PMe_3)_2]$, and one of its photolysis products *trans*-$[NiCl\{ClC{=}CCl(C_6H_4Me\text{-}4)\}(PMe_3)_2]$ have been determined by X-ray diffraction methods. Common structural features relating to the three complexes include square-planar coordination for Ni, the phosphorus ligands occupying *trans* positions, and two carbon ligands or one carbon ligand and one chloride ligand, occupying the remaining coordination sites in a *trans* configuration [67].

Chlorobis(*cis*-1,5-diphenyl-1,5-diphosphacyclooctane)nickel(II) chloride has been prepared and its crystal structure determined. The nickel atom was found to be pentacoordinated and revealed a distorted trigonal bipyramidal geometry, with the chloride ion occupying an equatorial position. Ni-P bond lengths were found to range from 2.202(1) to 2.237(1)*A*, while the Ni-Cl bond length was found to be 2.410(1)*A* [68].

A series of rather unusual coordinatively unsaturated diphosphine nickel(II) β-agostic ethyl cations have been prepared and isolated as their tetrafluoroborate salts. The complexes $[Ni\{L\}(C_2H_5)][BF_4]$ ($L = Bu^t_2P(CH_2)_2PBu^t_2$; $Bu^t_2P(CH_2)_3PBu^t_2$; *o*-$(Bu^t_2P(CH_2)_2C_6H_4)$ were characterised using elemental analysis and NMR spectroscopy. In addition, the X-ray crystal structure of $[Ni\{Bu^t_2P(CH_2)_2PBu^t_2\}(C_2H_5)][BF_4]$ was determined. The coordination geometry about Ni has been described as distorted square-planar in which the phosphine ligand functions in a didentate fashion. Relevant crystallographic data are: Ni-P = 2.181(1) and 2.214(1)*A*, Ni-C = 2.081(50 and 1.940(5)*A* [69].

1,8-bis(diphenylphosphino)anthracene has been prepared and reacted with nickel(II)chloride. The resultant complex (**17**) has been assigned square-planar geometry. Treatment with aqueous KCN did not remove Ni, but converted the complex to its cyanide analogue, with CN replacing Cl as a ligand, an indication of the stability of the cyclometallated complex [70].



(X =Cl, CN)

(17)

The synthesis, characterisation, disproportionation, and dynamic ligand exchange reactions of the bisphosphine complexes [Ni(P-P)X_2] (P-P = 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)ethylene (dppey); X = Cl, Br, I) and [Ni(P-P)$_2$]X_2 (X = I, NO_3) have been reported. For [Ni(P-P)X_2] the halide affinity was found to be Cl > Br > I, while dppey complexes were more stable than the corresponding dppe complexes [71].

7.3.3 *Complexes with oxygen donor ligands*

The coordination of water with Ni(II) has received noticeable attention in 1991. Several crystal structures have been published including the structure of hexaaquanickel(II) bromate [72], hexaaquanickel(II) bis[1,2,3-benzenetricarboxylate(1-)] tetrahydrate [73], and hexaaquanickel(II) 4-chlorobenzenesulfonate [74]. In all three structures, the nickel ion is coordinated in an almost regular octahedral array, with Ni-O bond lengths ranging from 2.022(2) to 2.061(2)Å.

The rather unusual complex, [$(H_2O)_5Ni(NC_5H_5)$]$_2$(Na)[calix[4]arene sulfonate].$3.5H_2O$, has been prepared by reaction of $Ni(NC_5H_5)_3(NO_3)_2$ with Na_5[calix[4]arene sulfonate] in deionized water. The crystal and molecular structure revealed two different [$(H_2O)_5Ni(NC_5H_5)$]$^{2+}$ cations. The Ni atom in both cations was octahedrally coordinated with four water molecules in the equatorial plane and a fifth water molecule and pyridine ligand occupying the axial positions. However, one cation had the pyridine ligand complexed in the hydrophobic cavity of the calixarene, while the other was located between two calixarene ligands [75].

The axial coordination of water, which is hydrogen bonded to dmso, with the nickel complex cation, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecanenickel(II), has been investigated in nitrobenzene. Interestingly, while water was only weakly coordinated to the cation in nitrobenzene, it coordinated quite easily to the complex cation when 0.05 mol fraction dmso is present, forming the pentacoordinate cation $[Ni(tmc)(WS)]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane; W = water; S = dmso; and WS is the 1:1 water/dmso species). The coordination constant for $[Ni(tmc)(WS)]^{2+}$ was found to be 24.0 dm^3/mol [76].

Nickel alkoxide complexes of the type $[ClNi\{Al(OBu^t)_4\}]$ and $[Ni\{Al(OBu^t)_4\}_2]$ have been prepared by the reaction of $K\{Al(OBu^t)_4\}$ with nickel(II) chloride in 1:1 and 1:2 ratios respectively. Further studies have been carried out using these complexes as precursors for the preparation of alkoxo derivatives such as $[(OBu^t)Ni\{Al(OBu^t)_4\}]$, $[\{Al(OEt)_4\}Ni\{Al(OBu^t)_4\}]$, and $[\{Al(O\text{-}Pr^i)_4\}Ni\{Al(OBu^t)_4\}]$. The complexes have been characterised using a number of analytical techniques [77]. The thermodynamics of complex formation between benzoate and nickel(II) have been studied in aqueous/1.0M sodium perchlorate solution. Stability constants were determined potentiometrically, from which, together with enthalpy changes, the free energy and entropy changes were calculated [78].

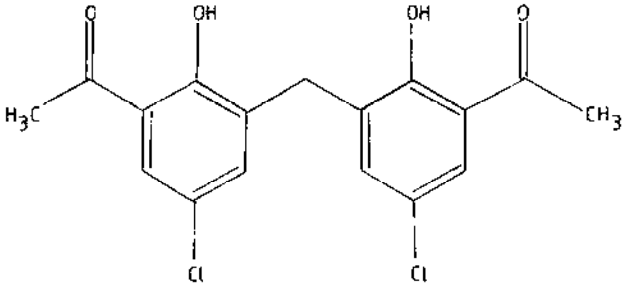
Triphenylarsine oxide has been complexed with nickel(II) bromide, yielding the complex $Ni(Br)_2(Ph_3AsO)_2$. The crystal and molecular structure of this complex was determined, revealing a distorted tetrahedral configuration for Ni coordinated to two Br and two Ph_3AsO ligands; Ni-Br = 2.364(8) and 2.39(1)Å, and Ni-O = 1.94(3) and 2.00(3)Å [79].

β-Diketone ligands, and their complexation with Ni(II), continue to attract interest, particularly in mixed ligand systems. These include (a) an ongoing study of mixed chelate nickel(II) complexes, comprising complexes with N,N,N',N'',N''-pentamethyldiethylenetriamine and the β-diketonates, acetylacetonate (acac), dipivaloylmethanate (dipm), pivaloyltrifluoroacetonate (pfac), trifluoroacetylacetonate (tfac), and hexafluoroacetylacetonate (hfacac) [80], (b) a study of the thermal behaviour of the mixed ligand complex $[Ni(acac)_2(L)_2]$ (L = 4-benzoylpyridine) [81], (c) a report on the thermodynamic and structural properties, relating to solvent and substituent effects of square planar Ni(II) complexes containing a diamine and a β-diketone ligand in general [82], as well as (d) a specific case concerning the nickel(II) complex containing tetramethylethylenediamine and acac as ligands [83].

The structures of two mixed nickel(II) complexes containing hexafluoroacetylacetonate have been reported. Bis(hexafluoroacetylacetonato)bis(tetrahydrofuran)nickel(II) was found to be octahedral in coordination geometry, with the thf ligands occupying *trans* axial positions (Ni-O = 2.011(5) and 2.041(12)Å), while the hfacac ligands coordinate in the equatorial plane (Ni-O ranges from 2.011(5) to 2.041(12)Å) [84]. In addition, the structure of the related complex (4-amino-2,2,6,6-tetramethylpiperidinyl-1-oxy)bis(hexafluoroacetylacetonato)(methanol)nickel(II) confirmed octahedral geometry for the Ni atom, with the hfacac ligands occupying the equatorial plane (Ni-O ranges from 2.014(5) to 2.042(5)Å). The methanol and nitroxyl ligands coordinate in a *trans* axial fashion with bond lengths of 2.094(6) and 2.075(6)Å respectively [85].

Isotopic substitution in neutron diffraction has been used to study the coordination environment of the Ni^{2+} ion in a 0.956M solution of $Ni(CF_3SO_3)_2$ in fully deuterated ethylene glycol (eg). It was shown that the eg molecules did not behave as monodentate ligands, but that tris chelate $[Ni(eg)_3]^{2+}$ complexes were formed. The number of second-shell eg molecules that participated in hydrogen bonding was estimated at six [86].

Ligands containing β-hydroxy aldehyde or ketone groups provide an ideal chelating environment, and a number have been complexed to Ni(II). 2,2'-dihydroxy-3,3'-diacetyl-5,5'-dichlorodiphenylmethane (H_2L)(**18**), has been prepared and complexed with nickel(II) perchlorate. Variation of the ligand to metal ratio gave rise to both mononuclear and dinuclear complexes, $[Ni(HL)_2].CH_3OH$ and $[Ni_2L_2].CH_3OH$ respectively. In addition, reaction of (**18**) with a stoichiometric amount of ethylenediamine in the presence of the nickel(II) perchlorate yielded a polymeric Schiff base complex [87].



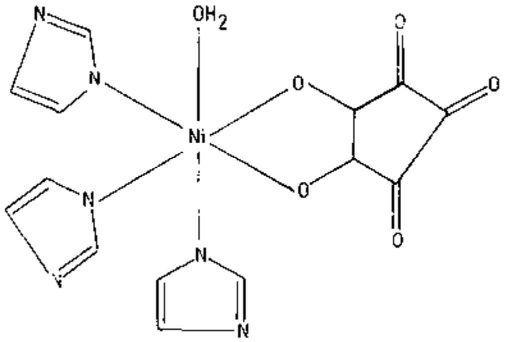
(**18**)

The complexation of 2,5-dihydroxy-1,4-benzoquinone with various metal ions has been investigated potentiometrically. Thermodynamic parameters such as enthalpy, free energy, and entropy changes, as well as stability constants were determined. The stability of the Ni(II) complex was evaluated with reference to other transition metal ions [88].

The mixed ligand complexes $[NiL_2L'_2]$ (HL = 9,10-dihydro-9,10-ethano-12-hydroxymethyleneanthracen-11-one; L' = H_2O, 4-benzoylpyridine, 4,4'-bipyridine) have been prepared and characterised using a number of spectroscopic and magnetic techniques. The complexes have also been compared with the parent acac complexes [89]. The same authors have examined the corresponding 2,2'-bipyridine and 1,10-phenanthroline adducts i.e where L' = 2,2'-bipyridine and 1,10-phenanthroline [90].

The metal ligand stability constants of ω-benzoyl-2-hydroxy-4-methoxy-3-methylacetophenone have been determined in acetone/water, ethanol/water, and dioxane/water media. Comparison of the Ni(II) complex with other transition metal complexes showed that the stability corresponded to the Irving-Williams series [91].

Aqua(4,5-dihyroxy-4-cyclopentene-1,2,3-trionato)tris(imidazole)nickel(II) monohydrate has been synthsized and its crystal structure reported. While the croconate ligand has the ability to function as a tetradentate ligand, coordination to the metal occurred only via two of the O donor groups (**19**). The coordination geometry is essentially octahedral with the following relevant data: Ni-O(croconate) = 2.135(2) and 2.166(2)Å, Ni-O(water) = 2.091Å, and Ni-N(imidazole) = 2.052(2), 2.061(3) and 2.065(3)Å [92].



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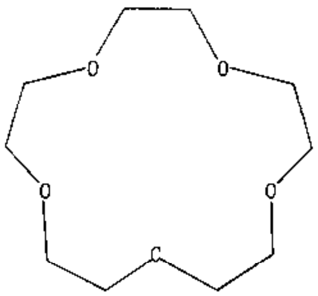
A number of ligands containing acid functional groups have been complexed with Ni(II). These include phthalic acid [93], mandelic acid [94], and a range of fulvic acids [95].

Calorimetric titration has been used to study the complexation of Ni^{2+} with $edtaH_4$ in aqueous medium. Various thermodynamic parameters were calculated and compared with those of the analagous Cd^{2+} and Cu^{2+} complexes [96].

FTIR spectroscopy has been employed to investigate the degree of complexation of *t*-butylcyclohexano-15-crown-5 (**20**) with divalent transition metal ions. Most of the metal ions complexed well with (**20**) in anhydrous carbon tetrachloride, but the presence of water made the complexation less complete. A qualitative order of stability for the complexes under water saturated conditions revealed the unusual trend of Mn > Zn > Cu > Co >Ni [97].



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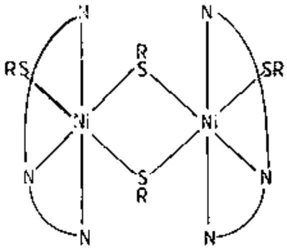
7.3.4 Complexes with sulfur donor ligands

Thiolate ligands have been reacted with [Ni(terpy)Cl$_2$] in methanol or acetonitrile. Different products were obtained depending on the basicity and bulk of the thiolate ligand employed. Thus, reaction with PhSH yielded the thiolato bridged dimer [Ni(terpy)(SPh)$_2$]$_2$.6CH$_3$OH (**21**), reaction with C$_6$F$_5$SH yielded the solvated monomer [Ni(terpy)(SC$_6$F$_5$)$_2$CH$_3$CN].3CH$_3$CN (**22**), while reaction with 2,4,6-(*i*-Pr)$_3$C$_6$F$_2$SH yielded the pentacoordinated complex [Ni(terpy)(S-2,4,6-(*i*-Pr)$_3$C$_6$F$_2$)$_2$].5CH$_3$CN (**23**). The crystal and molecular structures of these three complexes have been determined confirming distorted octahedral dimeric coordination in (**21**) (Ni-S = 2.410(2), 2.428(2) and 2.519(2)Å, Ni-N = 1.997(5), 2.090(5) and 2.108(4)Å), distorted octahedral coordination in (**22**) (Ni-S = 2.482(4) and 2.499(4)Å, Ni-N(CH$_3$CN) = 2.047(8)Å, Ni-N(terpy) = 1.987(70, 2.080(7) and 2.085(7)Å), and distorted trigonal bipyramidal coordination in (**23**) for which two similar and well separated molecules were obtained (Ni(1)-S = 2.274(3) and 2.332(2)Å, Ni(1)-N = 1.974(9), 2.085(5) and 2.113(7)Å, Ni(2)-S = 2.298(3) and 2.302(3)Å, Ni(2)-N = 1.986(6), 2.075(7) and 2.125(7)Å) [98].



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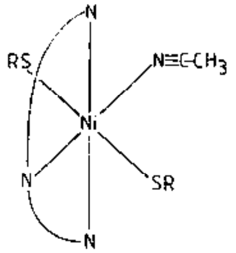

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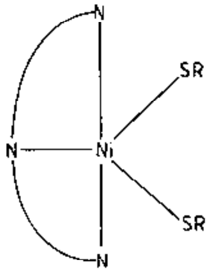

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A review covering novel solid state materials derived from transition metal bis-dithiolene complexes has been published [99]. The review covers the background to metal bis-dithiolene complexes, comments on combining these complexes with organic π-donors, and discusses their use in the preparation of molecular superconductors [99].

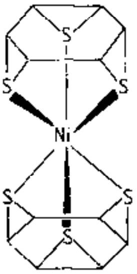
The chromophore bis(maleonitriledithiolato)nickelate(II) has been coated on a polymer electrode, and its photoelectrochemistry investigated. In the redox system investigated, an improvement in electronic conductivity was observed, but at the expense of lower ionic mobility [100].

A novel route for the synthesis of dithiocarbamate and xanthate nickel(II) complexes has been reported. The complexes $[NBu_4][Ni(C_6F_5)_2(S_2C\text{-}R)]$ (R = NHEt, NHPr, NMe_2, NEt_2, NC_4H_8, NC_5H_{10}, NC_4H_8O, OMe, OEt and O) have been prepared from the novel starting complex $[NBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$ in yields of over 70%. The complexes have all been characterised using a range of analytical techniques [101].

The adduct formation of $[Ni(dtp)_2]$ (dtp = $(C_2H_5O)_2PS_2$) with pyridine, 4-cyanopyridine, 2-aminopyridine, piperidine and benzylamine, has been invstigated in benzene using spectrophotometry and calorimetry. For 2-aminopyridine only the formation of the monoadduct $[Ni(dtp)_2L]$ was observed, while for the other bases, the formation of the mono- as well as the bisadduct $[Ni(dtp)_2L_2]$ was observed [102].

Related to the previous monoadduct complexes, the crystal structure of the pentacoordinated complex bis(O,O'-diethyldithiophosphato)(triphenylphosphine)nickel(II) revealed a distorted square pyramidal coordination geometry for Ni(II). The four S atoms form the base of the pyramid, with one P atom of triphenylphosphine at the apex. Relevant data are Ni-S = 2.433(2), 2.436(2), 2.395(2) and 2.391(2)*A*, Ni-P = 2.340(1)*A* [103].

Benzene trisulfide (BTS) has been complexed with nickel(II) perchlorate. The resultant complex $[Ni(BTS)_2](BF_4)_2$ was found to contain each BTS ligand functioning in a facially coordinating fashion (**24**). A comparison of this complex with other systems containing thioether ligand fields was made, and BTS was shown to generate the largest ligand field of any of the other thioether ligands examined. This was ascribed to its rigid endodentate conformation [104].



(**24**)

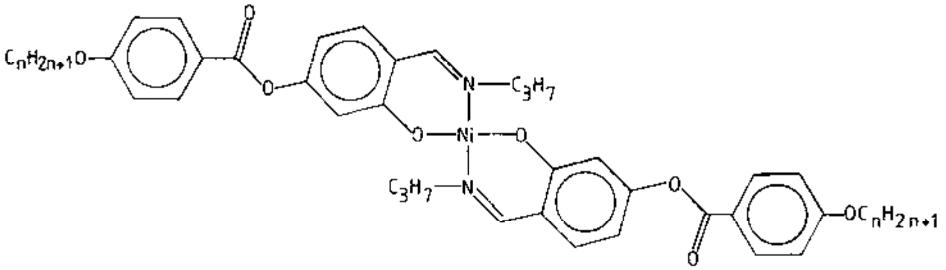
7.3.5 *Complexes with nitrogen-oxygen donor ligands*

Ligands derived from the condensation of aldehydes and ketones with amines and diamines, such as Schiff bases, hydrazones, carbazones, semi-carbazones, oximes, and azines continue to dominate this category. As in previous years most of the literature relates to the ubiquitous Schiff base.

The stability constants of the chelates of Ni(II) with the potentially didentate ligands, *o*-(N-α-pyrrolidimino)phenol, and *o*-(N-α-pyridimino)phenol, have been determined potentiometrically in 30% dioxane/water medium. In addition, the thermodynamic properties of complexation were also determined [105].

