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Nickel 1985

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Contents

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1. Introduction

This article reviews the coordination chemistry of nickel appearing in 1985 and includes volumes 102 and 103 of Chemical Abstracts. As with previous articles [1,2], the material has been arranged by oxidation state with further subdivision in terms of ligand donor type. An attempt has also been made to classify mixed-ligand complexes according to the fundamental theme of the article in which they appeared. As always, macrocycle and Schiff base complexes tend to dominate, although interest in higher oxidation state complexes, as well as those containing biological ligands, appears to be increasing.

Articles of general interest that have appeared include a review of Fe, Co and Ni which covers 1983 and contains 354 references [3], as well as one which compares the properties of Ni, Pd and Pt complexes [4]. In addition, the Ni(II) ion has been used in determining the "Coordination Power" (a measure for the donor ability) of various solvents. A good relationship between the "Coordination Power" and ligand field splitting parameter for the Ni(II) solvate ion was found [5].

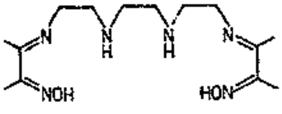
2. Nickel(IV)

Nickel(IV) chemistry continues to be dominated by complexes containing oxime functional groups. However, it appears that the study of the less stable, higher oxidation states of nickel is expanding in conjunction with the utilization of novel spectroscopic techniques. Electronic absorption and magnetic circular dichroism spectroscopy have been used to study the Waugh-structure ion, $[NiMo_9O_{32}]^{6-}$, in aqueous solution. The Ni(IV) ion in the polyanion was attributed a low-spin d^6 electronic configuration [6]. Continuing study of Ni(II)–Ni(IV) mixed-valence complexes reveals that these compounds may be obtained from the disproportionation reaction of the corresponding Ni(III) complex. The chloro-bridged one-dimensional Ni(II)–Ni(IV) mixed-valence complexes, $[NiL][NiCl_2L]$ (L = 3,7-diazanonane-1,9-diamine) [7] and $[NiL_2][NiCl_2L_2]$ (L = ethylenediamine) [8], have been analysed using XPS and ESR, respectively.

2.1. Complexes with nitrogen donor ligands

The preparation of $[Ni(HL)L](ClO_4)_2$ $\{H_2L = HON{:}C(CH_3)C(CH_3){:}N(CH_2)_2NH_2\}$ has been reported and compared with a number of other Ni(IV) compounds furnished by complexation with hexadentate and tridentate oxime-imine-amine ligands. The possibility of correlation between oxidation state stability, electroprotic equilibria, and reaction mechanisms, has been examined [9].

Pulse radiolysis has been used to study the kinetics of reduction of two nickel(IV)–oxime complexes, $[NiL]^{2+}$ $\{H_2L$ = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (1)$\}$ and $[Ni(dmg)_3]^{2-}$ (H_2dmg = dimethylglyoxime), using a series of organic radicals as reductant. In addition, the Ni(III) transients were observed and indications are that the electron is transferred to the metal centre [10].



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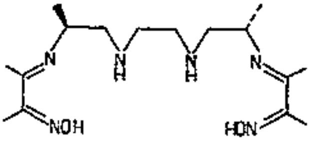
The electroprotic equilibria of $[NiL]^{2+}$ $\{H_2L = (\mathbf{1})\}$, ion-exchanged onto poly(*p*-styrenesulfonate) films attached to a basal pyrolytic graphite electrode, has been studied in aqueous solution over a pH range of 1–9 [11].

(*5S,12S*)-4,7,10,13-Tetraaza-3,5,12,14-tetramethylhexadeca-3,13-diene-2,15-dione dioxime (**2**), a chiral analogue of (**1**), has been complexed stereospecifically with Ni(II) and oxidized to the corresponding Ni(IV) complex, $[NiL]^{2+}$ $\{H_2L = (\mathbf{2})\}$, with retention of absolute configuration about the metal centre (ΛΔΛΛΔΛ). The reduction of this complex by $[CoL]^{2-}$ (H_4L = 1,2-diaminopropane-*N,N, N′,N′*-tetraacetic acid and 1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid) has also been investigated [12].



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2.2. *Complexes with sulfur donor ligands*

The oxidation of $[NiL_2]$ ($HL = R_2NCS_2H$; R = Et, Bu) with Br_2 and I_2 has been reported. Oxidation with Br_2 yielded the Ni(IV) complex, $[NiL_3]Br$, whereas oxidation with I_2 in non-polar media yielded the Ni(III) complex, $[NiL_2]I_3$. However, oxidation of $[NiL_2]$ with I_2 in polar media yielded the corresponding Ni(IV) complex, $[NiL_3]I_3$, which is thought to arise from disproportionation of $[NiL_2]I_3$ [13].

2.3. *Complexes with phosphorus and arsenic donor ligands*

A combination of EXAFS and electronic spectroscopy has been used to determine the structure of a variety of nickel(IV) complexes. This novel approach has been illustrated for the tetragonally distorted, pseudo-octahedral Ni(IV) complexes, $[NiCl_2\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{2+}$ (Ni–Cl = 2.26 Å, Ni–P = 2.22 Å) and $[NiCl_2\{o\text{-}C_6H_4(AsMe_2)_2\}_2]^{2+}$ (Ni–Cl = 2.27 Å, Ni–As = 2.36 Å) [14].

3. Nickel(III)

Interest has centred around the redox chemistry of Ni(III/II), with poly-aza macrocycles and didentate sulfur-donor ligands being used for stabilization of the higher oxidation states. This is exemplified by two reviews, one investigating the kinetic aspects of redox reactions of nickel(III) complexes [15], while the other looks at the stabilization of high oxidation states of metals through coordination by poly-aza macrocycles [16].