New Schiff base didentate ligands derived from the β-diketones acac and 1-phenyl-1,3-butanedionate (bzac), and the amine 2-phenylethylamine (2PEA) have been synthesized and characterised. Complexation with Ni(II) yielded the corresponding bis complexes [NiL_2] (HL = Schiff base ligand). The complexes have been assigned non-planar tetrahedral geometry, ascribed to steric factors arising from the flexible -CH_2-CH_2-Ph substituent on the nitrogen atom of 2PEA. A number of electrophilic substitution reactions such as chlorination, bromination, and phenylisocyanation at the γ-carbon of the β-diketoneimine chelate ring have also been reported [106].

A homologous series of new metallonematogens, bis[4-((4-alkoxybenzoyl)oxy)-*N*-*n*-propylsalicylaldiminato]nickel(II) (**25**) has been synthesized and their thermotrophic mesomorphism characterised by thermal analysis. All of the nickel complexes were found to exhibit enantiotropic phases over temperature ranges between 158-230°C (melting points) and 160-253°C (clearing points). It has also been revealed, by ^{1}H NMR, that the nematogenic nickel(II) complexes prepared in this study show association phenomena in solution [107].



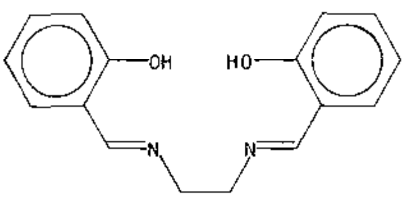
(n = 4 - 12, 14, 16, 18)

(25)

Coordination compounds of nickel(II) with potentially didentate Schiff bases derived from nitrofurfural and the bases sulfadimezine, norsulfazole, and ethazole, have been prepared. These complexes have been tested for antimicrobial activity [108].

Turning to tridentate Schiff base ligands and their Ni(II) complexes, the crystal structure of {1-[(2-hydroxyphenyl)iminomethyl]naphthalen-2-olato-O,O',N}piperidinenickel(II) has been determined. Nickel was found to be coordinated in a slightly distorted square-planar environment. The Schiff base functions as a tridendate O,N,O donor ligand, with the fourth coordination site being occupied by the piperidine ligand. Relevant data are: Ni-N(Schiff base) = 1.848(4)Å, Ni-O = 1.830(4) and 1.804(4)Å, Ni-N(pip) = 1.947(4)Å [109].

Potentiometric determination of the protonation/deprotonation equilibria of N,N'-ethylenebis(salicylideneimine) (H$_2$sal$_2$en) (**26**), the related Schiff base N-(2-aminoethyl)salicylideneimine (Hsalen) (**27**), and their organic constituents, salicylaldehyde (Hsal) and ethylenediamine (en), has been used to study the equilibria involved in the formation of the Schiff bases, and their complexation with nickel(II). Both sal$_2$en^{2-} and salen^{1-} are found to be stable towards disproportionation in the presence of the metal ion, and a planar configuration was adopted with Ni(II) [110].



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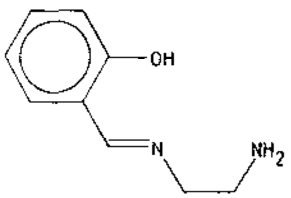
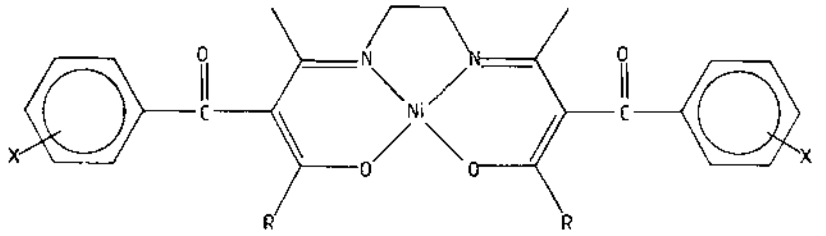


(27)

The Schiff base derived from 1-aminocyclopropanecarboxylic acid (ACC) and pyridoxal (PL), has been complexed with nickel(II)nitrate in the presence of water. The resultant complex [Ni(PL-ACC)(H$_2$O)$_2$].NO$_3$.H$_2$O, has been characterised by a single-crystal X-ray structure determination. The tetradentate Schiff base was found to coordinate to the square-pyramidal nickel atom through its carboxylate and phenolate oxygens and the imino nitrogen. The fourth basal donor is a water molecule, while the axial positions are occupied by the remaining water molecule and the hydoxymethyl oxygen from a neighbouring ligand molecule. Relevant data are: Ni-O(COO) = 2.024(4)Å, Ni-N = 2.013(5)Å, Ni-O(OH) = 1.976(5)Å, Ni-O(water) = 2.058(5) and 2.092(4)Å, Ni-O(adj) = 2.163(4)Å [111].

A variety of nickel(II) Schiff bases with isobutyl chains and benzoyl substituents have been prepared and characterised (**28**). The tetradentate ligands which contain a donor set of N$_2$O$_2$, exhibit planar coordination. Interestingly, the benzoyl substituents were found to be perpendicular to the chelate plane, while the isobutyl groups were found to move segmentally to facilitate approach to the benzoyl substituents [112].



(R = Me, X = H, *m*-NO_2, 3,5-$(NO_2)_2$; R = iso-Bu, X = H, *m*-NO_2, 3,5-$(NO_2)_2$)

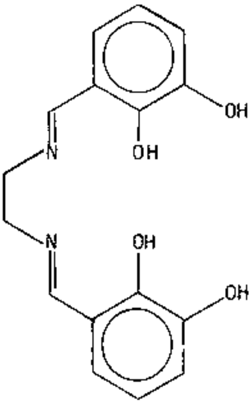
(28)

The electrochemistry of the Ni(II) complexes of a series of substituted N,N'-ethylenebis(mono-R-acetoimines) (R = $C_6H_4OCH_3$, $C_6H_4CH_3$, C_6H_5, CH_3, C_6H_4Cl, C_6H_4Br) has been investigated in methanol using cyclic voltammetry. A one electron anodic process was observed which was coupled with a subsequent chemical reaction [113].

In a study on ligand substitution in *trans*-N_2O_2 Schiff base bis(N-alkylsalicylaldiminato)nickel(II) complexes, the reaction of NiA_2 (NiA_2 = Phenylethylsalicylaldiminato)nickel(II), and cyclohexylethylsalicylaldiminato)nickel(II)) with the salen type ligands H_2B (H_2B = 1,2-diamino-N,N'-disalicylideneethane, 1,2-diamino-N,N'-disalicylidenepropane, 1,3-diamino-N,N'-disalicylidenepropane, 1,2-diamino-N,N'-disalicylidene-2-methylpropane, 2,3-diamino-N,N'-disalicylidenebutane, and 1,2-diamino-N,N'-disalicylidenecyclohexane) has been investigated. Normal and stopped-flow spectrophotometry was used to study the kinetics of the reaction, which was found to be a second order associatively controlled process, first order in both complex and ligand concentration [114].

Complexes of several 3-d transition metals with the asymmetrical tetradentate ligand 2-(2,5,8-triaza-1-octenyl)phenol (HL) have been studied using XPS. The nickel complex [NiL]ClO_4 was assigned a planar configuration with the ligand functioning in a tetradentate fashion, coordinating via an ON_3 donor set. Interestingly, the N 1s peak was asymmetric and appeared to consist of two components. The weaker component at a lower binding energy was attributed to the azomethine N atom, while the higher one was attributed to the two amino groups [115].

The potentially hexadentate compartmental ligand (H_4L = (**29**)), has been prepared by the reaction of 2,3-dihydroxybenzaldehyde and ethylenediamine. Reaction with nickel(II) acetate yields the mononuclear complex [Ni(H_2L)]. The nickel ion was assigned to the inner N_2O_2 compartment on the basis of physicochemical data. [Ni(H_2L)] functions as a ligand itself in the preparation of the heterodinuclear complexes [NiM(L)(X)(solv)$_n$] (M = La or Y; X = Cl or NO_3; solv = H_2O, methanol or dmso), and [NiM(L)(solv)$_n$] (M = UO_2 or Ba; solv = H_2O, methanol or dmso). Coordination of the second metal was found to occur via the outer O_2O_2 donor set [116].

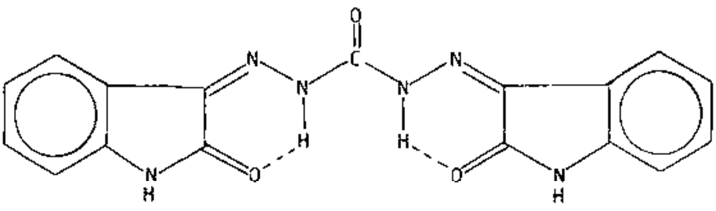


(**29**)

A selection of hydrazone ligands have been synthesized and complexed with nickel(II). These include the didentate hydrazones 2,4-pentanedione-1-(2-chlorophenylhydrazone) [117], 2-hydroxynaphthaldehyde phenylhydrazone [118], peonolphenylhydrazone [119], and the tridentate ligand diacetylmono(lepidyl)hydrazone [120]. In these studies, stability constants for complexation of each of the previously mentioned ligands with Ni(II) were determined.

Complexes of *o*-hydroxyacetophenone semicarbazone (HL) with Ni(II) have been prepared. Two complexes have been isolated *viz.* [NiLCl] and [Ni(HL)Cl_2]. The former has been assigned a square-planar configuration in which the deprotonated ligand functions as an ONO donor, while the latter complex has been assigned octahedral geometry in which the protonated ligand functions as an NO donor. The assignments have been based on spectral and magnetic analyses [121].

The carbohydrazone ligand (H_2L = (**30**)), formed by the condensation of carbohydrazide and isatin, has been synthesized and complexed with nickel(II). The resultant complexes [Ni(HL)Cl].$2H_2O$ and [Ni(L)(H_2O)$_2$] were isolated and characterised using a number of analytical techniques. It has been suggested that the ligand functions in a dibasic tetradentate fashion in [Ni(L)(H_2O)$_2$], which was assigned *trans* octahedral coordination geometry, but functions as a monobasic pentadentate ligand in [Ni(HL)Cl].$2H_2O$, with the remaining axial coordination site occupied by a water ligand (**31**) [122].



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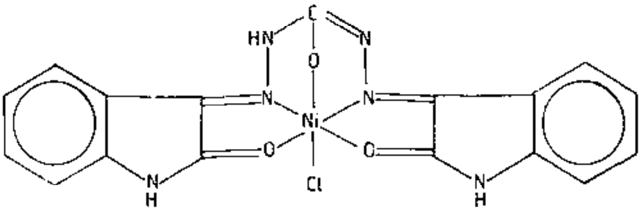


(31)

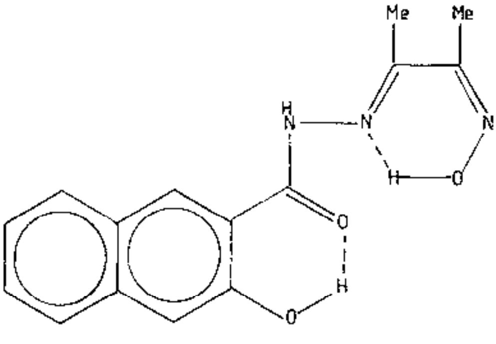
2-, 3-, and 4-chlorosubstituted benzohydrazide ligands have been complexed with Ni(II), yielding bis(benzohydrazonato)nickel(II) complexes in which the benzohydrazide ligands have undergone deprotonation. Of interest is the fact that, depending on the position of the Cl substituent, different isomers were obtained. Thus bis(2-chlorobenzohydrazide)nickel(II) was found to have a *cis* planar structure, while bis(3-chlorobenzohydrazide)nickel(II) and bis(4-chlorobenzohydrazide)nickel(II) exhibited *trans* geometry [123].

The ligand 1-butyroyl-1-phenyl-3-thiosemicarbazide (HL) has the potential to function as an ONS tridentate ligand. However, in its complexation with nickel(II) acetate, it formed a square-planar complex of the type [NiL(OAc)]. Spectral and magnetic data indicated that the ligand functions as a NO didentate ligand, and that the acetate ligand is coordinated in a didentate fashion as well [124].

Oxime ligands continue to find application in the area of metal ion solvent extraction. The distribution equilibria of the nickel(II) complexes of 1-phenyl-1,2-propanedione-2-oxime (HL) in the water-chloroform system have been studied. It has been deduced that nickel is extracted as its NiL_2 and $NiL_2(HL)$ complexes, for which the following equilibrium constants were obtained; NiL_2, $\log K_{ex} = -13.57 \pm 0.05$; $NiL_2(HL)$, $\log K_{ex} = -12.6 \pm 0.01$ [125].

The oxime-containing complexes $Ni(HL)_2X_2$ (HL = p-$MeOC_6H_4C(=NOH)P(O)(OEt)_2$; X = Cl, Br) have been prepared and characterised by IR, electronic, and NMR spectra. It was found that the ligand functions in a didentate fashion, binding via the oxime N and phosphoryl O atoms [126].

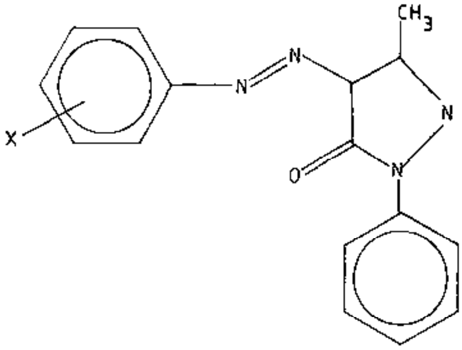
The potentially tetradentate ligand, biacetylmonoxime-3-hydroxy-2-naphthoylhydrazone (HL) (**32**), has been synthesized and complexed with nickel(II). Spectral evidence has been used to assign an octahedral structure to the complexes $[Ni(HL)_2]X_2$ (X = Cl, Br), and a square planar structure to the complex [NiL(OAc)]. The ligand functions as a tridentate ONN donor in $[Ni(HL)_2]X_2$, and as a didentate ON donor in [NiL(OAc)]. In the latter complex didentate coordination of the acetyl ligand was also suggested [127].



(**32**)

1-ethyl-3-p-nitrophenyltriazene-1-oxide has been complexed with nickel(II) acetate yielding the complex bis(1-ethyl-3-p-nitrophenyltriazene-1-oxide)nickel(II). The X-ray crystal structure of this complex has been determined and reveals *trans* square-planar coordination for Ni(II), in which the ligand acts in a didentate NO donor fashion. Relevant data are: Ni-O = 1.828(3)Å, Ni-N = 1.871(2)Å [128].

Some arylazo-5-pyrazolones of the general structure (**33**), have been complexed with nickel(II). The resultant complexes have the general formula $NiL(NO_3)(H_2O)$ when the ligand functions as a didentate NO donor, coordinating via the azo N and ketone O atoms. An exception occurred when the phenyl substituent was the *o*-OH group. In this case, the resultant complex, in which the ligand functions as a tridentate O,N,O donor had the formula NiL(H_2O), with coordination occurring via the hydroxyl O, azo N, and ketone O atoms [129].



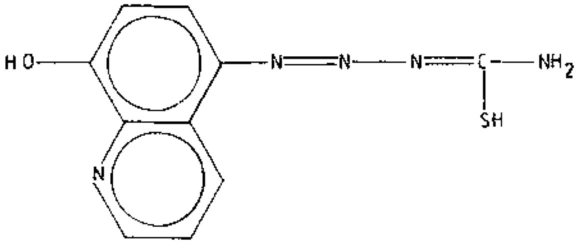
(X = *o*-OH, *m*-OH, *p*-COOH, *p*-SO_3H, *o*-COOH, *o*-CH_3)

(33)

The new pyridylazo ligands 1-(3,5-dichloro-2-pyridylazo)-2-naphthol, 2-(3,5-dichloro-2-pyridylazo)-5-(dimethylamino)phenol, and 2-(3,5-dichloro-2-pyridylazo)-5-(dimethylamino)-benzoic acid (HL) have been prepared, and their coordination with metal(II) ions investigated. The ligands function as tridentate NNO donors with complexation occurring via the pyridine N, azo N, and deprotonated OH atoms, resulting in hexacoordinate complexes of the type NiL_2 [130].

8-hydroxyquinoline and variously-substituted-8-hydroxyquinoline ligands provide an ideal source of potentially didentate chelating N,O donor groups. Potentiometric evidence for the formation of ternary chelates involving the complexation of 8-hydroxyquinoline and furan-2-carboxylic acid with Ni(II) has been cited. This study was carried out in 75% (v/v) aqueous ethanol at various temperatures [131].

In addition, the new azo-8-hydroxyquinolinesulfonamide ligands 5-phenyl- , 5-*p*-tolyl-, and 5-aminothioacetamide-8-hydroxyquinoline (HL) and their Ni(II) complexes have been synthesized. These ligands, which have the potential to function as either NO or NS donor monobasic ligands (**34**), were found to coordinate to Ni(II) in a didentate fashion via the NO donor set, forming complexes of the type [$NiL_2(H_2O)_2$]. TGA studies have been used to confirm the coordination of two water molecules [132,133].

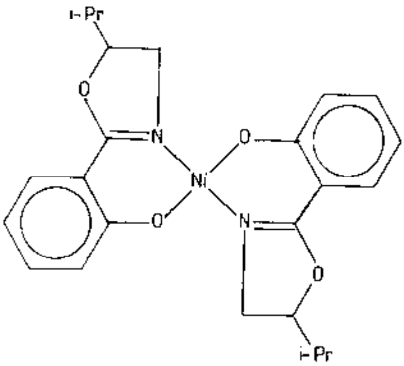


(34)

The reaction of formaldehyde with the nickel(II) chelate of L-threonine, results in the formation of $NiL_2(H_2O)_2$ (HL = 5-methoxyoxazolidine-4-carboxylic acid). On the basis of magnetic and spectral measurements, the complex was assigned octahedral geometry, the coordination of two water molecules being confirmed by the use of thermal analysis [134].

A number of solution studies involving iminodiacetic acid and related ligands have been undertaken. These include ternary complexes of Ni(II) with m-$RC_6H_4N(COOH)_2$ and 2,2'-bipyridyl or 1,10-phenanthroline [135], ternary complexes of Ni(II) with L-2-amino-3-(4-hydroxyphenyl)propionic acid and 2,2'-bipyridyl or 1,10-phenanthroline [136], complexes of Ni(II) with piperazine-N,N-di-β-propionic acid dihydrochloride [137], and ternary complexes of the type [NiAL] (A = 2,6-pyridinedicarboxylic acid, iminodiacetic acid; L = glycine, α-alanine, phenylalanine, tyrosine, tryptophan, en, 1,3-propanediamine, oxalic acid, catechol, catechuic acid, tiron, pyrogallol, *o*-aminophenol, *o*-phenylenediamine) [138].

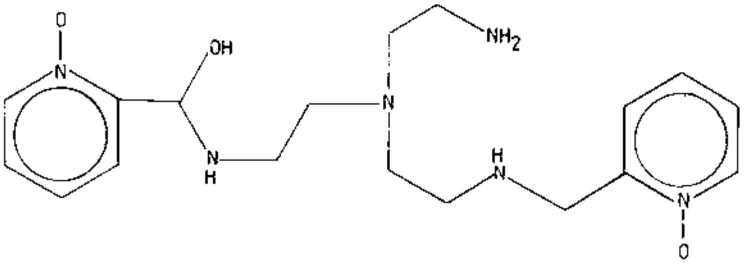
The optically active ligand (4S)-4,5-dihydro-2-(2'-hydroxyphenyl)-4-isopropyloxazole has been complexed with Ni(II), and the crystal structure of the resultant complex bis[(4S)-4,5-dihydro-4-isopropyl-2-(2'-oxidophenyl-χO)oxazole-χN]nickel(II) (35) has been determined. Two independent molecules per asymmetric unit were found for the distorted square-planar complex. Relevant data are: Ni-N = 1.870(3) and 1.878(5)Å, Ni-O = 1.838(4) and 1.834(5)Å [139].