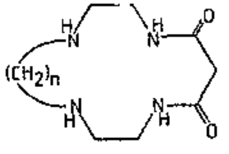
A number of biologically important Ni(III) complexes have been reported and are discussed in their relevant sections. Of particular interest is the EPR spectrum at 4.9 and 35 GHz of hydrogenase from *Chromatium vinosum*, in which intact enzyme molecules exhibit a complex EPR spectrum caused by a spin-coupled pair of Ni(III) ions and a $[4Fe–4S]^{3+}$ cluster. It was proposed that the Ni ion has five ligands provided by the protein in a square-pyramidal coordination [17].

Also of general interest is the complex anion, *trans*-$[Ni(CN)_4(H_2O)_2]^-$, which has been generated in aqueous solution by the oxidation of $[Ni(CN)_4]^{2+}$. It appears that this complex anion is an excellent precursor for the formation of a new series of nickel(III) complexes in which the axial ligands can be displaced [18].

3.1. Complexes with nitrogen donor ligands

Both EPR and electronic absorbance spectroscopy have been used to monitor the reaction of *trans*-dichlorobis(ethylenediamine)nickel(III) in aqueous HCl. The rate of Ni(III) reduction was influenced by both the H^+ and Cl^- concentrations. Use of H_2SO_4 resulted in the rapid displacement of Cl^- by HSO_4^- [19].

Turning to macrocyclic complexes, two articles have appeared that examined steric effects on the rates of Redox reactions involving the Ni(II/III) couple. One examines the effect of ring size and reaction medium on oxidation of the Ni(II) complex of the macrocycles (3) [20], while the other investigated the steric effects of several isomers of (5,12-dimethylcyclam)nickel(II) and one of the isomers of the 5,12-diethyl analogue [21].



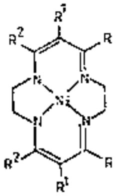
(n = 2,3)
(3)

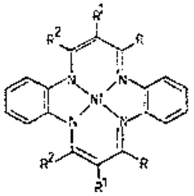
The kinetics of the reduction of a series of nickel(III) macrocycle complexes containing tetraaza and hexaaza moieties have been studied in acidic aqueous media using $Fe(H_2O)_6^{2+}$ and VO^{2+} (aq) as reductants [22]. In addition, a number of Ni(III) complexes containing triaza and tetraaza macrocyclic ligands have been employed as cross reactants in the study of outer-sphere electron-transfer reactions involving the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^{0/+}$ couple [23].

$[Ni(1,4,7\text{-triazacyclodecane})_2]^{3+}$ has been prepared by oxidation of the corresponding Ni(II) complex using either Co^{3+} (aq) in acidic aqueous media or NO^+ in CH_3CN. The octahedral NiN_6 chromophore is retained upon electron transfer, and outer sphere reactions of both the Ni(III) and Ni(II) species have been studied [24].

The crystal structure of $H_3O[NiL]$ (H_3L = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetic acid) has been determined. Of particular interest is the short Ni–N bond length of 2.04 Å. The unusual stability of the Ni(III) complex was attributed to the ligands preference for small metal ions [25].

The oxidation of **(4)** and **(5)**, using a number of oxidants, has been monitored by ESR spectroscopy. The choice of oxidant appears to be critical, since only oxidation by Br_2 yielded the desired Ni(III) species as primary oxidation product [26].





(R = Me, Ph; R^1 = H, COMe, CO_2Et, COPh; R^2 = Me,H)

(4) **(5)**

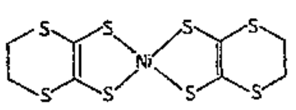
As is the case with Ni(IV), oxime-containing ligands have also been utilized in the stabilization of tervalent nickel. A series of Ni(III)-α-dioxime complexes have been used in the liquid phase catalytic oxidation of tetralin. Catalytic activity was found to be related to the structure of the Ni(III) complex [27].

The kinetics and mechanism of disproportionation of the nickel(III) complex, $[NiL]^+$ (H_2L = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime), have been investigated. Both the kinetics and mechanism are highly sensitive to pH [28].

3.2. Complexes with sulfur donor ligands

The dipotassium salt of 5,6-dihydro-1,4-dithiin-2,3-dithiolate (K_2L) reacted with Ni(II) yielding the Ni(III) complex anion, $[NiL_2]^-$ **(6)**, which has been isolated as its tetraethylammonium salt. A single-crystal X-ray study revealed that the coordination geometry of the nickel ion is essentially square planar (Ni–S = 2.148(2) Å) [29].

Similarly, the crystal and molecular structure of the related complex anion, $[NiL_2]^-$ (L = maleodinitriledithiolate) **(7)**, isolated as its *N*-methylphenazinium salt, has been determined. A square planar configuration was found for the Ni ion (Ni–S = 2.136(3) Å) [30].



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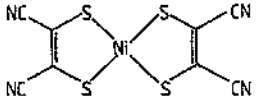


(7)

A number of variously-substituted nickel(II) dithiocarbamates, [Ni(RR^{1}NCS$_2$)] (R = Me, CH$_2$Ph; R^1 = Me, CH$_2$Ph, Ph; RR^1 = -[CH$_2$]$_4$-), have been oxidised in acetone-dichloromethane using Fe(III) salts as oxidant. The Ni(III) complexes, [Ni(RR^{1}NCS$_2$)$_2$]$^-$, were observed in solution, but could not be isolated in the solid state [31]. In addition, the oxidation of nickel(II)-bis(diethyldithiocarbamate) by *N,N,N′,N′*-tetraethylthiuramdisulfide has been described. The formation of the resultant Ni(III) complex, tris(diethyldithiocarbamate)nickel(III), is thought to proceed via a radical mechanism [32].