(35)

Titrations of tris(2-pyridyl)carbinol (HL) and di(2-pyridyl)carbinol (HL') in the presence of first row transition metals have been carried out. For tris(2-pyridyl)carbinol coordination can occur symmetrically, with two ligands bound via the N,N',N'' mode as observed in $[Ni(HL)_2]^{2+}$, or via a mixed donor mode, with one ligand bound in a symmetric N,N',N'' mode, and the second, in a non-symmetric N,N',O coordination mode, as observed in $[Ni(HL)(L)]^+$. This latter complex has been generated by making the -COH group acidic, effected by adjusting the pH during complexation. Di(2-pyridyl)carbinol was found to coordinate exclusively in a N,N',O fashion, and all the complexes were found to titrate as strong acids [140].

The structure of 2,2'-[5-(2-aminomethyl)-1-hydroxy-2,5,8-triazanon-3-ene-1,9-diyl]-bis(pyridine N-oxide)nickel hexafluorophosphate monohydrate has been prepared and its crystal and molecular structure determined. The novel tripodal ligand with three inequivalent arms (**36**) coordinates in a hexadentate fashion via a N_4O_2 donor set. The nickel atom is situated in a distorted octahedral environment, with Ni-N = 1.999(4), 2.065(4), 2.085(5), 2.132(4)Å, and Ni-O = 2.029(4) and 2.110(3)Å [141].



(36)

7.3.6 Complexes with nitrogen-sulfur donor ligands

The reaction between S_4N_4 and Ni^{2+} has been investigated in dmso. Reaction was found to proceed very slowly, but after several days, the nickel complex, $[Ni(S_2N_2H)_2]$, was formed with acidification of the solution. ^1H and ^{15}N NMR studies revealed that the protonated form of the complex, $[Ni(S_2N_2H_2)(S_2N_2H)]^+$, existed in the dmso solution. These studies also confirmed didentate coordination of the ligand S=N-S-NH_2, and that the proton binds at one NH group [142].

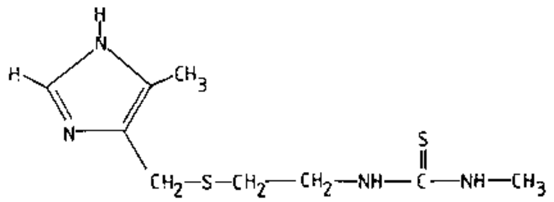
Thiosemicarbazide, $H_2NCSNHNH_2$ (HL), has been complexed with nickel(II) sulphate or chloride, yielding bis thiosemicarbazide complexes of the type $[NiL_2]$.xA (A = HCl, H_2SO_4). Both the *cis* and *trans* isomers of these complexes were isolated, and their electrical conduction measured as a function of temperature [143].

The structure of bis(thiocyanato-N)bis(thiosemicarbazide-N$_1$,S)nickel(II) has been redetermined, with a greater degree of precision than possible in its previous determination. The Ni atom was found to have an octahedral coordination geometry, with the thiocyanate ligands occupying *trans* axial positions. In addition, the thiosemicabazide ligands function as didentate N,S donors, and are coordinated in a *trans* configuration about Ni. Relevant data are Ni-N(NCS) = 2.071(2)Å, and for the thiosemicarbazide Ni-N = 2.093(2) and Ni-S = 2.429(1)Å respectively [144].

Similarly, the crystal and molecular structure of bis(2-methylthiosemicarbazide)nickel(II) nitrate has been reported. The Ni(II) ion was found to be coordinated in a *trans* square-planar configuration. The ligand functions in a didentate fashion, bonding via the S and hydrazine N atoms. Relevant data are: Ni-S = 2.177(1)Å, Ni-N = 1.894(3)Å [145].

X-ray crystallographic studies of the fluxional bis[1-isopropyl-3-methyl-4-N-alkyl(aryl)aldiminopyrazole-5-thionato]nickel(II) complexes, $[NiL_2]$ (HL = 1-isopropyl-3-methyl-4-N-R-aldiminopyrazole-5-thiol; R = methyl, phenyl, t-butyl), have been undertaken. All three complexes were found to possess pseudo-tetrahedral geometry. Ni-S bond lengths vary between 2.229(1) and 2.253(1)Å, while Ni-N bond lengths range from 1.975(7) to 1.995(4)Å. Comparison was also made with the previously reported structurally related complex, bis[1-isopropyl-3-methyl-4-N-cyclohexylaldiminopyrazole-5-thionato]nickel(II) [146].

N-methyl-N-[2-{(5-methylimidazol-4-yl)methylthio}ethyl]thiourea (L) (**37**) has been complexed with nickel(II). The crystal structure of the complex $[NiL_2(NCS)_2]$ reveals that the potentially tridentate ligand coordinates in a didentate fashion via the imidazole N atom and the thioether S atom. The thiourea S atom does not take part in coordination. The coordination geometry about Ni was found to be elongated octahedral, with the nitrogen atoms occupying the equatorial positions (Ni-N = 2.04 and 2.06Å), and the thioether S atoms occupying the apical positions (Ni-S = 2.58Å). Individual molecules are linked by a unique S···H-N hydrogen bond involving the uncoordinated thiourea S atom [147].

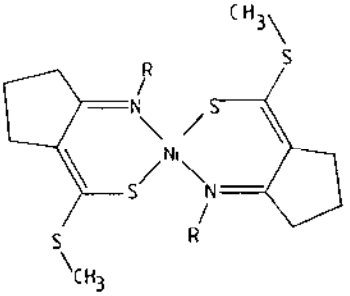


(37)

The heterocyclic thiones, oxadiazole thione and thiohydantoin (HL), have been complexed with Ni(II). Complexes of the type NiL_2 have been isolated and characterised using a number of analytical methods. The complexes were found to be diamagnetic, with the ligands functioning in a monobasic N,S didentate fashion [148].

Bis-ligand nickel(II) complexes with 4-amino-2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine (L) have been prepared by reaction between L and the corresponding nickel salt. The ligand functions either as a monodentate N donor, or as a didentate N,S donor, depending on the metal salt and conditions employed. Thus, it functions in a monodentate fashion in the octahedral complexes $[NiL_2(H_2O)_2Br_2].H_2O$, $[NiL_2(H_2O)_2I_2]$, $[NiL_2Cl_2].H_2O$ and a-$[NiL_2Br_2]$, but functions as a didentate N,S donor ligand in the complexes $[NiL_2(NCS)_2]$, $[NiL_2(H_2O)_2](ClO_4)_2$, $[NiL_2(H_2O)_2](BF_4)_2$, $[NiL_2(CH_3CN)_2](ClO_4)_2$, $[NiL_2(CH_3CN)_2](BF_4)_2$, $[NiL_2(H_2O)_2](NO_3)_2$, and b-$[NiL_2Br_2]$ [149].

In a sequence of papers, Bereman and Martin have investigated the synthesis and characterisation of N,S donor ligands with metal(II) ions. They have reported the preparation and characterisation of the nickel(II) complexes of methyl-2-amino-1-cyclopentenedithiocarboxylate (HL) and N,N'-pentamethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate (H_2L'). Methyl-2-amino-1-cyclopentenedithiocarboxylate was found to chelate in a didentate fashion via the thioketonate sulfur atom and an imine nitrogen atom, and formed a planar complex $[NiL_2]$. N,N'-pentamethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate coordinates with Ni(II) in a tetradentate fashion via a S,N,N,S donor set, yielding the complex [NiL']. Spectral data indicate that this complex has a pseudo-tetrahedral coordination geometry [150]. This work has been extended to include the effect of alkyl substituents on the imino N atom in the nickel(II) complexes of N-alkylmethyl-2-amino-1-cyclopentenedithiocarboxylate (alkyl = methyl, ethyl, n-propyl, n-butyl) $[NiL_2]$ (**38**). The alkyl substituents on the imine nitrogen atoms were found to drive the coordination stereochemistry from planar to tetrahedral [151]. In addition, they have determined the crystal and molecular structure of bis(methyl-2-amino-1-cyclopentenedithiocarboxylate)nickel(II). As predicted by earlier spectral studies, the complex exhibits *trans* planar coordination geometry. Relevant data are: Ni-S = 2.183(2)*A*, and Ni-N = 1.863(4)*A* [152].



(R = Me, Et, n-Pr, n-Bu)

(38)

$NiCl_2.6H_2O$ has been complexed with the thiolate ligands HSC_5H_3N-3-$SiMe_3$, HSC_6H_4-2-PPh_2, and HSC_6H_3-6-$SiMe_3$-2-$OPPh_2$, yielding the mononuclear complexes [$Ni(SC_5H_3N$-3-$SiMe_3)_2$], [$Ni(SC_6H_4$-2-$PPh_2)_2$], and [$Ni(SC_6H_3$-6-$SiMe_3$-2-$OPPh_2)_2$] respectively. All of the complexes have planar coordination geometry, as verified by their crystal and molecular structure determinations. However, the mode of coordination varied according to the ligand used. SC_5H_3N-3-$SiMe_3$ functions as a N,S donor in [$Ni(SC_5H_3N$-3-$SiMe_3)_2$] (Ni-S = 2.2281(8)*A*, Ni-N = 1.873(2)*A*), SC_6H_4-2-PPh_2 as a P,S donor in [$Ni(SC_6H_4$-2-$PPh_2)_2$] (Ni-S = 2.180(1)*A*, Ni-P = 2.181(2)*A*), and SC_6H_3-6-$SiMe_3$-2-$OPPh_2$ as a S,O donor in [$Ni(SC_6H_3$-6-$SiMe_3$-2-$OPPh_2)_2$] (Ni-S = 2.183(3) and 2.179(4)*A*, and Ni-O = 1.900(8) and 1.909(7)*A*) [153].

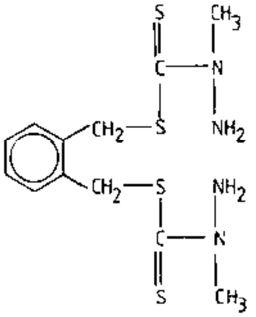
Turning to tridentate ligands, the N,S,N donor ligands 1,3-bis(5'-methyl-4'-imidazolyl)-2-thiapropane [154] and (4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane [155] have been complexed with Ni(II). Both ligands function in a tridentate fashion, yielding bis complexes of the type $[Ni(L)_2]X_2(H_2O)_n$ (X = Cl, NO_3, BF_4), while (4-(5-methyl-4-imidazolyl)-1-amino-3-thiabutane also yields the complex $[Ni(L)Cl_2(H_2O)]$ [155]. The related ligand 1,6-bis(3,5-dimethyl-1-pyrazolyl)-2,5-dithiahexane (L) has been reacted with a variety of nickel(II) salts. Complexes that have been isolated include $[NiLCl_2]$, $[NiL(NCS)_2]$, and $[NiL(NO_3)_2](H_2O)_2$. All of the complexes have been assigned octahedral geometry, in which the ligand functions in a tetradentate N,S,S,N donor fashion. In the complex $[NiL(NO_3)_2](H_2O)_2$ the nitrate ligands were assigned monodentate coordination [156].

Tetradentate dithioximide ligands of the general formula $RNHC(S)C(S)NH(CH_2)_n$-$NHC(S)C(S)NHR$ (R = c-C_5H_9 and c-C_6H_{11}, n = 2; n-$C_{12}H_{25}$ and $C_6H_5CH_2$, n = 2 - 4) (H_4L) have been prepared and reacted with Ni(II). Under acidic conditions, complexes of the type $[Ni(H_4L)]^{2+}$

were formed, isolated as their bromide salts, while under neutral conditions the neutral complexes $[Ni(H_2L)]$ were generated. Under basic conditions polymeric materials of approximate formula $([Ni_2L)_n$ were made. In addition, the crystal structure of the neutral complex $[Ni\{(c-C_5H_9)NHC(S)C(S)NH(CH_2)_2NHC(S)C(S)NH(c-C_5H_9)\}]$ has been determined. The ligand functions as a tetradentate S,N,N,S donor, and the coordination geometry about Ni was found to be distorted square-planar, approaching trapezoidal. Relevant data are: Ni-S = 2.171(4)Å, Ni-N = 1.86(1)Å [157].

Stepwise distortion from square-planar to pseudo-tetrahedral geometry has been observed in the series of complexes generated by the complexation of Ni(II) with N,N'ethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylate), N,N'-trimethylenebis(methyl-2-amino-1-cyclopentene-dithiocarboxylate) and N,N'-tetramethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylate) respectively. The ligands all function as tetradentate S,N,N,S donors, the only difference being the number of methylene groups bridging the imine nitrogens of each half of the ligand. The crystal structures of each of the complexes have also been determined. Systematic distortion from square-planar to tetrahedral geometry was observed as the number of methylene groups is increased [158].

α,α'-Xylene-bis(N-methyldithiocarbazate) (**39**), and the potentially sexidentate ligand (**40**), formed by the reaction of salicylaldehyde with α,α'-xylene-bis(N-methyldithiocarbazate), have been complexed with a variety of nickel(II) salts. (**39**) functions as a tetradentate N,S,S,N donor ligand forming octahedral complexes of the type $[NiLX_2]$ (L = (**39**); X = Cl, Br, I, or NCS). The doubly-deprotonated form of (**40**) functions as an O,N,S,S,N,O hexadentate donor ligand forming the octahedral complex [NiL] (H_2L = (**40**)) [159].



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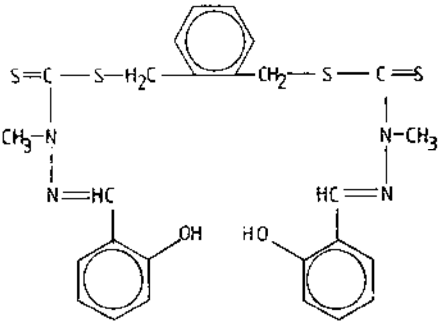

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7.3.7 *Complexes with oxygen-sulfur donor ligands*

2-mercaptopyridine N-oxide (H_2L) has been reacted with nickel(II) chloride in the presence of sodium methoxide. Deprotonation of the ligand occurred yielding the bis complex [NiL_2]. The crystal structure of this complex has been determined, revealing a square planar environment for Ni. The ligands function in a didentate fashion coordinating via the S,O donor set in a *cis* configuration. Relevant data are: Ni-S = 2.129(1) and 2.136(1)Å, Ni-O = 1.864(3) and 1.868(3)Å [160].

Potentiometry has been utilised to investigate mixed ligand complexes of nickel(II) containing thiosalicylic acid and a variety of polyamine ligands, including diethylenetriamine [161], ethylenetriamine, diethylenetriamine, or triethylenetriamine [162]. Studies were carried out in aqueous ethanol solution. The thiosalicylic ligand functions as a dibasic S,O donor ligand in all cases.

7.3.8 *Complexes with nitrogen-oxygen-sulfur donor ligands*

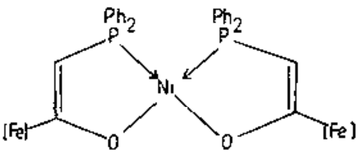
In a continuing study on the transition metal complexes of Schiff bases derived from S-alkyldithiocarbazate with 2-pyridinecarboxaldehyde N-oxide, a series of mononuclear nickel(II) complexes of the two tridentate ligands S-methyl-β-N-(pyridine N-oxide-2-ylmethylidene)-dithiocarbazate (SMPDH) and S-benzyl-β-N-(pyridine N-oxide-2-ylmethylidene)dithiocarbazate (SBPDH) was prepared and characterised. Complexes that were isolated include [Ni(SMPD)L](ClO_4) and [Ni(SBPD)L](ClO_4) (L = imidazole, pyridine), [Ni(SMPD)X] and [Ni(SBPD)X] (X = N_3, SCN, Cl), [Ni(SMPD)$_2$]·H_2O and [Ni(SBPD)$_2$]. Both square-planar and octahedral configurations were found to occur. In all of the complexes both ligands were found to function in a monobasic O,N,S donor fashion. The crystal structure of [Ni(SMPD)(imH)](ClO_4) was also reported, revealing a square-planar configuration for Ni. Relevant data are: Ni-S = 2.143(1)Å, Ni-N(SMPD) = 1.840(3)Å, Ni-O = 1.860(3)Å, and Ni-N(imH) = 1.888(4)Å [163]. In addition, in a separate report, the crystal and molecular structure of [Ni(SMPD)(py)](ClO_4) has been described. Ni was found to be in a square-planar coordination environment, with the deprotonated ligand SMPD coordinated via its O,N,S donor atoms. The pyridine ligand occupies the fourth coordination site. Relevant data are: Ni-S = 2.140(2)Å, Ni-N(SMPD) = 1.845(4)Å, Ni-O = 1.843(4)Å, and Ni-N(py) = 1.912(4)Å [164].

Acetylacetone thiobenzoylhydrazone (H_2L) has been complexed with nickel(II) forming the square-planar complexes [NiL($NHEt_2$)] and [NiL(NH_3)]. In each of the complexes, the doubly-deprotonated ligand functions in a tridentate fashion coordinating through its O,N,S atoms. The fourth coordination site is occupied by the monodentate N-containing ligand [165].

The complexation equilibria of the potentially didentate (N,O), or tridentate (N,O,S) ligands, 2-(*p*-chlorophenyl)thiazolidine-4-carboxylic acid, 2-(*p*-tolyl)thiazolidine-4-carboxylic acid, 2-(*p*-hydroxyphenyl)thiazolidine-4-carboxylic acid, and 2-(*o*-hydroxyphenyl)thiazolidine-4-carboxylic acid, with Ni(II) have been investigated in aqueous media. The mode of coordination was found to vary depending on the pH employed [166].

7.3.9 Complexes with ***phosphorus–oxygen*** *donor ligands*

The complex (η-C_5H_5)Fe(CO)(PPh_3)C(O)CH_2PPh_2, when reduced in the presence of LiBu, can be complexed with $NiCl_2$, to yield the bis(phosphino enolato)nickel(II) complex, *cis*-[Ni[Ph_2PCH=C(O)Fe(η-C_5H_5)(CO)(PPh_3)]$_2$ (**41**). The crystal structure of (**41**) has been determined, revealing a distorted square-planar coordination about Ni, with *cis* coordination occurring via the P and O atoms (Ni-P = 2.175(3) and 2.167(2)*A*, Ni-O = 1.903(5) and 1.881(7)*A*). The coordination sphere about the two Fe atoms is essentially pseudo-octahedral [167].



[Fe] = FeCp(CO)(PPh_3)

(**41**)

7.3.10 Complexes with ***phosphorus*** *-sulfur donor ligands*

5,8 Diphenyl-5,8-diphospha-2,11-dithiadecane (L) has ben complexed with nickel(II) tetrafluoroborate yielding the complexes [Ni(*meso*(P)-L)$_2$](BF_4)$_2$ and [Ni(*rac*(P)-L)$_2$](BF_4)$_2$. The crystal structure of the latter complex has been determined, and is a racemate consisting of [Ni(*RR*(P)-L)$_2$]$^{2+}$ and [Ni(*SS*(P)-L)$_2$]$^{2+}$. The ligand functions as a P_4S pentacoordinate donor, with the coordination sphere about Ni found to be a slightly distorted square pyramid, with the four P atoms constituting the basal plane, and the S atom located at the apical position. Relevant crystallographic data are: Ni-S = 2.603(2)*A*, Ni-P = 2.214(2), 2.227(2), 2.228(2), and 2.233(2)*A* [168].

7.3.11 Complexes with halide or pseudo-halide ligands

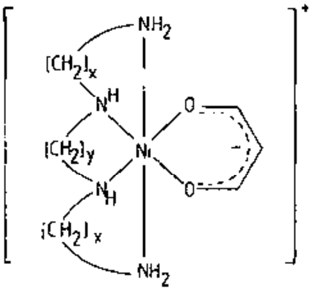
The crystal and molecular structure of bis(ethylenediamine)copper(II) tetracyanonickelate(II) has been reported. The structure was found to consist of tetracoordinate Ni(II) species alternating with axially distorted Cu(II) groups. Two of the CN ligands function in a monodentate fashion, while the other two fulfil a bridging role between the Cu and Ni complexes. Relevant data are: Ni-C = 1.850(4) and 1.864(4)Å [169].

Continuing with structural studies of the tetracyanonickelate(II) anion, the crystal structures of (18-crown-6)-(2-hydroxyethylammonium)tetracyanonickelate(II) and 10-aminodecylammonium tetracyanonickelate(II) have been determined. Square-planar coordination was found for both tetracyanonickelate(II) ions, which made them favourable to form hydrogen bonds *via* N with the hydroxyl group in (18-crown-6)-(2-hydroxyethylammonium)tetracyanonickelate(II), and *via* N with the amino group in 10-aminodecylammonium tetracyanonickelate(II) [170].

7.4 NICKEL(II) MACROCYCLE COMPLEXES

7.4.1 Macrocycles with nitrogen donor atoms

By way of introduction to this section, a study has been reported in which the mechanism of ring closure in the template synthesis of tetraaza macrocyclic complexes was examined. The study looked at the conditions necessary to optimise the synthesis of the non-condensed tetramine-diketonate complexes (**42**), and whether or not these noncyclic products could be used as precursors to the macrocyclic complexes. Precursor complexes that were prepared include [Ni(L)(acac)]X (L = N,N'-bis(2-aminopropyl)-1,3-propanediamine; N,N'-bis(2-aminopropyl)-1,3-ethanediamine, N,N'-bis(2-aminoethyl)-1,3-propanediamine; X = PF_6, I) [171].



(x =2,3; y =2,3)

(42)

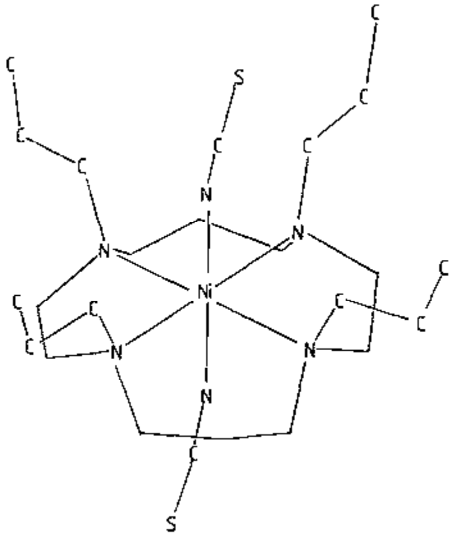
Molecular mechanics is increasingly being applied to the study of nickel(II) macrocyclic complexes. A systematic study aimed at extending the Allinger MM2 force field for use with N_4-macrocyclic complexes of low-spin Ni(II) has been undertaken. The study has incorporated the X-ray data for twenty low-spin Ni(II) complexes, and the extended force field has been applied to a re-examination of the configurational isomers of $[Ni(cyclam)]^{2+}$ and their N,N,N,N-tetramethylated derivatives [172]. In addition, a molecular mechanics study of the nickel(II) complexes of the hexidentate macrocycles *cis*- and *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine, has been reported. Interestingly, the study shows that the *trans* isomer exhibits a preference for small metal ions, while the *cis* isomer can coordinate a wider range of metal ions without significant intramolecular strain [173].

Turning to synthetic methods, a general synthetic route to prepare fully N-alkylated azamacrocycles has been reported. The synthesis involves two steps, as shown below.

$$R_2NH + R'COCl + Et_3N \Leftrightarrow R_2NCOR' + [Et_3NH]^+Cl^-$$

$$R_2NCOR' + BH_3/thf \rightarrow R_2NCH_2R'$$

where R_2NH represents a secondary amine or secondary amino group of an azamacrocycle. The generality of this method was shown by the synthesis of a number of alkylated cyclam ligands, which were prepared in good yield. In addition, the crystal structure of *trans*-(*R,S,R,S*)-$[NiL(NCS)_2]$ (L = 1,4,8,11-tetrapropyl-1,4,8,11-tetraazacyclotetradecane), prepared *via* this route, has been determined. Ni was found to be hexacoordinate, with the macrocycle adopting *trans*-(I) geometry (**43**) with the propyl groups located on the same side of the plane, rather than the more usual geometry for hexacoordination (Ni-N(L) = 2.170(4), 2.170(6), 2.183(5), 2.210(5)Å, Ni-N(NCS) = 2.137(5) and 2.017(4)Å) [174].

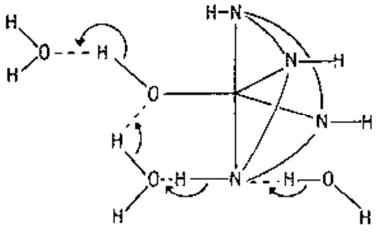


(43)

The kinetics of the colligation reaction between *R,R,S,S*-NiL^{2+} (L = 1,4,8,11-tetraazcyclotetradecane) with a variety of alkyl radicals (R = Me, Et, n-propyl, i-propyl, n-butyl, i-butyl) have been reported. The reaction, which occurs with the trans-III isomer of NiL^{2+}, yielded the species $RNiL(H_2O)^{2+}$. Rate constants were found to vary in the order Me > primary > secondary in aqueous perchloric acid at 25°C [175].

Continuing with coordination of axial ligands to square-planar 1,4,8,11-tetrazacyclotetradecanenickel(II) and its alkylated analogues, Kummamaru and co-workers have investigated the coordination of acetonitrile to 1,4,8,11-tetrazacyclotetradecanenickel(II) and (*1R,4R,8S,11S*)-tetramethyl-1,4,8,11-tetrazacyclotetradecanenickel(II) in nitrobenzene. Compared with dmf and dmso, acetonitrile was found to coordinate strongly to (*1R,4R,8S,11S*)-tetramethyl-1,4,8,11-tetrazacyclotetradecanenickel(II) [176]. The same group have examined the solvation and ionic association of (*1R,4S,8R,11S*)-tetramethyl-1,4,8,11-tetrazacyclotetradecanenickel(II) perchlorate in mixed solvents of dmf and N,N-dimethylacetamide (dma) with nitrobenzene and 1,2-dichloroethane. They concluded that the main site for ion pairing for $[NiL]^{2+}$ was the axial pocket surrounded by the four N-methyl groups. Dmf was found to solvate via coordination, whereas dma solvated without coordination [177]. Finally, as part of this on-going study, they have examined the reaction of 1,2-dichloroethane with pyridine using the (*1R,4S,8R,11S*)-tetramethyl-1,4,8,11-tetrazacyclotetradecanenickel(II) cation as a probe. The reaction is monitored by a change in the visible spectrum of the (*1R,4S,8R,11S*)-tetramethyl-1,4,8,11-tetrazacyclotetradecanenickel(II) cation, caused by axial ligation of the chloride ions [178].

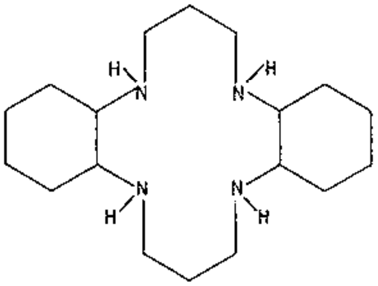
The base catalysed isomerisation of *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$ to planar $[Ni(cyclam)]^{2+}$ has been studied in the pH range 7-8, in an attempt to define the mechanism of the reaction. Results obtained in the study suggest that the conversion of *cis*-$[Ni(cyclam)(H_2O)_2]^{2+}$ to $[Ni(cyclam)]^{2+}$ occurs via an intermediate which involves coordinated hydroxide (**44**), and the conversion of the folded tet *b* ligand in the *trans*-V configuration to the planar *trans*-III configuration [179].



(44)

In a continuing study looking at macrocyclic ring size effects, a comparative study of the high- and low-spin complexes of Ni(II) with two tetraaza dibenzosubstituted macrocycles, has been carried out. Results obtained for the complexes $[NiL][BF_4]_2$ and $[NiL(NCS)_2]$ (L = 5,6,7,8,15,16,17,18-octahydro-7-methyl-9H,14H-dibenzo[b,i][1,4,8,11]tetraazacyclotetradecine, and 5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine) have also been compared with the analogous nickel(II) complexes of cyclam. The X-ray structures of $[NiL][BF_4]_2$ and $[NiL(NCS)_2]$ (L = 5,6,7,8,15,16,17,18-octahydro-7-methyl-9H,14H-dibenzo[b,i][1,4,8,11]tetraazacyclotetradecine), $[NiL][BF_4]_2$ (L = 5,6,7,8,9,10,15,16,17,18-decahydrodibenzo[e,m][1,4,8,11]tetraazacyclotetradecine), $[Ni(cyclam)]I_3$, as well as the free ligand, have been determined. These data together with molecular mechanics calculations have been used to assess the effects of spin state and ligand substituent on the hole size and ring conformations adopted by each complex [180].

The macrocycle dicyclohexylcyclam (**45**) has five feasible conformational isomers. Two of the five conformational isomers have been isolated *viz.* the *cis-anti-cis* form, and the *cis-syn-cis* form. The complexation behaviour of these two isomers towards Ni(II) was investigated by pH-titration. It was found that *cis-anti-cis* form was more stable than the *cis-syn-cis* form when complexed to Ni(II). In addition, the cyclohexyl groups increase the macrocyclic effect relative to cyclam for the *cis-anti-cis* form, but not for the *cis-syn-cis* form [181].

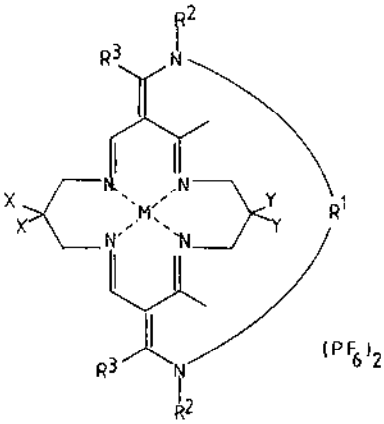


(45)

The crystal and molecular structure of *catena*-5,7,12,14-tetramethyl-5-*aci*-nitromethyl-1,4,8,11-tetraazacyclotetradec-11-enenickel(II) perchlorate dihydrate has been determined. Ni is found to be octahedrally coordinated with the macrocyclic N_4 ring occupying the equatorial plane. The two remaining apical coordination sites are occupied by *aci*-nitro groups, one belonging to the coordinated ligand, and one belonging to a neighbouring ligand molecule, with the result that a linear polymeric structure was obtained for the complex (Ni-N ranges from 2.029(4) to 2.089(5)Å, while Ni-O = 2.108(5) and 2.122(5)Å) [182].

2,4,4,10,12,12-hexamethyl-1,5,9,13-tetraazacyclohexadeca-1,9-diene (L) has been complexed with Ni(II), and the acid assisted dissociation kinetics of $[NiL]^{2+}$ studied in aqueous perchloric acid. Two possible pathways for the cleavage of each Ni-N bond were evaluated *viz.* the protonation pathway and the solvent dissociation pathway. It was concluded that the dissociation of the complex occurs *via* a dissociatively activated reaction [183].

Six new cyclidene ligands have been prepared and reported together with their nickel(II) complexes (**46**). The crystal structure of one of these complexes, (2,3,11,12,14,17,17,20,24,24-decamethyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.$1^{5,9}$]octacosa-1,5,7,9(28),12,14,19,21,26-nonaene-κ^4N)nickel(II) hexafluorophosphate, was determined, revealing an essentially square-planar coordination geometry for Ni(II) (Ni-N = 1.902(6), 1.864(8), 1.884(6) and 1.900(8)Å) [184].



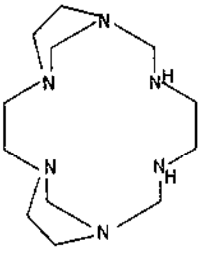
(X = Me, Y = H, $R^2 = R^3$ = Me; X = H, Y = Me, $R^2 = R^3$ = Me;
X = Me, Y = Me, $R^2 = R^3$ = Me; X = Me, Y = H, $R^2 = PhCH_2$, R^3 = Ph;
X = H, Y = Me, $R^2 = PhCH_2$, R^3 = Ph; X = Me, Y = Me, $R^2 = PhCH_2$, R^3 = Ph)

(**46**)

Turning to pentaaza macrocyclic complexes, the crystal and molecular structure of the low-spin complex (3-methyl-1,3,5,8,12-pentaazacyclotetradecane)-$\kappa^4N^1,N^5,N^8,N^{12}$)nickel(II) diperchlorate has been reported. The complex, which was synthesized via the template reaction of 3,7-diazanonane-1,9-diamine, formaldehyde and methylamine, in the presence of nickel(II) perchlorate, exhibits a regular square-planar coordination geometry, with only the four secondary amine nitrogen atoms of the azacyclam ligand bound to the metal. Relevant data are: Ni-N = 1.921(60, 1.933(6), 1.938(6), and 1.937(6)Å [185].

The macrocyclic ligands 1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, 15-ethyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione, and 15-benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione have been prepared and the stability constants of their Ni(II) complexes determined potentiometrically. The dioxygen affinities of the nickel(II) macrocycles have been measured, and these compounds were found to form 1:1 superoxo-type dioxygen adduct complexes. In addition, all three Ni(II) dioxygen complexes facilitated hydroxylation of the macrocyclic ligand at the electron-rich 15-carbon position, thereby providing some new examples of oxygen insertion via activation of the coordinated oxygen [186].

Square-planar Ni(II) complexes of the macrotricyclic ligands 1,3,6,8,11,14-hexaazatricyclo[12.2.1.1^{8,11}]octadecane (**47**) and 1,3,6,8,12,15-hexaazatricyclo[13.3.1.1^{8,12}]eicosane (**48**) have been prepared *via* the template condensation of formaldehyde and ethylenediamine with 2,2,2-tetramine and 3,2,3-tetramine respectively, in the presence of Ni(II). The crystal structures of both nickel(II) complexes, $[NiL](ClO_4)_2$ (L = (**47**); Ni-N = 1.913(4), 1.933(4), 1.920(4), 1.925(4)Å) and $[NiL](ClO_4)_2.1/2H_2O$ (L = (**48**); Ni-N = 1.939(2), 1.945(2), 1.952(2), 1.969(2)Å), have also been reported. The coordination geometry about Ni is distorted square-planar in both cases, with the level of distortion being slightly greater for the former complex. Coordination occurs via the four N atoms in a mode similar to the analogous cyclam complexes, and each six-membered chelate ring has an amino function at the bridgehead position [187].



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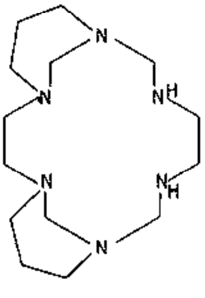
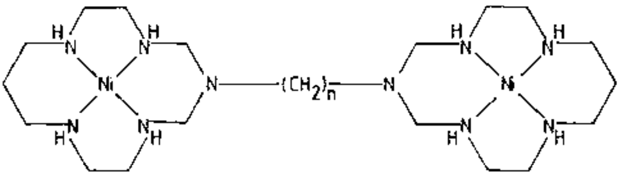


(48)

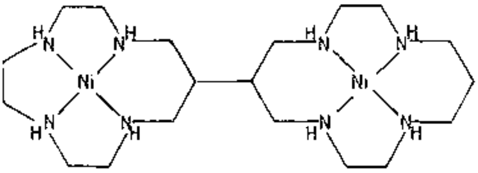
Continuing with tricyclic ligands, 1,5,8,12,15,19,22,26-octaazatricyclo[17.9.2.2^{5,15}]-dotriacontane has been prepared and complexed with Ni(II). The resultant dinuclear complex, $[Ni_2L](ClO_4)_4$, has been assigned a distorted square pyramidal coordination geometry on the basis of the crystal structure of its analogous Cu complex. Coordination was found to occur via four N atoms of the ligand, forming the base of the pyramid for each Ni atom, with the apical positions occupied by the chlorate ligands [188].

Bis(macrocyclic) complexes have received some attention recently. A new "one-pot" synthesis for the preparation of nickel(II) complexes with bis(pentaazamacrocyclic) ligands (**49**) has been reported. The synthesis involves the template condensation of $[Ni(2,3,2\text{-tetramine})]^{2+}$ with formaldehyde and the appropriate aliphatic diamine [189]. In addition, the new bimacrocyclic ligand, (1,4,7,10-tetraaza-12-cyclotridecyl)-1,4,8,11-tetraazacyclotetradecane (**50**), in which the 13- and 14-membered rings are linked together by a C-C bond, has been synthesized and complexed with nickel(II). The resultant dinuclear complex $[Ni_2L](ClO_4)_4$ (L = (**50**)) was found to exhibit the properties of both the 13- and 14-membered rings. Interestingly, it was shown that the complex could serve as an electrocatalyst for water reduction to produce H_2 [190].



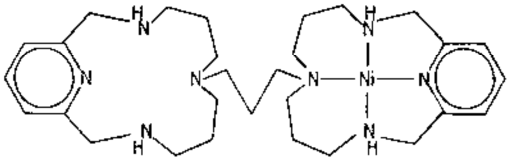
(n = 2, 3, 4)

(**49**)



(**50**)

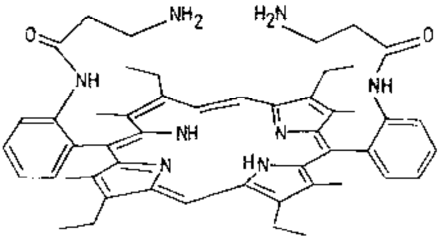
Of particular interest is the very novel electrochemical synthesis of the "lariat" mononuclear Ni(II) complex with a bimacrocyclic ligand. The complex was prepared from the heterobinuclear complex $[CuNiL](ClO_4)_4$ (L = 7,7'-trimethylenebis[3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene), by selective electrolytic reduction of the Cu(II) using a Hg pool. The resultant product $[NiL](ClO_4)_2$ was isolated and characterised as the mononuclear Ni(II) complex (**51**) [191].