3.3. Complexes with nitrogen–oxygen donor ligands

Nickel(III)–peptide complexes of Gly$_4$, Gly$_3$, GlyAlaGly and GlyGlyAla (Gly = glycyl, Ala = alanyl) have received considerable attention lately. Bis(tripeptido)nickelate (III) complexes, formed by the addition of excess tripeptide to solutions of (tripeptido)nickel(III), have been observed in solution. Coordination was found to be a function of pH, with N$_5$O coordination occurring at a pH of 6–11 [33]. Attention has also been given to the reaction of Ni(III)-peptides with acid [34] and a series of polypyridine and polyamine ligands [35].

4. Nickel(II)

4.1. Complexes with halide ligands

A general route for the synthesis of alkali metal trifluoronickelate (II) monohydrates, MNiF$_3 \cdot$H$_2$O (M = NH$_4$, Na or K), has been reported [36]. In addition, X-ray electron spectroscopy has been used to study the fluoride layer on the surface of nickel in its reaction with gaseous fluorine [37].

^{1}H-NMR has been used to study the composition and stability constants of the chloro complexes of Ni(II) in solutions of HCl in aqueous acetonitrile, aqueous acetone, and aqueous dioxan [38].

4.2. Complexes with oxygen donor ligands

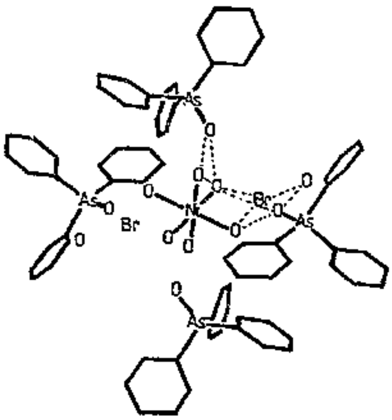
A variety of nickel alcoholates, Ni(OR)$_2$ (R = Me, Et, Pr, *iso*-Pr), have been prepared and characterized by X-ray diffraction, IR and diffuse reflectance spectroscopy. Ni(OMe)$_2$ and Ni(OPr-*iso*)$_2$ were assigned octahedral and tetrahedral structures, respectively, whereas both types of environment were observed for

$Ni(OEt)_2$ and $Ni(OPr)_2$ [39]. The structure of the related complex, tetrakis[μ_3-methoxo-(2,4,6-trichlorophenolato)(methanol)nickel(II)], has been reported. The nickel atoms were found to possess a distorted octahedral environment [40].

Numerous carboxylic acids have been complexed with Ni(II). These include 2,5-dihydroxybenzoic acid [41], 2-nitrophenoxyethanoic acid [42], 2,3-xylylamino- and 2,4-xylylamino-*N*-monoacetic acid [43]. The complexes, $[NiL_2(H_2O)_4]$ (HL = carboxylic acid), all exhibit *trans*-tetragonally-distorted octahedral coordination, with the carboxylic acid ligands functioning in a unidentate fashion.

Dimethylacetamide (L) has been reacted with $NiCl_2$. The resultant complex, $[NiL_2Cl_2(H_2O)_2]\cdot 4H_2O$, was found to have an octahedral structure [44].

The synthesis and crystal structures of two novel complexes, resulting from the reaction of $NiBr_2$ with Ph_3AsO, have been reported. One complex, formulated as $NiBr_2\cdot 4(Ph_3AsO)\cdot 8H_2O$, consists of a Ni(II) ion octahedrally coordinated to six water molecules which, in turn, are hydrogen bonded to the Ph_3AsO and Br^- moieties, thereby forming a second coordination sphere (**8**). The second complex, formulated as $[NiBr(P_3AsO)_4]\cdot Br\cdot 3/2(C_6H_5CH_3)\cdot H_2O$, exhibits square-pyramidal coordination in which the Ni(II) ion is coordinated to four Ph_3AsO molecules and a bromide ion (**9**) [45].



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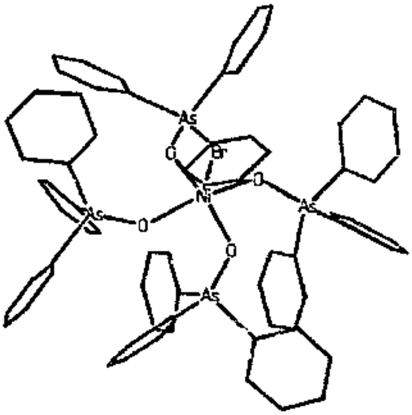


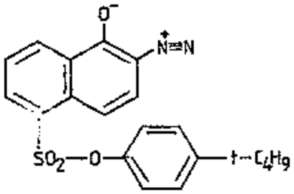
(9)

Anhydrous $Ni(ClO_4)_2$ and its chloryl and nitryl salts, $ClO_2Ni(ClO_4)_3$, $NO_2Ni(ClO_4)_3$, and $(NO_2)_2Ni(ClO_4)_4$, have been prepared by reacting Cl_2O_6 with the corresponding anhydrous or hydrated nickel chloride or nitrate. An octahedral environment was suggested for Ni(II) [46]. This has been substantiated by further work in which the behaviour of ClO_4^- as a ligand was studied using EXAFS, IR and Raman spectroscopy [47].