(**51**)

Porphyrin and variously-substituted porphyrin complexes of nickel(II) have been examined using Resonance Raman and optical spectroscopy. Shelnutt and co-workers have investigated the relationships between structural parameters such as non-planarity, core size, and $C_\alpha NC_\alpha$, and the Raman frequencies of some planar and nonplanar Ni(II)porphyrin complexes. These include the complexes of octamethyltetraphenylporphyrin, octaethyltetraphenylporphyrin, octapropyltetraphenylporphyrin, tetracyclopentenyltetraphenylporphyrin, tetracyclohexenyltetraphenylporphyrin, tetracycloheptenyltetraphenylporphyrin, and dodecaphenylporphyrin. In addition, they have included the nickel(II) complexes of porphine, octaethylporphyrin and tetraphenylporphyrin for comparison. Existing molecular mechanics and X-ray structures of these complexes were used in the investigation, with the exception of the octapropyltetraphenylporphyrin complex, the crystal structure of which was determined [192].

The synthesis and characterisation of the new multi-chelating bis-alanyl-appended porphyrin ligand, *cis*-5,15-bis(*o*-[β-alanylamido]phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin (H_2L =(**52**)) has been reported. Complexation of (**52**) with nickel(II) acetate yielded the complex $[NiL].CHCl_3.CH_3OH$, the crystal and molecular structure of which has been determined. The coordination environment about Ni is essentially square-planar with Ni-N bond lengths ranging from 1.91(1) to 1.93(1)Å. The terminal amines are not coordinated, and it was shown that their chelating ability is maintained, making further metallation possible [193].



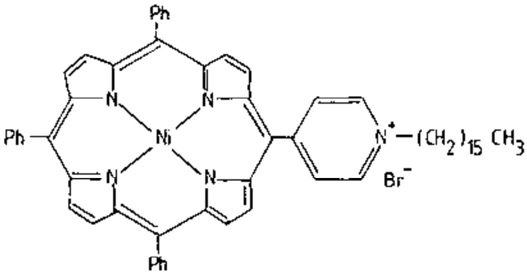
(52)

Similarly, the amido-appended porphyrin ligand, 5-(*o*-pivalamidophenyl)-10,15,20-(tritolyl)porphyrin (H_2L), has been complexed with nickel(II). The mechanism of a reversible two-electron oxidation reaction of this complex [NiL] was investigated using cyclic voltammetry and UV-vis-near-IR and Fourier transform IR thin layer spectroelectrochemistry. The reaction product was found to be an endogenous isoporphyrin resulting from the formation of an oxazine ring formed via condensation of a meso carbon of the porphyrin dication with the oxygen of the amide group [194].

The synthesis and spectroscopic characterisation of the pyridinium-appended porphyrin ligand, 5-(4-N-hexadecylpyridinuimyl)-10,15,20-triphenylporphyrin bromide $[H_2L]^+Br^-$, and its nickel complex $[NiL^+Br^-]$ (**53**), have been reported. The complex was shown to be monomeric in neat ethanol or dmf, but micelle formation was found to occur in mixtures of ethanol/water, or dmf/water [195].

Continuing with solution interface studies, the role of tetraphenylporphyrin and its nickel complex in the transfer of Fe^{3+} across the water/nitrobenzene interface has been investigated [196].

Optical absorption and Raman scattering have been used to compare the electronic and vibronic characteristics of metalloporphycenes with those of their analogous metalloporphyrins. In particular, the electronic and vibrational spectra of the nickel(II) complex of 2,7,12,17-tetrapropylporphycene were compared with those of the analogous nickel(II) complex of octaethylporphyrin [197].



(**53**)

Novel gas phase synthetic methods have been employed to prepare metalloporphyrin ions including NiP^+ and NiP^- (P = porphine) [198]. In addition, the gas phase charge-transfer reactions of the radical anions of the nickel(II) complexes of tetraphenylporphyrin and salicylethylenediimine have been described. It was found that facile electron transfer to an organic electrophile was characteristic of these anionic species and in fact in some cases reversible electron-transfer reactions were observed [199].

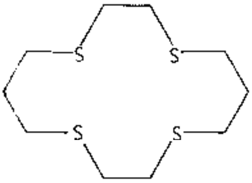
Tetra-*t*-butylphthalocyanine and its nickel(II) complex have been oxidised using $NOBF_4$, and dichloro-5,6-dicyano-*p*-benzoquinone. The ease of oxidation was compared with analogous Cu, Zn, and Co complexes. The ease of oxidation was found to follow the order Co(II) > Ni(II) = Cu(II) < Zn(II) [200].

In a continuing study of phthalocyanine and related compounds, the synthesis and properties of tetra- and octanitrophthalocyanine have been reported. The complexes were prepared by the reaction of 3-, 4-nitro-, or 3,5-dinitrophthalic acid with nickel(II) acetate in the presence of $(NH_4)_2MoO_3$. The effect of the nitro groups on the electronic spectra, basicity and the coordination of HX (X = Cl, Br) to the nickel atom was studied [201].

7.4.2 Macrocycles with sulfur donor ligands

The conformational and nickel(II) binding properties of 1,4,8,11-tetrathiocyclotetradecane (**54**), and its dimethyl derivatives bearing gem-dimethyl pairs at the 6-position (**55**), or at the 6- and 13-positions (**56**), have been compared. The synthesis and crystal structures of $[NiL](ClO_4)_2$ (L =

(55), **(56)**) have been determined and compared with the analogous complex of **(54)**. All three nickel complexes exhibit square-planar geometry with similar 14-membered ring conformations and bond lengths as follows: Ni-S = 2.178(1), 2.175(1)*A* (L =(**54**); Ni-S = 2.172(4), 2.179(4), 2.182(4), 2.179(4)*A* (L = (**55**)); Ni-S = 2.176(2), 2.184(2)*A* (L = (**56**)). The relative binding of each ligand to Ni(II) was determined in CD_3NO_2 using NMR. (**56**) was found to bind most strongly, followed by (**55**) and (**54**) respectively [202,203].



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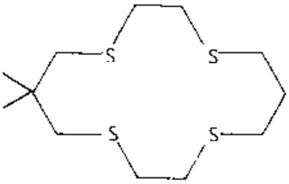

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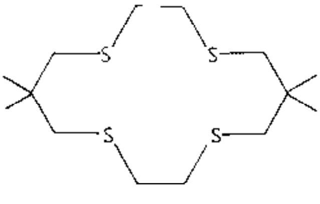
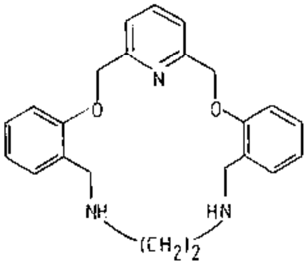


(56)

7.4.3 Macrocycles with nitrogen-oxygen donor ligands

The interaction of Ni(II) with the two macrocycles (**57**) and (**58**), which each contain a N_3O_2 donor group, has been investigated. Spectrophotometric studies in dmso revealed the formation of both 1:1 and 1:2 (metal:ligand) complexes. In addition, the X-ray crystal and molecular structures of the free macrocycle (**57**), the 1:1 complex $[Ni(L)I]I.CH_3OH$ (L = (**57**)), and the 1:2 complex $[NiL_2(NO_3)]NO_3.2CH_3OH$ (L = (**57**)) were reported. $[NiL(I)]I.CH_3OH$ was found to contain a distorted octahedral geometry, with three N atoms and two O atoms of the macrocycle coordinated to Ni(II), as well as one coordinated iodide ligand completing the coordination sphere (Ni-N = 1.994(15), 2.032(16), 2.124(17)Å; Ni-O = 2.114(15), 2.111(15)Å; Ni-I = 2.838(19)Å). Similarly, the structure of $[NiL_2(NO_3)]NO_3.2CH_3OH$ reveals hexacoordination for Ni(II), with two macrocycles coordinating via their aliphatic N atoms (exo coordination), and didentate coordination of a nitrate ion. Relevant data are: Ni-N = 2.140(19), 2.145(26)Å; Ni-O = 2.208(22)Å [204].



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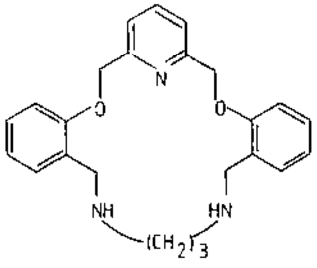
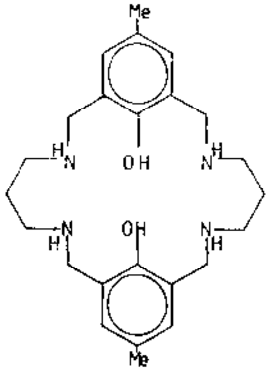


(58)

The crystal and molecular structure of 1,4,7-tris[(2*S*)-2-hydroxypropyl]1,4,7-triazacyclononanenickel(II) dibromide monohydrate has been reported. The coordination sphere about Ni was found to be octahedral with coordination occurring via the *fac*-N_3O_3 donor set of the macrocyclic ligand. Relevant data are: Ni-N = 2.059(6), 2.062(6), 2.065(6)Å; Ni-O = 2.083(5), 2.073(5), and 2.083(5)Å [205].

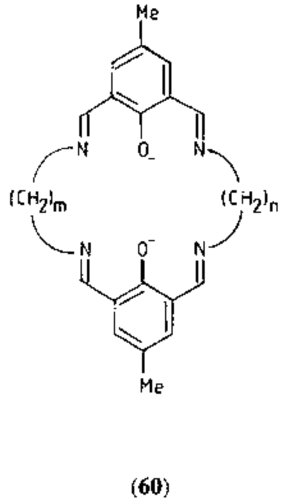
A number of dinuclear macrocyclic complexes have been synthesized. The novel complex $[Ni_2L(CH_3OH)(ClO_4)_2].2(C_2H_5)_3NH(ClO_4)$ has been prepared from the tetraamino-diphenolic ligand H_2L (**59**). The X-ray crystal and molecular structure of the complex revealed pseudooctahedral geometry for the two nickel(II) centres, which are coordinated to two secondary amine N atoms

(Ni-N = 2.064(3), 2.057(5)Å), and two bridging phenoxide O atoms (Ni-O = 2.028(4)Å), which complete the NiN_2O_2 plane. The remaining axial coordination sites are occupied by *trans* axially disposed methanol molecules (Ni-O = 2.105(5)Å) and perchlorate ions (Ni-O =2.411(5)Å) [206].



(59)

The complexes [N,N'-ethylene-1,3-diylbis(3-formyl-5-methylsalicylideneiminato)]-nickel(II) and [N,N'-propane-1,3-diylbis(3-formyl-5-methylsalicylideneiminato)]nickel(II) have been reacted with the diamines, en, propane-1,3-diamine, butane-1,4-diamine, or pentane-1,5-diamine in the presence of Pb(II). The resultant trinuclear macrocyclic complexes have the general formula $[Pb(NiL^{m,n})_2]X_2$, where H_2L = macrocycle formed by the condensation of two molecules of 2,6-diformyl-4-methylphenol and two diamines $H_2N(CH_2)_mNH_2$ and $H_2N(CH_2)_nNH_2$ (m =2 or 3; n=2 - 5) (**60**), and X = ClO_4, PF_6, BPh_4 or BF_4. Structural analysis indicates that the Ni(II) ion is bound at one of the N_2O_2 donor sites, and that Pb(II) is sandwiched by the vacant N_2O_2 sites of the two NiL entities [207].

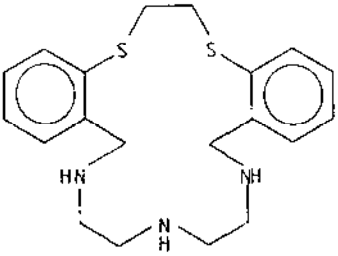


(**60**)

7.4.4 Macrocycles with nitrogen-sulfur donor ligands

Nickel template synthesis has been employed in the preparation of pentadentate and macrocyclic nitrogen-sulfur ligands. A pentadentate ligand complex (2,6-bis(((2-mercaptophenyl)thio)methyl)pyridinato)nickel(II) has been prepared by the reaction of $[Ni(bdt)_2]^-$ (bdt = benzenedithiolate) with 2,6-bis(chloromethyl)pyridine. The coordination sphere of the Ni ion consists of an aromatic amine N atom, two thioether S atoms, and two thiolate S donor atoms. A hexadentate macrocyclic ligand complex (1,10-diaza-4,7,13,16-tetrathia-5,6:14,15-dibenzocyclooctadecane)nickel(II)bis(tetraphenylborate), has been prepared by the reaction of $[Ni(bdt)_2]^-$ (bdt = benzenedithiolate) with bis(2-chloroethyl)amine. The coordination sphere of this complex, consists of a distorted octahedron in which coordination occurs *via* four thioether S donor atoms in the equatorial plane (Ni-S = 2.398(2) and 2.440(2)Å), with the axial positions occupied by the nitrogen atoms (Ni-N = 2.082(4)Å) [208].

The X-ray crystal and molecular structure of the Ni(II) complex containing the pentadentate 17-membered macrocycle 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dithiacycloheptadecane (L = (**61**)). The complex $[NiL(H_2O)](ClO_4)_2$ was found to display octahedral coordination, in which the macrocyclic ligand is meridionally coordinated. Coordination occurs via all five N_3S_2 donor atoms, with the water molecule occupying the remaining coordination site. Relevant data are: Ni-S = 2.396(5) and 2.428(5)Å; Ni-N = 2.070(13), 2.083(13) and 2.092(12)Å [209].



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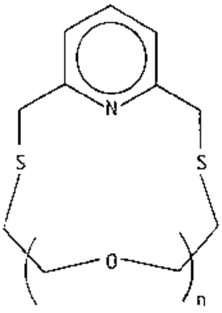
7.4.5 Macrocycles with nitrogen-oxygen-sulfur donor ligands

The pyridine based macrocycles containing N, O, and S donor atoms (**62**), have been synthesized and complexed with a variety of Ni(II) salts. Complexes that have been isolated include $NiLCl_2$ and $Ni(NCS)_2$. Spectroscopic data indicate that all of the complexes contain Ni in a distorted octahedral environment, verifying that the macrocycles coordinate as N,S,S,O donor ligands [210].



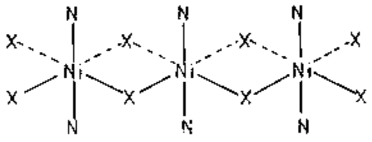
(n = 1, 2, 3)
(**62**)

7.5 NICKEL(II) POLYNUCLEAR COMPLEXES

Polynuclear complexes continue to attract considerable interest. Complexes ranging from dinuclear to polymeric, and homonuclear to heteronuclear, have been prepared. Bridging ligands and functional groups that have been utilised include halides and pseudo-halides such as azides and thiocyanates, alkoxides, Schiff base and related ligands, polyfunctional acids, azines, and phosphorous- and sulfur-containing ligands. For clarity we have divided the complexes into homonuclear and heteronuclear complexes and, wherever possible, into the nature of the bridging moiety.

7.5.1 Homonuclear complexes

Halides and pseudo-halides have been used to great effect in the synthesis of polynuclear complexes. The synthesis, spectroscopic and magnetic properties of the dinuclear complexes NiL_2X_2 (L = 5-methyl[1,2,4]triazolo[1,5-*a*]pyrimidin-7-ol; X = Cl, Br) have been described. On the basis of these data, the complexes were assigned a psuedo-octahedral polynuclear structure (**63**), in which the halide ions function as bridging groups [211].



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A series of chloride bridged complexes bis[[1,2,3-η^3-1-[(trialkylsilyl)oxy]-2-propenyl]-(μ-chloro)nickel(II)] has been prepared. The high yield synthesis gave yields ranging from 63 to 83%. In addition, the methyl analogue bis[[1,2,3-η^3-1-[(trimethylsilyl)oxy]-2-propenyl]-(μ-chloro)nickel(II)] has been characterised by single crystal X-ray crystallography [212].

The dinuclear complexes $[NiLX_2]_2$ (L = N-(6-methyl-2-pyridylmethylene)-2-(2-pyridyl)-ethylamine; X = N_2, NCS) have been synthesized. Spectroscopic and magnetic data suggest a bridged dinuclear structure with Ni centres being linked by azide bridges or end-to-end thiocyanate ligands. In addition, magnetic susceptibility measurements suggest the existence of ferromagnetic exchange interactions in the two complexes [213].

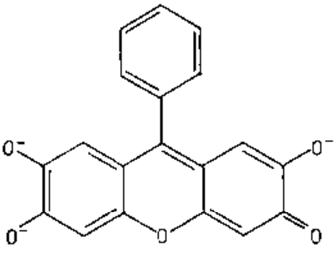
Two new dinuclear nickel(II) complexes, $[\{Ni(terpy)(NCX)_2\}_2]$ (X = S, Se), have been prepared from 2,2':6',2''-terpyridine. The crystal and molecular structure of $[\{Ni(terpy)(NCS)_2\}_2]$ was determined, revealing a dimer consisting of two Ni atoms coordinated to two terpy ligands, two terminal NCS ligands, and two end-to-end NCS bridging ligands. Each Ni atom was found to have a distorted octahedral coordination environment with Ni-N(terpy) = 2.08(1), 1.97(1), 2.09(1)Å; Ni-NCS(terminal) = 2.04(2)Å; Ni-NCS(bridging) = 1.99(2) and Ni-SCN(bridging) = 2.625(5)Å [214].

$[NiMe(OMe)(PMe_3)]_2$ has been used as starting material for the preparation of a range of mono- and dinuclear complexes that contain bridging linkages. The square-planar complexes *trans*-$NiMe(OR)(PMe_3)_2$ (R = 3-NO_2-C_6H_4, 4-NO_2-C_6H_4, 3-CHO-C_6H_4, C_6F_5, and 4-$C_6H_5N_2$-C_6H_4) were prepared by addition of the appropriate phenol to $[NiMe(OMe)(PMe_3)]_2$ in the presence of trimethylphosphine. In the absence of the phosphine, only the dinuclear phenoxide complex, $[NiMe(OC_6F_5)(PMe_3)]_2$, was isolated, while reaction with triphenylsilanol yielded the dinuclear complexes *cis/trans*-$[NiMe(OSiPh_3)(PMe_3)]_2$ or *cis*-$Ni_2Me_2(OMe)(OSiPh_3)(PMe_3)_2$ [215]. Reaction of

$[NiMe(OMe)(PMe_3)]_2$ with various carboxylic acids was also found to yield the dinuclear complexes $[NiMe(OOCR)(PMe_3)]_2$ (R = cyclohexyl, $CH(C_6H_5)_2$, $C(C_6H_5)_3$, 9-anthracenyl, bicyclo-[3.2.2]nonane-1-yl, C_6H_5, 2-NH_2-C_6H_4, 4-OH-C_6H_4, 1-naphthyl, 2-naphthyl, CF_3, CH_2Cl, $CHCl_2$, CH_2Br). In addition, the crystal and molecular structure of $[NiMe(OOCC_6H_5)(PMe_3)]_2$ has been determined. The molecule was found to contain two square-planar nickel centres, parallel to each other, with the following data: Ni-C = 1.907(7)*A*, Ni-P = 2.119(2)*A*, Ni-O = 1.955(5) and 1.919(6)*A* [216]. Finally, $[NiMe(OMe)(PMe_3)]_2$ has been reacted with 1,2-hydroxobenzene and a number of related dihydroxo ligands. Dinuclear complexes that were isolated include (O--O)$[NiMe(PMe_3)]_2$ (O--O = benzene-1,2-dioxo, benzene-1,2-dioxo-4-methyl, benzene-1,2-dioxo-3-methoxo), and (O--O)$Ni_2Me_2(PMe_3)_3$ (O--O = benzene-1,2-dioxo, benzene-1,2-dioxo-4-methyl, benzene-1,2-dioxo-3-methoxo, naphthaline-2,3-dioxo). In addition, the crystal and molecular structure of (benzene-1,2-dioxo-3-methoxo)$Ni_2Me_2(PMe_3)_3$ was determined. The molecule was found to contain two square-planar nickel centres, perpendicular to each other, with the following data: Ni-C = 1.920(7)*A*, Ni-P = 2.104(2)*A*, Ni-O = 1.919(5) and 1.900(4)*A* [217].