$[Ni(O_2PF_2)_2 \cdot HPO_2F_2]$ has been prepared by reaction of nickel metal with anhydrous difluorophosphoric acid. The nickel atom is coordinated to the oxygen atoms and was assigned an octahedral coordination environment [48].

The reactions of bis(acetylacetonato)nickel(II) with a number of ligands have been studied, both in the solid state and in solution [49,50]. Complexes that have been isolated in the solid state include $[Ni(acac)_2L_2]$ (L = 2-, 3-, 4-pyridinecarboxylic acid hydrazide) [50], $[Ni(acac)(O_2CCCl_3)]$, and $[Ni(acac)(O_2CCCl_3)L_2]$ (L = γ-picoline, imidazole, 2-picoline N-oxide and thiourea) [51]. The complexes are all high-spin octahedral, with the exception of $[Ni(acac)(O_2CCCl_3)]$, which has been assigned a tetrahedral structure. In addition, an XPS and IR study of $[Ni(acac)_2]$ (Hacac = acetylacetonate) has been undertaken [52].

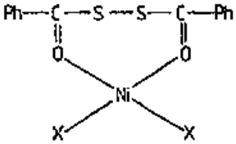
Turning to solution studies, ^{14}N-NMR has been used to study the exchange of pyridine (py) with $[NiL_2(py)_2]$ (HL = acetylacetone, thenoyltrifluoroacetone). In this study, it was observed that the electron-withdrawing power of the substituent group on the β-diketonate ring correlates with a more favourable exchange activation [53]. Similarly, the reaction of *p*-*t*-butylphenyl-1,2-naphthoquinonediazide-(2)-5-sulfonate (**10**) with bis(acetylacetonato)nickel(II) has been studied by NMR [54].



(**10**)

Cyclic voltammetry and controlled potential electrolysis have been used to investigate the cathodic behaviour of bis(acetylacetonato)nickel(II). The complex undergoes a complicated reduction process in which mono(acetylacetonato)nickel(II) and tris(acetylacetonato)nickel(II) species were observed [55].

Dibenzoyldisulfide has been reacted with NiX_2 (X = Cl, Br), yielding the 1:1 adducts $[NiLX_2]$ (L = dibenzoyldisulfide). The complexes were assigned tetrahedral stereochemistry and are unusual in that they contain a seven-membered chelate ring (**11**) [56].



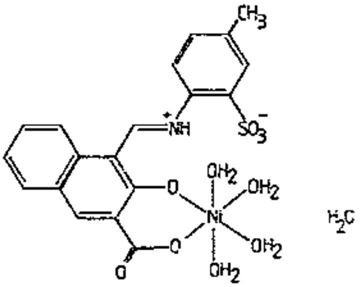
(**11**)

Salicylic acid and its substituted analogues have been reacted with a number of nickel salts. Coordination usually occurred via a deprotonated carboxylic acid function and a hydroxyl or deprotonated hydroxyl moiety. Complexes that have been isolated consist of $[Ni(HL)_2]$ and $[NiL_2]$ (H_2L = salicylic acid) [57,58], $[Ni(HL_2)_2(H_2O)_2]$ (H_2L = 4-aminosalicyclic acid [59], 5-sulfosalicyclic acid [60]), $[Ni(H_2L)_2(H_2O)_2]$ (H_3L = γ-{3-carboxy-4-hydroxybenzoyl}butanoic acid) [61] and $(Ni(L)(L^1)_2]$ (H_2L = 5,5′-thiodisalicylic acid, $L^1 = H_2O$, NH_3, $MeNH_2$ or py) [62]. In addition, the stability constants of the Ni(II) complexes of a series of alkyl-salicylic acids, alkyl-4-hydroxyisophthalic acids [63], as well as mandelic acid [64], have been determined potentiometrically.

The interaction of a number of diacetic acid ligands with Ni(II) has been studied in solution and in the solid state. Precision calorimetry was used to determine the thermodynamics of the complexation of iminodiacetic acid with Ni(II) [65], while the stability constants for the Ni(II) complexes of thiodiacetic, thiodipropionic, dithioacetic, oxydiacetic and iminodiacetic acids [66], as well as *N*-hexyl-iminodiacetic acid [67], have been determined potentiometrically. Turning to the solid state, 2,6-xylyliminodiacetic acid (H_2L) has been reacted with Ni(II) yielding the complex, $[NiL(H_2O)_2]$ [68].

While on the subject of dicarboxylic acids, in an ongoing study, the complexes of nickel(II) succinate with a number of amines and diamines, have been prepared. These include $[NiLL^1_2(H_2O)_2]$ (H_2L = succinic acid; $L^1 = PhNH_2$, 4-chloroaniline, *o*-, *m*-, *p*-toluidine, *o*-anisidine, pyridine, β-picoline) and $[NiLL^1_2]$ (L^1 = ethylenediamine, propylenediamine) [69].

The Schiff base *N*-(2-hydroxy-3-carboxy-1-naphthylidene)-4-methyl-2-sulfonic acid (H_3L) has a number of sites available for coordination. Reaction with Ni(II) yielded the octahedral complex, $[Ni(HL)(H_2O)_4]$, with coordination occurring via the deprotonated hydroxyl and carboxylic acid functions, as shown below (**12**) [70].



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2-(Ethoxycarbonylamino)pyridine N-oxide (L) has been reacted with a variety of nickel salts, yielding complexes of the type $[NiL_2X_2]$ (X = Cl, Br, NCS) and $[NiL_3]X_2$ (X = I, ClO_4, NO_3). Both series of complexes were assigned octahedral coordination [71]. However, the related ligand 2,2′-biquinolyl-*N*,*N*′-dioxide (L), only yielded tris complexes of the type $[NiL_3]X_2$ (X = ClO_4, CF_3SO_3, NO_3) [72].

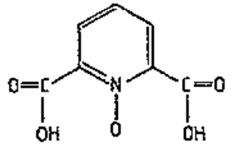
Mixed-ligand complexes of the type $[NiL_2L^1_2]$ (HL = *o*-hydroxyacetophenone; L^1 = quinoline, isoquinoline, morpholine) have been prepared and characterized using a number of spectroscopic techniques [73]. In addition, the interaction of

Ni(II) with the related ligands 3,5-dichloro-2′-hydroxychalcone [74] and *N*-2′-diphenylacetohydroxamic acid [75] has been investigated in solution. Other ligands that have been studied in solution include 1,2-dihydroxy-4-nitrobenzene [76] and hexachlorophene [77].

The synthesis of ethylenediammonium bis(dithioxalato) nickelate(II) has been reported. Its crystal and molecular structures have also been determined and reported [78].

Heptane-2,4,6-trione has the ability to function as a didentate or tridentate ligand depending on the experimental conditions employed. A series of articles have been published in which both the formation constants for the reaction of heptane-2,4,6-trione, 1-phenylhexane-1,3,5,-trione, 1,5-diphenylpentane-1,3,5-trione and 2,2′-dihydroxybenzophenone with Ni(III) [79], as well as the kinetics and mechanism of the reaction of Ni(II) with heptane-2,4,6-trione [80] have been investigated. Both 1:1 and 2:2 complexes were formed in solution.

The potentially tridentate ligand, pyridine-2,6-dicarboxylic acid *N*-oxide (**13**), has been reacted with nickel acetate yielding the complex, $[NiL(H_2O)_2]$ $\{H_2L = (\mathbf{13})\}$. UV spectra indicate an octahedral environment for the nickel atom with a 10 Dq value of 907 cm^{-1} being reported [81].



(**13**)

Potentiometric and spectrophotometric studies have been carried out on the complexation of *o*-phenylenediamine-*N*,*N*,*N*′,*N*′-tetraacetic acid with Ni(II) [82].

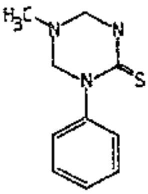
4.3. Complexes with sulfur and selenium donor ligands

A series of nickel thiolates has been prepared by reaction of the sodium salt of an appropriate thiol with $(NEt_4)_2[NiX_4]$ (X = halide). Complexes that have been isolated include $(NEt_4)_2[Ni(SPh)_4]$, the crystal structure of which has been determined, as well as the trimeric and dimeric complexes, $(NEt_4)_3[Ni_3(SEt)_{12}]$ and $(NEt_4)_2[Ni_2L_3]$ (L = ethane-1,2-dithiol), respectively [83].

N,*N*′-Diphenylthiourea (H_2L) has been reacted with Ni(II) yielding the neutral complex, $[Ni(HL)_2]$, which has been characterized using spectroscopic and thermogravimetric analysis. In addition, the stability constants for $Ni(HL)^+$ and $Ni(HL)_2$ have been determined spectrophotometrically [84].

5-Methyl-1-phenylhexahydro-1,3,5-triazine-2-thione (**14**) has the capability of coordinating via a number of donor atoms. IR and Raman spectra of the tetrahedral complex $[NiL_2Cl_2]$ (L = (**14**)) indicated that coordination occurs via the sulfur atom [85].

A variety of 1:1, 2:1 and 3:1 thiosemicarbazide complexes of Ni(II) have been



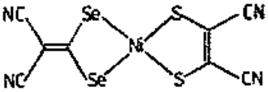
(14)

studied using IR spectroscopy. The relative stability of the Ni–S bond was found to decrease for the metal:ligand ratio in the series 1:1 > 1:2 > 1:3 [86].

The stability constants for the Ni(II) complexes of 2-methyl-hydrazinedithiocarboxylic acid, 3,3-dimethyl-hydrazinedithiocarboxylic acid, and 3-methyl-3-phenylhydrazine-dithiocarboxylic acid have been determined in aqueous solution. Both 1:1 and 1:2 complexes were observed [87].

Interest in the chemistry of Ni(II) complexes containing 1,2-dithiolate ligands has been sustained. This is exemplified by an article which discusses the structural diversity of homoleptic ethane-1,2-dithiolato complexes of the first transition series [88]. Of particular interest is the bis Ni(II) complex of maleonitrile dithiolate which has been studied in some detail. Studies include the crystal and molecular structure of its tetraethylammonium salt [89], as well as its photoelectrochemical [90], electrical conduction [91], and charge transfer properties [92]. In addition, it has been used to prepare the mixed-ligand complex, bis-tetraethylammonium(1,2-dicyanoethylene-1,2-dithiolato)(1,1-dicyanoethylene-1,1-diselenato)nickelate(II) (**15**), the crystal structure of which has been determined. The complex is essentially square planar with (Ni–S = 2.16 Å and Ni–Se = 2.23 Å) [93].

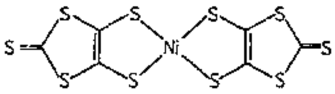
While on the subject of diselenolenes, a simplified procedure for the preparation of metal diselenolenes has been reported [94].