3,4-dihydroxyphenylpropionic acid (H_2L) has been complexed with nickel(II). The resultant dinuclear complex $K_2[NiL_2Cl_2]$ was characterised using spectroscopic and magnetic methods. These data indicate a tetrahedral coordination sphere for each Ni atom, with catechol-like coordination by the 3,4-dihydroxyphenylpropionic acid ligand [218].

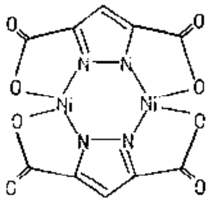
The dinuclear complex $Ni_2(CTH)_2(PTHF)ClO_4$ (CTH = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, H_3PTHF = 9-phenyl-2,3,7-trihydroxy-6-fluorone (**64**)), as well as its one electron oxidation product $Ni_2(CTH)_2(PTHF)(ClO_4)_2$, have been synthesized. Octahedral coordination geometry has been assigned to each of the Ni atoms, which are bridged by the tetraoxalene radical $PTHF^{3-}$, with the two macrocycles in a folded configuration occupying the remaining octahedral coordination sites [219].



(64)

Complexes of Ni(II) with the potentially polydentate ligand tetrazolyl-1-acethydrazide (L) have been prepared and characterised using IR spectroscopy. The complexes have the general formula $[NiL_2](ClO_4)_2$ and $[NiL_3](ClO_4)_2$. Spectral data indicate that L functions both as a didentate and tridentate ligand. On the basis of a comparison with its Cu analogue, the structure of $[NiL_2](ClO_4)_2$ was assumed to be a polymeric chain with the ligand coordinating to one Ni atom via the N and O atoms of the acethydrazide function, and to an adjacent Ni atom via the N atom of the tetrazol function [220].

The dinuclear complex cation $[Ni_2L_2]^{2-}$ (H_3L = 3,5-pyrazoledicarboxylic acid) has been prepared and isolated as its tetrabutylammonium salt. Comparison with its Cu and Pd analogues suggests that the complex is essentially planar, with the two N atoms of the pyrazole ring functioning as the bridging groups (**65**) [221].



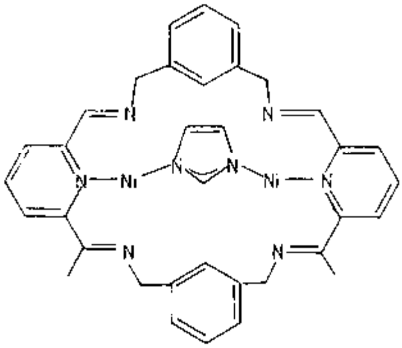
(**65**)

Schiff base and related ligands have been employed in the synthesis of multinuclear Ni complexes. The polySchiff base ligand H_2L, derived from 4,4'-dihydroxy-3,3'-diacetylbiphenyl and 1,3-propanediamine, complexes with Ni(II), forming solid polychelates of the type $[NiL.nH_2O]_x$. The structural, thermal and electrical properties of this polychelate were investigated [222].

New mono- and dinuclear nickel(II) complexes have been prepared by a nucleophilic substitution reaction of the C-H methine-containing complex, mono-pyridine-S-methyl-N-acetylacetonehydrazine-carbodithioate nickel(II), with benzoyl chloride and phthaloyl dichloride respectively. The mono- and dinuclear nickel(II) complexes were found to display magnetic and spectroscopic behaviour characteristic of square-planar coordination. The Schiff base ligands were found to function as S,N,O donor ligands, with py completing the coordination sphere for each Ni atom [223].

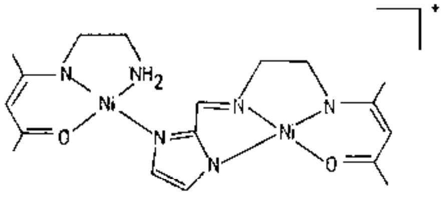
1-(3-hydroxy-2-naphthoyl)-4-phenyl-3-thiosemicarbazide (H_2L) coordinates with nickel(II) yielding the complexes [$NiL(H_2O)_2$] and [NiL]H_2O. In [$NiL(H_2O)_2$], H_2L behaves as a binegative bridging tetradentate ligand with coordination occurring via the phenolic O atom and the N atom of the NH group from one end, and the S atom and N atom from the NH group on the other, with loss of both protons. Two water molecules complete the octahedral coordination sphere for each Ni atom. In [NiL]H_2O, H_2L once again is found to behave as a binegative bridging ligand, but now functions in a tridentate fashion coordinating via the phenolic O atom, the NH nitrogen, and the CS sulfur atom in the enol form. The S atom functions as the bridging moiety, completing the square-planar geometry proposed for this complex [224].

Continuing with Schiff base bridging ligands, reaction of 2,6-diacetylpyridine and *m*-xylylenediamine in the presence of Ni(II) and imidazole has been shown to yield the imidazole bridging dinuclear complex (**66**). Substitution of imidazolate by acetate yielded the analogous dinuclear complex, but with acetate as the bridging moiety. Square-planar geometry was assigned to each of the nickel atoms on the basis of its Cu analogue, the crystal structure of which has been determined [225].



(**66**)

The synthesis of (4(5)-methylimidazole)(7-amino-4-methyl-5-aza-3-hepten-2-onato-nickel(II) perchlorate has been reported and its crystal and molecular structure determined. The related dinuclear complex (μ-5-methylimidazolato)bis(7-amino-4-methyl-5-aza-3-hepten-2-onato-dinickel(II) perchlorate has also been isolated and its crystal and molecular structure reported. In both mononuclear and dinuclear complexes, the Ni centre was found to display essentially square-planar geometry with some tetrahedral distortion, coordination involving the N,N,O donor atoms from the 7-amino-4-methyl-5-aza-3-hepten-2-onato ligand, and an N atom from the imidazole ligand. The imidazole ligand functions as the bridging moiety in the dinuclear complex (**67**) [226].



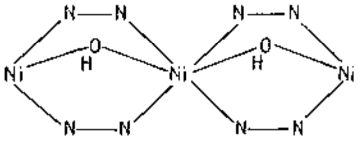
(67)

N,N',N'',N'''-Tetramethylsulfonyl-1,4-benzoquinonediimine-2,5-diamine (H_4L) has been prepared by the reaction of 1,2,4,5-tetraaminobenzene and methylsulfonyl chloride, and complexed with Ni(II) acetate in pyridine. The resultant complexes have been assigned the molecular formulae $[Ni_2(py)_4(\mu\text{-}L)]$, and $[Ni_2(py)_4(\mu\text{-}L)]^{2+}$. The ligand functions as a tetradentate tetrabasic ligand in the former complex, and as a tetradentate dibasic ligand in the complex cation [227].

The dicyanomethanide-bridged anionic Ni(II) complex, $[\{Ni(C_5H_5)_2(\mu\text{-}NCCHCN)\}_2]^{2-}$, has been prepared and isolated as its tetrabutylammonium salt. The X-ray crystal structure of the complex reveals a distorted square-planar environment for both the Ni atoms, which are coordinated to the N atoms of the bridging $[CH(CN)_2]^-$ ligands. Relevant data are: Ni-C = 1.88(1) and 1.90(1)Å; Ni-N = 1.87(1) and 1.98(1)Å [228].

Three different dinuclear nickel(II) complexes were prepared using the acyclic polyamine ligand 5,5-bis(4'-amino-2'-azabutyl-3,7-diazanonane-1,9-diamine) (L). The complexes $[Ni_2L](ClO_4)_4$, $[(NiCl_2)_2L].2H_2O$ and $[NiCl(OH_2)L](ClO_4)_3.H_2O$, have been characterised by their crystal and molecular structures. $[Ni_2L](ClO_4)_4$ was found to exhibit square-planar geometry for both the Ni atoms, with Ni-N bond lengths varying from 1.914(11) to 1.939(8)Å. The nickel coordination sphere was found to be octahedral for both Ni atoms in the neutral complex $[(NiCl_2)_2L].2H_2O$. The Ni atoms and N atoms of the ligand are co-planar, while the Cl ligands occupy *trans* axial coordination sites. Ni-N distances are longer than in the previous complex, ranging from 2.079(4) to 2.097(5)Å, while Ni-Cl distances range from 2.494(2) to 2.519(2)Å. The third complex, $[NiCl(OH_2)L](ClO_4)_3.H_2O$, is unusual, as it is found to contain two Ni centres with different coordination geometry. One Ni atom exists in a square-planar coordination environment, coordinated to the four N atoms of the ligand (Ni-N ranges from 1.907(10) to 1.945(8)Å), while the other Ni atom is octahedrally bound, coordinating to the four N atoms of the ligand in the plane, with Cl and OH ligands occupying the remaining coordination sites in a *trans* axial fashion (Ni-N ranges from 2.074(7) to 2.094(8)Å; Ni-Cl = 2.556(3)Å; Ni-OH = 2.202(9)Å) [229].

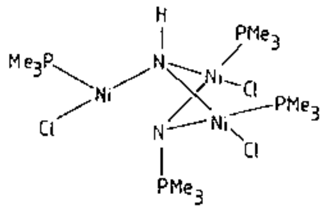
The synthesis, crystal and molecular structure, and magnetic properties of $[Ni_3L_4(NCS)_4(OH)_2(H_2O)_2]$ (L = 2,5-diamino1,3,4-thiadiazole) have been reported. The structure was found to consist of centrosymmetric trimeric discrete molecules, in which the Ni(II) atoms are coordinated in a slightly distorted octahedral geometry by two N atoms of the thiadiazole ligands, two N atoms of the thiocyanate groups, and by two O atoms (**68**). The central Ni atom is linked to the terminal Ni atoms via two planar thiadiazole ligands, and one bridging OH molecule. Relevant data are: Ni-N(thiadiazole) ranges from 2.080(5) to 2.138(5)Å; Ni-NCS = 2.064(6)Å; Ni-OH = 1.997(4) and 2.047(4)Å; Ni-OH_2 = 2.153(5)Å [230].



(68)

The related trimeric complex $[NiLNi(H_2O)_2LNi](ClO_4)_2$, and its heteronuclear Cu analogue $[CuLNi(H_2O)_2LCu](ClO_4)_2$ have also been prepared by the same group. In both complexes, the central Ni^{2+} is octahedrally coordinated by two pairs of oxamidate O atoms, with two water molecules occupying *cis* positions, making up the coordination sphere. The two terminal Ni(II) ions are four coordinate, with four oxamidate N donor atoms, of which two are negatively charged, constituting the coordination sphere. The same discussion applies to the Cu analogue [231].

Photochemical activation of $(PMe_3)_2ClNi(N_3)$ has resulted in the formation of the new trimetallic and tetrametallic diamagnetic nickel clusters (**69**) and (**70**) with phosphorane-imido and imido ligands in capping positions. The crystal structure of (**69**) revealed a planar triangle of Ni atoms which are diamagnetic. The average bond lengths are Ni-N 1.953Å, Ni-Cl = 2.223Å, and Ni-P = 2.161Å [232].



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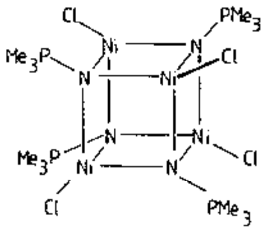


(70)

The complex NiL (H_2L = N,N'-bis(3'-pyridazinecarboxamide)-1,3-propane) has the potential to coordinate to metals *via* the uncoordinated pyridazine N atoms. Reaction of NiL with nickel(II) chloride (2:1) yielded the trinuclear complex $[NiL]_2NiCl_2$. This complex was found to exhibit magnetic properties which are consistent with two diamagnetic metal centres and one paramagnetic metal centre [233].

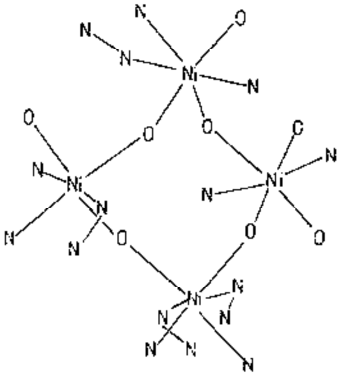
A structurally related Ni trimer, $[Ni_3L_4Cl_2]$ (HL = bis(2-pyridyl)amide), has been prepared and characterised. The crystal and molecular structure revealed a nearly linear Ni_3 unit, in which L functions as a tridentate N_3 donor ligand. The central Ni atom was found to be tetracoordinate involving the four N atoms of L, while the outer Ni atoms were found to be pentacoordinate involving four N atoms of L as well as a fifth chloride ligand, in a square pyramidal conformation. Ni-N distances range from 1.892(7) to 2.443(4)Å, with Ni-Cl = 2.340(2) and 2.331(2)Å respectively [234].

Poly(2-acrylamido-1,2-diaminobenzene) homopolymer has been reacted with a variety of nickel(II) salts. Reaction with nickel(II) chloride yielded complexes in which the polymer functions in a neutral fashion. Spectral and magnetic data indicate that the coordination environment about the Ni atoms is octahedral, with the Cl ligands bound in a *trans* axial manner. However, reaction with nickel(II) acetate yielded complexes which are diamagnetic, indicating a square-planar configuration about Ni in these complexes. In this case, the polymer functions in a uninegative fashion, bonding via two N atoms, while the acetate group functions as a didentate ligand [235].

The preparation of the bis(ethylenediamine)nickel(II) complex of permethylpolyazine has been reported. The synthesis employed was found to produce a polymer with alternate diimine sites complexed to Ni(II). IR spectra of the monomer and polymer indicate that during complexation, the metal has changed the polymer geometry from all-*trans* to a mixture of *cis* and *trans* bonds. Octahedral coordination has been assigned to the metal complexes, with two en ligands coordinated as well as the azine polymer which functions in a didentate fashion for each Ni atom [236].

Dithiooxamide has been copolymerised with 1,4-diaminobutane, and the copolymer has been complexed with nickel(II) acetate and chloride respectively. The complexes, which exhibit a partially aromatized coordination structure, were characterised using a variety of analytical techniques [237].

Reaction of nickel(II) perchlorate with the ligand 7-[(3,5-dichloro-2-pyridyl)azo]-8-hydroxyquinoline-5-sulfonic acid (HL), yielded the most unusual complex $[Ni_4L_4(H_2O)_4].20H_2O$. Single crystal X-ray analysis revealed that this complex contains four Ni(II) atoms and four ligand molecules with a novel oxygen bridged configuration (**71**). The geometry about each of the Ni atoms approximated distorted octahedral, with the ligands exhibiting N,N,O or N,O chelate coordination. The remaining coordination sites are occupied by water molecules [238,239].



(71)

Turning to S and Se bridging ligands, the reaction between Ni^{2+} and 1,2-bis(diphenylphosphino)ethane and NaSH or NaSeH afforded the trinuclear clusters $[Ni_3S_2(dppe)_3](BPh_4)_2.MeCN$ and $[Ni_3Se_2(dppe)_3](BPh_4)_2.MeCN$. The X-ray crystal structures of $[Ni_3S_2(dppe)_3](PF_6)_2.MeCN$ and $[Ni_3Se_2(dppe)_3](BPh_4)_2.MeCN$ were determined revealing three square-planar NiX_2P_2 (X = S, Se) coordination planes sharing two μ_3-X ligands. Relevant data are: $[Ni_3S_2(dppe)_3](PF_6)_2.MeCN$; Ni-P = 2.158(4), 2.173(4) and 2.196(4)Å, Ni-S = 2.195(4) and 2.190(3)Å; $[Ni_3Se_2(dppe)_3](BPh_4)_2.MeCN$; Ni-P = ranges from 2.172(8) to 2.195(8)Å, Ni-Se ranges from 2.318(4) to 2.300(4)Å [240].

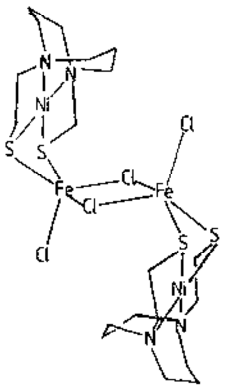
Dimeric 4-phenyl-1,2,3,5-dithiadiazole, $(PhCN_2S_2)_2$, has been reacted with $[\{Ni(Cp)(CO)\}_2]$, yielding the dinuclear complex $[Ni_2(Cp)_2(PhCN_2S_2)]$. The crystal structure of this complex revealed a Ni_2S_2 tetrahedral core in which $(PhCN_2S_2)_2$ functions as the bridging moiety. Indications are that a Ni--Ni interaction exists indicating formally 19-electron nickel centres [241].

Phosphorus-containing ligands have also been employed as bridging moieties. 1,2,4,5-tetrakis(dimethylphosphino)benzene (L) has been prepared and reacted with nickel(II) chloride, yielding a complex of formula $[NiClL]_n$ (n = 20-30). In addition, reaction of the related complex $NiL'Cl_2$ (L'= 1,2-bis(methylphosphino)benzene) with L afforded the mixed-ligand dinuclear complex $[L'NiCl(\mu\text{-}L)NiClL']Cl_2$ [242].

7.5.2 Heteronuclear complexes

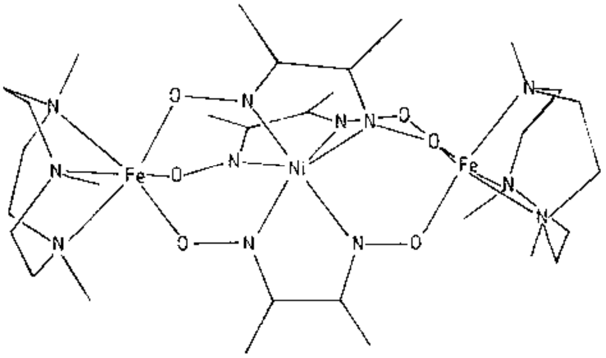
3-Hydroxysalicylaldehyde has been converted into a series of 3-alkoxy-N-methylsalicylaldemine derivatives (alkyl = CH_3, $CH_2CH_2OCH_3$, $CH_2CH_2OCH_2CH_2OCH_3$) (HL), and complexed with Ni(II), yielding complexes of the type NiL_2. Complexes with the alkoxy side arms were found to bind Na^+ and Ni^{2+}, and evidence indicates a "crown-like" cage structure, which the authors suggest may be fairly common [243].

A number of complexes containing Ni and Fe have been prepared. N,N'-bis(mercaptoethyl)-1,5-diazacyclooctane has been used in the preparation of the bimetallic complex $[LNiFeCl_2]_2$ (L = N,N'-bis(mercaptoethyl)-1,5-diazacyclooctane). The crystal structure of this complex revealed a Ni_2Fe_2 core (**72**) which contains two square-planar Ni atoms and two Fe atoms in a square-based pyramidal configuration. Relevant data are: Ni-N = 1.974(8) and 1.966(9)Å, Ni-S = 2.172(3) and 2.165(3)Å, Fe-S = 2.552(3) and 2.462(3)Å, Fe-Cl = 2.286(30, 2.422(3) and 2.547(3)Å [244].