(15)

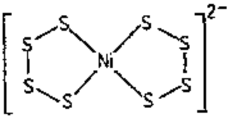
Variations on the dithiolate theme have manifested themselves in the publication of a number of unusual crystal structures. The molecular structure and solid-state properties of the two-dimensional mixed-valence complex, $[NBu_4]_{0.29}[NiL_2]$, and its neutral analogue, $[NiL_2]$ (**16**) (H_2L = 4,5-dimercapto-1,3-dithiole-2-thione), have been reported [95]. Similarly, the crystal structures of the $[Ni(S_4)_2]^{2-}$ (**17**) and $[Ni(CS_4)_2]^{2-}$ (**18**) anions have been determined as their tetraethylammonium salts [96], while the structure of the $[Ni(S_3N)(CN)_2]^-$ (**19**) anion has been determined as its tetramethyl ammonium salt [97].

A number of interesting analytical techniques have been used to study Ni(II)–dithiocarbamate complexes. ^{59}Ni and ^{62}Ni isotopic labelling has been applied in an infrared study carried out on a variety of heterocyclic dithiocarbamate nickel



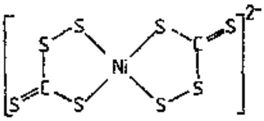
(Ni-S = 2.144(2) and 2.150(2)Å)

(16)



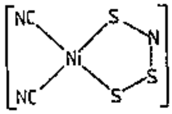
(Ni-S = 2.146(7) and2.179(3)Å)

(17)



(Ni-S = 2.174(2) and 2.165(2)Å)

(18)



(Ni-S = 2.131(4) and 2.139(6)Å)

(19)

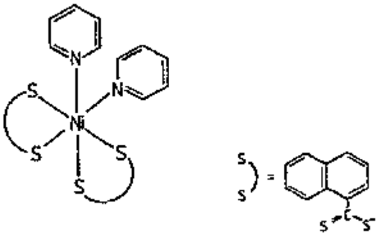
complexes, $[Ni(CH_2CH_2XCH_2CH_2NCS_2)_2]$ ($X=CH_2$, O, S, NH, H_3CN, C_6H_5CH, C_6H_5N). Assignment of the Ni-ligand vibrational modes revealed that the Ni–S bond strength is practically independent of the X substituent in the heterocycle [98]. In addition, XPS and infrared spectroscopy have been used to study a number of dithiocarbamate and xanthate complexes of nickel(II) [99]. An interesting development of this study is a correlation of the shifts in the infrared spectra with those observed for atomic core levels in the X-ray photoelectron spectra [100].

The crystal and molecular structures of bis[*N*,*N*-bis(2-hydroxyethyl)-dithiocarbamato]nickel(II) [101] and bis(pyrrolidinedithiocarbamato)nickel(II) [102] have been determined. Both complexes are essentially square planar with Ni–S bond lengths of 2.209(1) and 2.193(1) Å for the former complex and 2.214(1) and 2.198(1) Å for the latter.

ESR spectroscopy has been used to study the ligand exchange reaction between $[NiL_2]$ (L=diethyldiselenocarbamate) and a series of copper(II) dithiolene complexes. Kinetic data indicate a simple second-order rate law [103].

Turning to nickel xanthate complexes, the crystal structures of the benzene inclusion compound of the 2,2′-dipyridylamine (2,2′-dpa) nickel ethylxanthate adduct, $[Ni(S_2COEt)_2(2,2'\text{-dpa}) \cdot C_6H_6]$, and the carbon tetrachloride inclusion compound of the 4,4′-bipyridyl (4,4′-bipy) nickel butylxanthate adduct, $[Ni(S_2COBu)_2(4,4'\text{-bipy}) \cdot 2CCl_4]_n$, have been determined by single crystal X-ray diffraction methods. The coordination geometry of the nickel atom was found to be octahedral in both cases [104]. Other xanthate complexes that have been prepared are $[NiL_2]$ ($HL=ROCS_2H$; R=*iso*-Pr, *iso*-Bu, *iso*-amyl), and their corresponding mixed-ligand complexes, $[NiLL^1]$ (HL^1=oxine, 2-picolinic acid). $[NiL_2]$ were found to be square planar, whereas $[NiLL^1]$ were assigned tetrahedral stereochemistry [105].

$[NiL_2]$ (HL=α-dithionaphthoic acid) has been reacted with pyridine yielding the mixed-ligand complex, $[NiL_2(py)_2] \cdot py$, the crystal structure of which has been determined. The complex has a distorted octahedral structure with the pyridine molecules occupying *cis* positions (**20**) [106]. In addition, the structure and properties of [Ni(S_2CR)$_2$] (R = H, F, Me, Ph, MeO, MeS, Me_2N) have been studied by LCAO MO methods [107].



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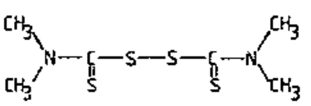
N,N,N′,N′-Tetramethylthiuramdisulfide (L) (**21**) has been complexed with a variety of nickel salts. The resultant complexes, [NiL$_2$X$_2$] (X = Cl, Br, NO_3, NCS, OAc) and [NiL$_3$]X$_2$ (X = I, ClO_4) are hexacoordinate with (L) functioning in a didentate fashion [108]. Structurally similar to (**21**), 1,1-diethyl-3-(thiobenzoyl)thiourea (**22**) reacted with Ni(II) yielding [NiL$_2$] {HL = (**22**)}. The crystal structure of this complex revealed square planar coordination with an average Ni–S bond length of 2.153 Å in the monoclinic form, and 2.163 Å in the triclinic form [109]. The complexation of a similar ligand, methylenebis(thioacetic acid) (**23**), has been studied in aqueous solution [110].



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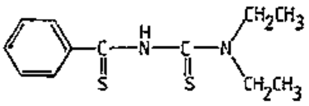

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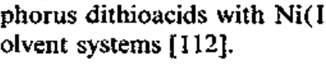

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The crystal and molecular structure of bis(*O,O′*-diisopropylphosphorodithioata)nickel(II), [NiL$_2$] {HL = $HS_2P(O\text{-}i\text{-}C_3H_7)_2$}, has been reported. Coordination about the Ni atom is square planar with equivalent Ni–S distances of average value 2.221(1) Å [111]. In addition, the stability constants of the complexation of a number of phosphorus dithioacids with Ni(II) have been determined in two-phase water–organic solvent systems [112].

4.4. *Complexes with nitrogen donor ligands*

Heterocyclic *N*-donor ligands such as pyridine, imidazole and their substituted analogues, remain the most widely used ligands in this category. Table 1 lists a

Table [illegible]
Some pyridine and substituted-pyridine complexes of Ni(II)

Ligand (L)	Complex	Comments	Ref.
Pyridine, 3-, 4-methylpyridine	$[Ni(A)_2L_2]$	(A) = *N,N*-diethyl- and piperidyl-*N'*-benzoylthiourea	[113]
4-R-Pyridine (R = H, CH_3, CH_3CO, Cl, Br, NH_2, CHO, CO_2Me, CO_2Et)	$[NiL_2X_2]$ ($X = N_3$, NCS) $[NiL_4X_2]$ ($X = N_3$, NCS)	*Trans*- or *cis*-octahedral depending on the substituent and anion used	[114]
2-R-Pyridine (R = CH_3, NH_2)	$[Ni(A)_2L_4]$	Octahedral complexes. (A) = phthalimide, succinimide	[115]
6-Methyl-pyridine-2-phosphonic acid	Various	NMR study in aqueous solution	[116]
4-Vinylpyridine	$[NiL_4(NCS)_2]$	X-ray crystal structure. Study of the clathration properties for liquid *o*-, *m*-, and *p*-xylene at 25°C	[117]

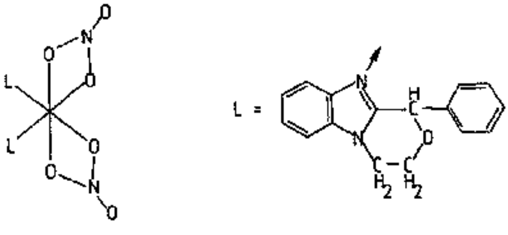
variety of substituted pyridine ligands and their nickel(II) complexes [113–117]. Of particular interest is a study of the clathrogenic properties of the $[NiL_4(NCS)_2]$ (L = 4-vinylpyridine) host [117].

While on the subject of clathrate complexes, the inclusion compounds of diisothiocyanatotetrakis(α-arylakylamine)nickel(II) complexes have been reviewed [118]. In addition, the crystal and molecular structure of $[NiL_4(NCS)_2]$ (L = α-phenyl-ethylamine) have been determined. The complex has a *cis*-octahedral structure which converts to *trans*-octahedral on clathration of *S*-butylbenzene [119].

The interaction of substituted imidazole and benzimidazole ligands with Ni(II) has been studied in a variety of ways. The stability constants of the complexation of *N*-methylimidazole [120] and series of variously-substituted benzimidazoles [121,122] with nickel(II), have been determined potentiometrically. In a related study, the extraction of nickel(II) with *N*-butylimidazole from sulfate solutions, has been examined [123].

Turning to the solid state, the crystal and molecular structure of $[NiL_2(NO_3)_2] \cdot CH_3CN$ (L = 1,2-dihydro-4-phenyl-4*H*-[1,4]oxazino[4,3-a]benzimidazole) have been reported. The coordination geometry is hexa-coordinate with the unidentate benzimidazole ligands occupying *cis* positions (**24**) [124].

A number of pyrazole derivatives have been complexed with a variety of nickel



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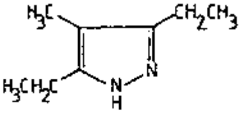
salts. Reaction of 3,5-diethyl-4-methylpyrazole (**25**) with NiX_2 (X = Cl, Br, I) yielded octahedral complexes of the type $[NiL_4X_2]$ {L = (**25**)} [125], whereas reaction of 1-methyl-3,4-diphenylpyrazole (L) (**26**) with NiX_2 (X = Cl, Br, I, NO_3) yielded $[NiL_2X_2]$ (X = Cl, NO_3), $[NiL_3Br_2]$ and $[NiL_4I_2]$, which have a variety of stereochemistries depending on the anion used [126]. A similar ligand, 3,5-diamino-1,2,4-triazole (**27**), when reacted with nickel nitrate, yielded the complex $[NiL_2(NO_3)_2]$ {L = (**27**)}, in which L is coordinated via the heterocyclic N atoms [127].



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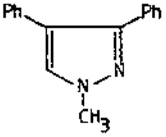

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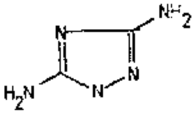

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The thermal behaviour of a number of nickel(II)–morpholine complexes has been studied. Complexes prepared and investigated include $Ni(CN)_2 \cdot 1.5L$, $NiBr_2 \cdot 3L$, $NiI_2 \cdot 4L$ and $Ni(NCS)_2 \cdot 4L$ (L = morpholine) [128].

A number of primary amines have been complexed with Ni(II). The hepta- and octaammoniates of nickel(II) thiocyanate, $Ni(NCS)_2 \cdot nNH_3$ ($n = 7,8$), have been prepared by the reaction of NH_3 with $Ni(NCS)_2$ at −35.4°C [129]. In addition, 4-aminobenzophenone (L), which has the ability to coordinate via its N or O donor atoms, has been complexed with a number of Ni(II) salts. Coordination occurs via the primary amine moiety in the complexes $NiL_2Cl_2 \cdot H_2O$, $NiLX_2$, NiL_2X_2 and NiL_6X_2 (X = NO_3), while in the remainder of the complexes it occurs via the carbonylic oxygen atom [130].