(72)

The trimetallic complex, $[L_2Fe_2Ni(dmg)_3](PF_6)_2.0.5CH_3OH$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane, H_2dmg = dimethylglyoxime) has been synthesized and its structure determined using X-ray methods. The crystal structure showed that $Ni(dmg)_3$ functions as a bridging moiety with two O atoms from each dmg complexing to an adjacent Fe atom (**73**). The high spin Fe centres exhibit hexacoordinate N_3O_3 coordination (Fe-O varies from 1.927(12) to 1.953(8)$\mathring{A}$, Fe-N varies from 2.231(16) to 2.261(12)$\mathring{A}$), while the Ni centre is N_6 hexacoordinate (Ni-N varying from 2.023(17) to 2.050(17)$\mathring{A}$) [245].



(**73**)

Turning to Co,Ni bimetallics, the kinetics and mechanism of complex formation between (oxalato)pentaamminecobalt(III) and Ni(II) have been investigated in aqueous medium. It was postulated that the partially coordinated oxalate ligand functions as the bridging moiety [246]. Similarly, the kinetics of the analogous reaction between histidinatopentaamminecobalt(III) and Ni(II) have been determined in aqueous medium. In this case, the formation of the dinuclear species was found to occur *via* proton-independent and proton-dependent paths, the latter arising out of the protonation equilibrium of the pendant amine function of the histidine moiety bound to Co(III) *via* the carboxylate group. Chelation of Ni(II) was found to occur via the tertiary N and primary amine group of the histidine bridging ligand [247].

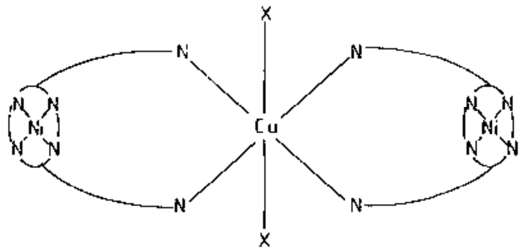
The multimetallic complexes, $M^1M(M'EDTA)_2.4H_2O$ (M^1,M,M' = Ni(II), Co(II), Zn(II)), have been prepared and their magnetic properties examined in the very low temperature range. The structures of these compounds are regarded formally as ordered bimetallic layers of alternating chelated and hydrated octahedral sites M and M', with tetrahedral sites M^1 connecting the different MM' layers [248].

A variety of bimetallic complexes containing Ni and Cu have been reported. Ligand migration, leading to irreversible thermochromism, has been observed in the complex $[Ni(phen)_3][CuCl_4]$ using TGA, EPR, UV-visible and IR spectroscopic methods [249].

The tetranuclear copper(I) complexes $[CuLCl]_4Y_2$ (L = monodentate N,N-diethylnicotinamide; Y = 3,4,5,6-tetrachlorocatecholate) and $L_4Cu_4(OH)_2Cl_4Y\,3H_2O$ have been reacted with $Ni(NS)_2$ (NS = monoanionic S-methyl isopropylidenehydrazinecarbodithioate). The resultant tetranuclear mixed metal complexes have been isolated as the copper-nickel homologues $N_4Cu_{4-x}Ni_x(OH)_2Cl_4Y\,3H_2O$ (x = 1 - 4) [250].

Seven new heterodinuclear Ni(II)-Cu(II) complexes have been synthesized from the planar monomer fragments Cu(oxpn) (oxpn = N,N'-bis(3-aminopropyl)oxamido) or $Cu(Me_2oxpn)_2$ (Me_2oxpn = N,N'-bis(2,2'dimethyl-3-aminopropyl)oxamido). The complexes have the general formula $[CuLNi(cyclam)](ClO_4)_2$ (L = oxpn or Me_2oxpn) or $[CuLNi(L')_2]$ (L' = bipy, phen). Magnetic measurements between 4K and ambient temperature were carried out and it has been shown that a strong antiferromagnetic coupling exists in all cases [251].

Linear trinuclear complexes have been prepared using the potentially binucleating ligand *cis*-5,15-bis[o-(β-alanylamido)phenyl]-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, $[H_2(DPE)](NH_2)_2$. The porphyrin core of the ligand was coordinated to nickel yielding the complex $[Ni(DPE)](NH_2)_2$, which was then further coordinated to a variety of nickel(II) salts. Complexation with Zn(II) perchlorate yielded the complex $[\{[Ni(DPE)](NH_2)_2\}_2Zn](ClO_4)_2$, while complexation with Cu(II) chloride or thiocyanate yielded the complexes $[\{[Ni(DPE)](NH_2)_2\}_2CuX_2]$ (X = Cl, NCS) (**74**) [252].



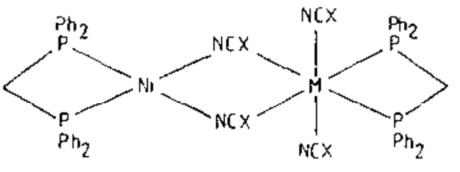
(X = Cl, NCS)

(**74**)

The crystal and molecular structure of poly[nickel(II)-μ-(cyano-C:N)-{(ethylenediamine-N,N')zinc}-tri-μ-cyano(N,C)] has been reported. The structure is composed of an infinite three-dimensional network of Zn and Ni atoms linked by bridging cyano groups. The Ni geometry was found to be square-planar, with coordination to four bridging cyano groups (Ni-C = 1.879(5) and 1.870(5)Å), while the coordination geometry of the Zn atom was found to be extended tetragonal bipyramidal, with coordination to two N atoms from the en ligand (Zn-N = 2.142(5)Å) and two N atoms from bridging cyano groups (Zn-N = 2.160(5)Å) in the equatorial plane. The remaining axial positions are occupied by two N atoms from bridging cyano groups at longer distances (Zn-N = 2.271(5)Å) [253].

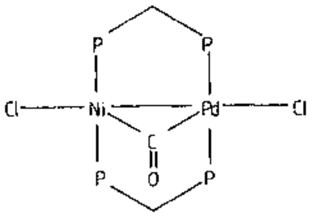
The nickel(II) complexes, $NiX_2(RNC)_2$ (X = Cl, Br, I; R = 2,6-$Me_2C_6H_3$, 4-Br-2,6-$Me_2C_6H_2$, 2,4-*t*-Bu-6-$Me_2C_6H_2$, 2,4,6-*t*-Bu-6-$Me_2C_6H_2$), have been reacted with RNC or PPh_3, yielding complexes of the type $NiX_2(RNC)_3$ or $NiI_2(PPh_3)(RNC)_2$ respectively. The crystal structure of $NiI_2(2,6\text{-}Me_2C_6H_3NC)_3$ was determined revealing a trigonal bipyramidal structure for this complex, a structure not revealed by the chloro and bromo analogues. Reaction of the complexes $NiX_2(RNC)_2$ with Hg in the presence of isocyanide gave the mixed-metal donor complexes $[Ni(RNC)_4HgX_2]_2$ (X = Cl, Br, I). An X-ray analysis of $[Ni(4\text{-}Br\text{-}2,6\text{-}Me_2C_6H_2RNC)_4HgI_2]_2$ revealed a donor-acceptor complex containing a Ni-Hg bond as well as bridging I atoms. The coordination sphere about Ni was found to be trigonal bipyramidal, while the Hg atom displayed distorted tetrahedral coordination [254].

Bimetallic complexes of the type $[NiM(XCN)_4(dppm)_2]$ (M = Cd(II), Hg(II); X = S, Se; dppm = 1,1-bis(diphenylphosphino)methane) have been synthesized and characterised using a variety of analytical techniques. On the basis of spectral and magnetic data, the complexes have been assigned the dimeric structure (**75**), in which both monodentate and bridging thiocyanate groups are present [255].



(**75**)

The synthesis, characterisation, and reactivity of the heterodinuclear complex [NiPd(μ-dppm)$_2$(μ-CO)Cl$_2$] have been reported. On the basis of spectral data, the complex was assigned the structure (**76**), in which both dppm ligands as well as the CO ligand function as bridging groups [256].



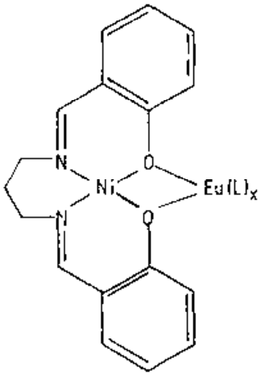
(76)

Ligand migration, leading to irreversible thermochromism, has been observed in the complexes [Ni(L)$_3$][PdCl$_4$].nH$_2$O (L = 1,10-phenanthroline, 4,7-diphenyl-1,10-phenanthroline) using TGA, EPR, UV-visible and IR spectroscopic methods. The thermal stability and non-isothermal decomposition kinetics of these complexes have also been determined [257].

The high yield synthesis of the novel cubane-type mixed-metal cluster cation [Mo$_3$NiS$_4$(H$_2$O)$_{10}$]$^{4+}$ has been reported. Reaction of the incomplete cubane-type aqua ion [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ with nickel metal results in the formation of this complex, which has been further converted to [Mo$_3$NiS$_4$(Hnta)(nta)$_2$Cl]$^{5-}$ (H$_3$nta = nitrilotriacetic acid). Crystal structures have been determined for the complex cations [Mo$_3$NiS$_4$(H$_2$O)$_{10}$]$^{4+}$, isolated as its paratoluenesulfonate salt, and [Mo$_3$NiS$_4$(Hnta)(nta)$_2$Cl]$^{5-}$, isolated as its calcium salt [258]. In addition, the reaction of [Mo$_3$NiS$_4$(H$_2$O)$_{10}$]$^{4+}$ with Cu^{2+} has also been reported. Displacement of the Ni^{2+} ion was found to occur yielding the complex cation [Mo$_3$CuS$_4$(H$_2$O)$_{10}$]$^{4+}$ [259].

A comparative study of the thiomolybdate and the thiotungstate complexes [Ni(MS$_4$)$_2$]$^{2-}$ (M = Mo, W) has been undertaken. The electronic structures and bonding properties of these complexes were investigated, and transition and ionization energies were evaluated [260].

The nickel(II) complex of N,N'-disalicylidene-1,3-propanediamine has been shown to exhibit significant fluorescence quenching of Eu(III). This effect, which was not observed when a simple nickel(II) salt was used, is attributed to the formation of the mixed Ni-Eu complex **(77)**, in which the O atoms of the ligand function as the bridging moieties [261].



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7.6 *NICKEL(II) COMPLEXES WITH BIOLOGICAL LIGANDS*

A significant number of ligands with biological implications have been complexed with Ni(II). These include amino acids, amino acid derivatives, including peptides, proteins and enzymes, nucleic acid bases, and carbohydrates.

A range of amino acids and amino acid derivatives have been complexed with Ni(II). The structure of pentaaqua(glycine)nickel(II) sulfate monohydrate has been reported. Coordination about Ni was found to be distorted octahedral, with bonds to one glycine O atom (Ni-O = 2.068(2) Å) and five water molecules (Ni-O ranges from 2.047(2) to 2.056(2)Å). It was suggested that this may be the first case of monodentate oxygen coordination by the glycine zwitterion [262]. In addition, the heats of formation of nickel(II) ternary complexes containing glycine and oxalic acid ligands have been determined [263].

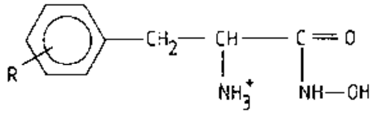
The mixed complex Ni(gly)(β-ala).$2H_2O$ (Hgly = glycine, Hβ-ala = β-alanine) has been observed on the crystal face of the complex Ni(β-ala)$_2$.$2H_2O$, when the latter complex is crystallised in the presence of glycine [264].

In a study of the coordination behaviour of N-protected aminoacids, the complexing properties of N-(4-aminobenzoyl)glycine (HL) with Ni(II) have been investigated. Based on the crystal structure of the analogous Co complex, the nickel complex $[\{NiL_2(H_2O)_2\}_n]$ was found to exist as a polymeric one dimensional chain in which the ligand functions in a bridging didentate fashion. The coordination geometry about Ni is essentially distorted tetragonal-octahedral, with two water molecules and two carboxylate O atoms coordinating in the basal plane, and two amino N atoms occupying the apical coordination sites [265].

In a continuing study, N,N-bis(2-hydroxyethyl)glycine, a "Good's" buffer, has been complexed with Ni(II) in aqueous solution. The stability constants of the 1:1 and 2:1 complexes were determined and were found to be very similar to those obtained for glycine. From these data it was concluded that alcohol group coordination was occurring [266].

Ternary complexes of metal(II) ions with aliphatic amino acids (alanine, α-aminobutyric acid, norvaline, norleucine) and purine nucleosides (inosine and xanthosine) have been studied in aqueous solution. Potentiometric pH measurements have been made and the stability constants and species distributions determined [267].

Similarly, the complexation of Ni(II) with the hydroxamic acid derivatives of phenylalanine, tyrosine and 3,4-dihydroxyphenylalanine (**78**) has been investigated in aqueous solution using pH-metric, spectrophotometric and e.s.r. methods. The formation constants and binding modes have been reported, as well as the effect of the phenyl and hydroxyl groups on complex formation [268].



(R = H, 4-OH, 3,4-$(OH)_2$)

(78)

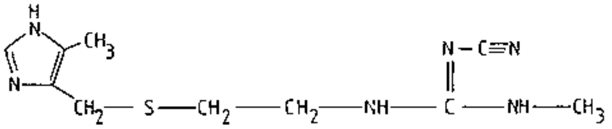
The stability constants of the binary complexes of nickel(II) with L-proline, L-valine, α-aminoisobutyric acid, and oxalic acid have been determined in aqueous solution [269].

The synthesis, structure, and properties of potassium bis(L-cysteinato-N,S)nickel(II) sesquihydrate have been reported. The crystal structure determination revealed square-planar coordination geometry for Ni. The two ligands are coordinated via their N and S donor atoms in a *trans* configuration (Ni-N = 1.906(9) and 1.928(9)Å; Ni-S = 2.209(4) and 2.199(3)Å). In addition, a secondary interaction between the carboxylate O atoms and the K^+ ions was observed [270].

Turning to histidine, a calorimetric study of the complexation of L-histidine (HL) with Ni(II) has been undertaken. The formation constants and thermodynamic parameters for the formation of the bis complex [NiL_2] have been reported [271].

A variety of complexes of Ni(II) formed with histidine and uracil, and thyamine or 2-thiouracil, have been synthesized and characterised using various of analytical techniques. The resultant complexes had the general formula [$Ni(his)(ur)(H_2O)_2$].$5H_2O$ (hisH = histidine, ur = uracil), [$Ni(his)(thy)(H_2O)_2$].$3H_2O$ (thy = thyamine), and [$Ni(his)(tur)(H_2O)$]$\cdot 2H_2O$ (tur = 2-thiouracil). Histidine was found to function as a didentate ligand in all of the complexes coordinating *via* the α-amino N atom and carboxylate group. Uracil and thyamine function as didentate ligands coordinating through their carbonyl O and one N atom, whereas thiouracil coordinates in a tridentate fashion coordinating via its carbonyl O, thiocarbonyl S, and one N atom [272].

The potent histamine H_2-receptor antagonist cimetidine (L) (**79**) has been complexed to Ni(II) in methanol. The resultant complex cation [NiL_2]$^{2+}$ has been isolated as its diperchlorate salt. Coordination to the metal ion most likely occurs *via* the imidazole N, thioether S and amino N atoms [273].



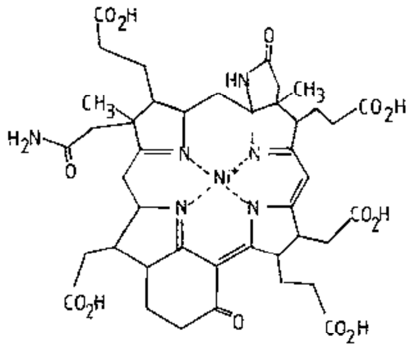
(79)

The stability constants of the binary complexes of L-canavanine and L-arginine with Ni^{2+} have been determined in aqueous solution. Spectroscopic measurements indicated the presence of the mono, bis and tertiary complexes, NiL, NiL_2, and NiL_3. The ligands generally function as tridentate donors, with the exception of the tris complex where they function in a didentate manner [274].

A monomeric nickel complex of D-penicillamine (H_2L) has been prepared, and its structure determined. The crystal structure of $K_2[NiL_2]4H_2O$ reveals square-planar coordination geometry for Ni. The two ligands are coordinated *via* their N and S donor atoms in a *cis* configuration (Ni-N = 1.956(9) and 1.949(9)Å; Ni-S = 2.155(3) and 2.147(3)Å). In addition, a strong secondary interaction between the carboxylate O atoms and the K^+ ions was observed. The use of D-penicillamine as an antidote for nickel poisoning was suggested by the authors [275].

Potentiometric and EPR studies have been carried out on the Ni(II) complexes of several imidazopyridine ligands. These studies have shown that the oxine type of donor set (N,O^-), is an effective binding site for metal ions, even though the complexes are weaker than oxine itself [276].

Ni-enzyme complexes have attracted considerable interest. Factor 430 (**80**), the nickel tetrahydrocorphinoid cofactor used with the enzyme methyl-coenzyme M reductase, found in many of the methanogenic bacteria which produce methane, has been the subject of a number of studies. Generally the work has concentrated on synthesizing models of F430.



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Berkessel has synthesized a series of nickel chelates as models for an interaction of the S-containing substrates with F430. As a common feature, the model complexes contain a pentadentate ligand that positions the S atom of the thioether at an axial coordination site of the Ni ion. For comparison , the S donor was replaced by an O donor. Electrochemical studies revealed that electron transfer can easily take place from the S atom to Ni [277].

Similarly, the reductive chemistry of a series of progressively more saturated Ni(II) porphyrins, derived from anhydromesorhodochlorin XV methyl ester, has been examined as models of F430. Electrochemical studies revealed that, within the Ni(II) porphyrin, chlorin, isobacteriochlorin, and hexa- and octahydroporphyrin series, only the isobacteriochlorins are reduced to Ni(I). In addition, the crystal structure of the anhydromesorhodoisobacteriochlorin methylester nickel(II) complex was determined [278].

The crystal structure of the bromide salt of 12,13-diepi-F430, a derivative of coenzyme F430, has been reported. The complex Was shown to adopt a highly ruffled, saddle-shaped conformation, with short equatorial Ni-N bonds (1.86Å). The coordination sphere about Ni was found to be slightly distorted from planar [279]. In addition, a methylnickel(II) derivative of coenzyme F430 has been proposed as an intermediate in the enzymic process catalysed by methyl-CoM reductase. Indirect evidence supports the formation of a CH_3-F430 nickel(II) complex in which the methyl group is bound to the complexed metal [280].

Considerable work has been published concerning the nickel coordination site in hydrogenase enzymes. EXAFS has been used to investigate the mode of coordination of Ni in the hydrogenases isolated from *D. gigas*, *T. roseopersicina* and *D. baculatus*, as well as the CO dehydrogenase isolated from *C. thermoaceticum*. Comparison with model compounds suggests that the coordination sphere for Ni is square-planar in these enzymes [281].

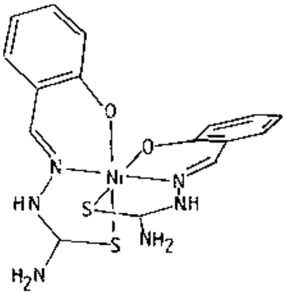
EXAFS has also been utilised, in a more detailed study, to investigate the Ni site in *T. roseopersicina* hydrogenase. The results obtained in this study suggest a Ni ligand environment composed of 3+1 N,O donor atoms at 2.06Å and 2+1 S donors at 2.21Å. In addition, a strong similarity was observed between these data and those from the Fe,Ni,Se enzyme isolated from *D. baculatus* [282].

The structure of the Ni site in *T. roseopersicina* hydrogenase has been further investigated by the use of XANES. By comparison with 44 model compounds, the authors were able to ascertain that the coordination environment in *T. roseopersicina* hydrogenase was probably distorted bipyramidal, with a mixed O,N- and S-donor ligand environment for the biological Ni site [283].

A Q-band ENDOR study of the Ni site in *D. gigas* hydrogenase has been undertaken. The enzyme was examined "as-isolated", reduced with hydrogen, and in its reoxidized form. Through proton and deuteron ENDOR experiments, the authors were able to detect and characterise two distinct types of exchangeable protons, the possible products of heterolytic cleavage of H_2. It was suggested that one proton may be linked directly to the reduced metal centre, while the other could be associated with H_2 or OH^- bound to Ni [284].

A new method of metal replacement has been utilised to prepare a Ni-substituted rubredoxin. The Ni centre was found to be coordinated to four cysteine residues in a distorted tetrahedral geometry. Oxidation of this complex resulted in the Ni site exhibiting EPR signals resembling those obtained from the Ni-containing hydrogenases. These results suggest that the amino acid sequences which appear to be involved in the Ni fixation of the substituted rubredoxin are homologous with the cysteine-containing moieties present in the Ni hydrogenase sequences [285].

The complex $[NiL_2]Cl_2$ (L = o-$C_6H_4(OH)CH{=}NNHCSNH_2$) was found to be an excellent model compound for hydrogenase. The N,O,S-donor Ni(II) complex was found to exist in an octahedral configuration in the solid state, but reverted to a square-planar configuration in solution. In addition, it could be reduced to an air-stable Ni(I) form and, like hydrogenase itself, catalysed hydrogen/deuterium exchange. The crystal structure of the octahedral complex was determined and reveals *cis* coordination with both ligands in the phenol, rather than phenolate form (**81**) [286].



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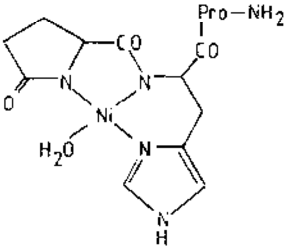
A series of nickel complexes of formula $[Ni(L)X]^+$ (L = the tripodal ligand $N(CH_2CH_2SR)_3$, R = *i*-Pr, *t*-Bu; X = Cl, Me, COMe, CO, H) has been prepared with a view to investigating their structural and reaction chemistry in relation to CO dehydrogenase. This series includes rare examples of stabilised Ni-methyl, -acyl, -hydride, and -carbonyl ligands in the absence of nonphysiological coligands such as C, P and As donor ligands. The crystal and molecular structures of five complexes (R = Cl, Me, COMe, CO, H) were determined, revealing trigonal-bipyramidal stereochemistry for all of the complexes. This work forms part of an attempt to simulate acetyl-coenzyme A synthase activity [287].

Nickel(II) carbonic anhydrase, and its adducts with nitrate, acetate, cyanate and azide have been investigated using ^1H NMR and electronic absorption spectroscopy. The anions were found to bind to the metal ion forming 1:1 adducts. The coordination geometry of Ni has been examined at varying pH. At neutral pH it appears to be pseudo-octahedral, whereas at higher pH a five-coordinate geometry was suggested [288].

The relationship between the concentration of bovine serum albumin (BSA) and the structure of its complex with Ni(II) has been examined using UV spectrometry. Increasing the concentration of free BSA was shown to transform the coordination geometry from pentacoordinated square-pyramidal into tetracoordinated square-planar. The O atom of the carboxyl group of the aspartate in BSA appears to be involved in coordination to Ni [289].

The complex formation of L-pyroglutamyl-L-histidyl-L-prolinamide (HL) with Ni(II) has been studied using pH-metry, UV spectroscopy and circular dichroism. Different metal species were formed depending on the pH employed. Thus, complexes of the type NiL, $NiH_{-2}L$, and $NiH_{-3}L$ were formed as the pH was increased from 5.5 to above 11.0. Monodentate coordination of the ligand via the imidazole N3 atom is suggested for the 1:1 complex, which has been assigned an octahedral structure on the basis of its electronic spectrum, with H_2O molecules completing the coordination sphere. $NiH_{-2}L$ has been assigned a square-planar structure (**82**), as has $NiH_{-3}L$ which also has a deprotonated pyrole N atom (**83**) [290].



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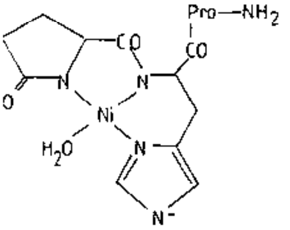


(83)

pH-metry has also been used to investigate the complexation of humic acid (HL) with metal(II) ions. Complex stability was found to decrease with an increase in the number of coordination centres on HA, with an increase in ionic strength of the solution, as well as with an increase in the molecular weight of HA. Complex stability was found to rise as the pH was increased, this increase being ascribed to the increasing contribution of weakly acidic functional HA molecules. The values of the Hills coefficient and the number of coordination centres followed the Irving-Williams series i.e. $Pb^{2+} > Ni^{2+} > Zn^{2+} > Co^{2+} > Cd^{2+} > Mn^{2+} > Ca^{2+} > Mg^{2+}$ [291].

Turning to carbohydrate ligands and their derivatives, chelate complexes of Ni(II) with fructose and fructose high syrup have been prepared and characterised. The chelates were not homogeneous, and three species of molecular weight 68 000, 37 000 and 20 000 were obtained for Ni-fructose, and two species of molecular weight 66 000 and 50 000 were found for Ni-high fructose [292].

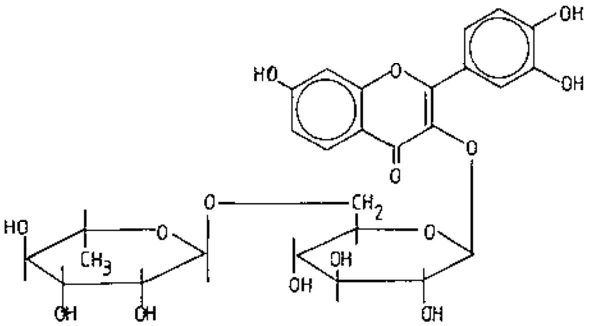
Gluconic acid (H_3L) has been complexed with Ni(II). The resultant complexes, $Ni(II)(H_2L)_2 2H_2O$ and $[Fe(III)_2Ni(II)L_2(HL)]5H_2O$, were characterised using elemental chemical analysis, electronic and IR spectroscopy, and magnetic measurements [293].

The formation constants of the binary and ternary complexes of Ni(II) with citric acid and $edtaH_4$ have been determined in aqueous solution. Complex formation was examined at varying temperatures and pH [294].

A kinetic study of the complexation of Ni(II) with α-amino-δ-ureido-*n*-valeric acid has been undertaken using the stopped flow technique. Data were obtained at varying temperature and pH, and overall as well as specific rate constants were calculated [295].

Coordination of Ni(II) to nucleosides and related compounds has generated considerable interest. The stability constants of the 1:1 complex of Ni with orotidine 5'-monophosphate has been determined using potentiometric pH titrations in aqueous media. Comparison of the coordinating properties of orotidine 5'-monophosphate was made with uridine 5'-monophosphate, adenine 5'-monophosphate, and thymidine 5'-monophosphate. Increased stability for the orotidinate complex was found. This was ascribed to the involvement of a further binding site, located on the base [296].

The equilibrium reactions between rutin (**84**) and quercetin (**85**) with Ni(II) have been studied in aqueous solutions using potentiometric and spectrophotometric methods. Rutin is a potentially hexadentate O donor ligand, whereas quercetin is a potentially heptadentate O donor ligand [297].



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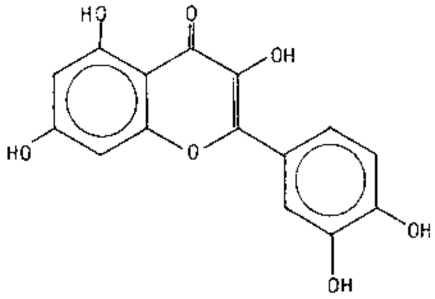

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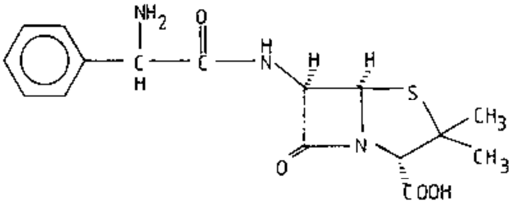
In a study investigating the ability of nickel(II) complexes to effect oxidative DNA modification, the intrinsic selectivity of a number of Ni(II) complexes has been examined. A purified oligonucleotide having the 15-base sequence d(CATGCGCTACCCGTG) was used as substrate. Square-planar Ni(II) complexes of tetraazamacrocycles were found to be highly active for DNA modification under oxidative conditions, compared to the analogous copper complexes or octahedral Ni(II) complexes. In addition, oxidation was found to occur specifically at G residues [298].

Resonance Raman and optical spectroscopy have been used to elucidate the bonding of nickel(II) porphyrins to anionic biopolymers. In particular, the binding of the nickel(II) porphyrins to double-stranded DNA, single-stranded DNA and RNA, polypeptides, and sulfated carbohydrates has been investigated [299].

Turning to sulfur-containing biological ligands, the complexation of ampicillin (**86**) with a number of metal ions has been investigated in aqueous solution using the pH-titration technique of Calvin-Bjerrum, as modified by Irving and Rossotti. The stoichiometry and stability of the resultant nickel(II) complexes were ascertained [300].

A thermochemical study of the complexation of sodium N-chlorobenzenesulfamide with Ni(II) has been reported. The stability constants and heats of formation of the resultant complexes were determined [301].

6-Ethoxybenzothiazole-2-sulfonamide (HL) has been reacted with Ni(II). The resultant complex $[NiL(H_2O)_2(\mu\text{-OH})]_2$ was characterised by elemental chemical analysis, IR and UV-visible spectroscopy, and magnetic measurements. This complex was found to be a strong inhibitor of red cell bovine carbonic anhydrase [302].



(86)

7.7 *NICKEL (I)*

Macrocycles and phosphorus-donor ligands continue to be used to stabilise nickel in the +1 oxidation state.

In a study concerning Ni(II), Ni(I), and Ni(I)-CO tetraazamacrocycles, EXAFS and UV-visible spectroscopy have been used to examine a number of Ni(II)-tetraazamacrocyclic complexes, the nature of the reduced species derived from these complexes, and the Ni(I)-CO adducts. It was found that reduction of Ni(II) to Ni(I) caused an expansion of the macrocyclic core, as well as a distortion. However, conversion of the Ni(II)-complex to the Ni(II)-complex anion radical was found to leave the coordination geometry about the nickel atom unchanged. Interestingly, the anion radical of NiL^+ (L = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) was found to dimerise in solution forming diamagnetic adducts. EXAFS data on the CO adducts of N(I)L (L = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) clearly showed pentacoordination with the presence of a short Ni-C bond (1.78-1.80Å). In addition, the crystal and molecular structure of (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I) perchlorate was determined, revealing a square-planar coordination sphere about Ni(I) [303].

A similar study on the site of electroreduction in nickel metalloporphyrins has been undertaken. The effects of temperature, porphyrin macrocycle, and solvent on the electroreduction of [Ni(II)L] (H_2L = *meso*-tetrakis(*p*-(diethylamino)phenyl)porphyrin or *meso*-tetrakis(*o,o,m,m*-tetrafluoro-*p*-(dimethylamino)phenyl)porphyrin) were examined. Results obtained in this study demonstrated that, depending on the temperature, the type of porphyrin macrocycle, the solvent used, and the nature of potential axial ligands, electroreduction could lead to the formation of Ni(I) porphyrins, Ni(II) porphyrin π-anion radicals, or Ni(II) porphyrin π-anion radicals with some Ni(I) character [304].

The crystal and molecular structure of chlorotris(triphenylphosphine)nickel(I) toluene has been reported. Distorted tetrahedral coordination geometry was revealed for the Ni(I) ion with the following relevant data: Ni-Cl = 2.2785(9)Å, Ni-P = 2.2987(9), 2.3029(9) and 2.3148(9)Å [305].

Nickel complexes of the type $[Ni(L)_2](BF_4)_2$ (L = 1,1-bis(diphenylphosphino)methane (dppm), 1,2-bis(diphenylphosphino)ethane (dppe), 1,2-bis(diphenylphosphino)ethene (dppv), 1,2-bis(diphenylphosphino)benzene (dppb), 1,3-bis(diphenylphosphino)propane (dppp)), $[Ni(L)(L')](BF_4)_2$ (L = dppe, dppp, dppb; L' = dppm, dppp) and $[Ni(dppm)_2(CH_3CN)](BF_4)_2$ have been prepared and characterised. The half-wave potentials for the Ni(II)/Ni(I) couple were measured for each of the complexes, and were found to become more positive as the bite size of the diphosphine was increased. X-ray crystal structural studies of $[Ni(dppm)_2](BF_4)_2$ and $[Ni(dppb)_2](BF_4)_2$ revealed that increasing the bite size results in larger tetrahedral distortion. In addition, the most stable Ni(I) complex, $[Ni(dppp)_2](PF_6)$, was isolated and characterised, while complexes containing dppm were shown to have a tendency to become pentacoordinate, as verified by the structural determination of $[Ni(dppm)_2(CH_3CN)](BF_4)_2$ [306].

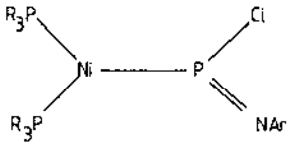
7.8 NICKEL (0)

Phosphine-containing ligands continue to be used with great effect in the stabilisation of nickel in the zero valent state.

The crystal and molecular structure of bis[μ-(3,4-η,κP^5)-5-chloro-2,2,6,6-tetramethyl-3-phenyl-4,5-diphospha-2-silahept-3-ene]biscarbonylnickel(0)} has been reported. The structure determination revealed an "anti-parallel" arrangement of two PPCNi(CO) moieties, with each Ni atom being σ-coordinated to the phosphino fragment of one diphosphapropene, and η^2 coordinated by the π system of the second phosphino-methylenephopsphane [307].

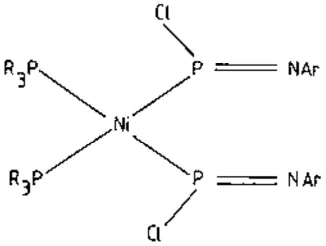
SO_2 coordination geometry in the Ni(0) complexes $Ni(PR_3)_2(SO_2)$ (R = alkyl or aryl) has been examined using IR and ^{31}P-NMR spectroscopy. The X-ray crystal structure of $Ni(PCy_3)_2(SO_2)$ (Cy = cyclohexyl) has also been described [308].

Chloro(2,4,6-tri-*t*-butylphenylimino)phosphine, Cl-P=N(2,4,6-$Bu^t_3C_6H_2$), has been reacted with a variety of Ni(0) complexes, yielding the first examples of σ-complexes containing P-functionalised iminophosphines. Reaction of one equivalent of Cl-P=N(2,4,6-$Bu^t_3C_6H_2$) with $[Ni(R_3P)_2(C_2H_4)]$ (R = Ph, Bu^n, Et) was found to give (**87**), whereas reaction with two equivalents yielded (**88**), both structures being confirmed by ^{31}P and ^1H NMR. A third compound, $[(Ph_3P)Ni(ClP=N(2,4,6\text{-}Bu^t_3C_6H_2)_3]$, was also observed spectroscopically. Reaction with $[(R_3P)_2Ni(CO)_2]$ yielded (**89**), with only one ligand being substituted. The structure of this complex was also confirmed using ^{31}P and ^1H NMR [309].



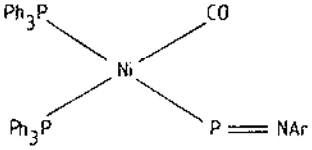
(R = Ph, Bu^n, Et; Ar = 2,4,6-$Bu^t_3C_6H_2$)

(**87**)



(R = Ph, Bu^n, Et; Ar = 2,4,6-$Bu^t_3C_6H_2$)

(**88**)



(R = Ph, Bu^n, Et; Ar =2,4,6-$Bu^t_3C_6H_2$)

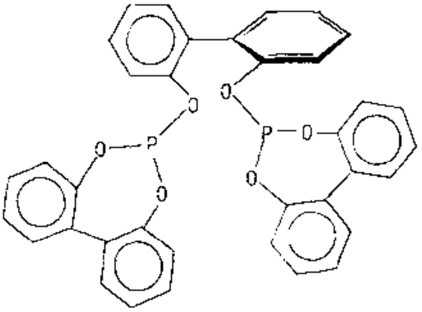
(**89**)

"Ab initio" calculations have been carried out on the model compounds, (dinitrogen)nickel(0) and bis(phosphine)(dinitrogen)nickel(0), to investigate the relative stability of end-on and side-on coordination of dinitrogen to Ni(0). The presence of ligands appears to affect the mode of coordination, with side-on coordination being preferred when ligands are present, and end-on coordination being preferred in the absence of other ligands [310].

An improved method for the preparation of $Ni(CO)_2(PR_3)_2$ has been reported. The preparation involves reaction of the dithiocarbamate, $[Ni(S_2COEt)_2]$, with the relevant phosphine PR_3. Yields of up to 50% have been recorded [311].

Protonation of a number of Ni(0) phosphine complexes has been carried out using $H_2C(SO_2CF_3)_2$. The resultant complex cations $[L_3NiH]^+$ (L = Ph_3P, Ph_2PMe, Et_3P) were isolated as their $HC(SO_2CF_3)_2^-$ salts. However, protonation of $[Ni\{(OEt)_3P\}_4]$ was found to yield $[(OEt)_3P\}_4NiH][HC(SO_2CF_3)_2]$. In addition, the compounds $[(Et_3P)_4NiH][HC(SO_2CF_3)_2]$ and $[(Ph_3P)_4NiH][HC(SO_2CF_3)_2]$ were found to be stereochemically nonrigid in CH_2Cl_2 solution [312].

The synthesis, stability and hydrocyanation catalytic activity of the nickel(0) complex of the diphosphite ligand (L) (**90**), derived from 2,2'-biphenol, have been described. The complex $[NiL_2]$ was prepared by the reaction of (**90**) with $[Ni(cod)_2]$. It has also been shown to be a very active and stable catalyst for the hydrocyanation of butadiene, exhibiting higher activity than the presently used commercial catalyst [313].



(90)

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