Diamines continue to be the most prominent ligand in this category (see Table 2), with the emphasis moving away from ethylenediamine to its variously-substituted analogues. Ligands that have been complexed with Ni(II) include variously-substituted ethylenediamines [131–134], propanediamines [135–137] and butanediamines [138–141]. In addition, the kinetics of ternary complex formation between (triethylenetetramine)nickel(II) and ethylenediamine, 2,2′-bipyridine, and sarcosine, has been studied [142].

The synthesis of the new amine ligand, 3-(aminoethyl)-3-methylazetidine (L) (**28**), and its complex with Ni(II), $[NiL_3](ClO_4)_2 \cdot H_2O$, have been reported. Both meridional and facial configurations are possible for the complex [143].

Dioxime ligands, like their diamine counterparts, have the ability to chelate in a

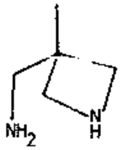

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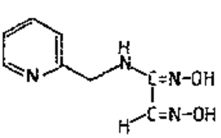
Table 2
Various diamine ligand complexes of Ni(II)

Ligand (L)	Complex	Comments	Ref.
$H_2NCH_2CH_2NH_2$	$[NiL_2(NO_2)_2]$	$[NiL_2(NO_2)_2] \rightleftharpoons [NiL_2(NO_2)]NO_2$ isomerism	[131]
meso-$H_2NCH(Ph)CH(Ph)NH_2$	$[NiL_2]Cl_2 \cdot 2H_2O[NiL_2]X_2$	Square planar; crystal structure	[132,133]
	$(X = Cl, Br, I, NO_3, ClO_4)$	Square planar-octahedral transformations	
dl-$H_2NCH(Ph)CH(Ph)NH_2$	$[Ni(H_2O)_2L_2]X_2$ $(X = Cl, Br, NO_3)$	Octahedral	[133]
$(CH_3)_2NCH_2CH_2NH_2$		Potentiometric study	[134]
$H_2NCH_2CH_2CH_2NH_2$	$[NiL_3](NO_3)_2$	Octahedral; crystal structure	[135,136]
$H_2NCH_2CH(NH_2)CH_3$	$[NiL_3](NO_3)_2$		[136]
$H_2NCH_2C(NH_2)(CH_3)_2$	$[NiL(CN)_2][NiL_2]^{2+}$	Kinetic study Potentiometric study	[137,138]
$H_2NCH_2CH_2NH(i\text{-}Pr)$	$[NiL]^{2+}$	Potentiometric study	[138]
$H_2NCH_2CH_2N(R)_2$ $(R = CH_3, CH_3CH_2)$	$[NiL_3](NO_3)_2$		[136]
$H_2N(CH_2)_4NH_2$	$[NiL_3]Cl_2 \cdot H_2O[NiL_2(H_2O)_2]$ $Br_2[NiL_2(NCS)_2]$	Thermal investigation	[139]
meso-$CH_3CH(NH_2)CH(NH_2)CH_3$		Potentiometric study	[140]
$H_2N(CH_2)_2N(H)(CH_2)_2Cl$	$[NiL_2 Cl_2]$	Infrared study	[141]

didentate fashion, usually via their nitrogen donor atoms. A variety of dioxime ligands, including bis(diethylamino)glyoxime [144], amino(methyl)glyoxime [145], 1,2-benzoquinone dioxime [146], iminobis(acetamidoxime) [147], and dibenzo-[f,o]-2,3-bis(hydroxyimino)-1,4-diazo-8,11,14-trioxa-2,3,9,10,12,13-hexahydrocylo-heptadecine [148], have been complexed with Ni(II). Preference for coordination via the dioxime moiety over other functional groups is manifested in the Ni(II) complexes of *N*-(2-methylpyridyl)aminoglyoxime (**29**) [149] and 2-oxime-3-oximatopiperazine (**30**) [150].

In an ongoing series, the spectral and magnetic properties of Ni(II) complexes of quinoline-2-aldoxime and isoquinoline-3-aldoxime have been investigated. The complexes, $[NiL_2X_2]$ (L = quinoline-2-aldoxime, isoquinoline-3-aldoxime; X = Cl, Br, I, NCS, NCSe, OAc, $1/2SO_4$) were assigned a dimeric halo-bridged *cis*-octahedral structure for halo complexes, while the remaining complexes were assigned a monomeric *cis*-octahedral structure [151].



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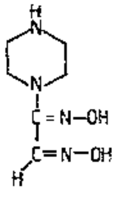

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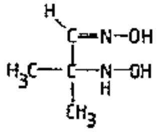
The complexes, $[Ni(HL)_2]$, have been prepared from the sterically hindered oximes {HL = (**31**), (**32**)}. Reaction with oxidizing agents yielded the dehydrogenated complexes, $[NiL_2]$, which have been assigned square planar stereochemistry [152].



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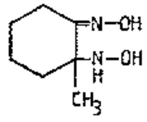

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The complexation of Ni(II) with a number of azo-ligands containing heterocyclic fragments has been studied both in the solid state and solution. Complexes that have been isolated are tetrahedral $[NiL_2]$ {HL = 2-(2′-*N*-phenylaminonaphthylazo)-1-methylbenzimidazole, 2-(2′-hydroxynaphthylazo)-1-benzimidazole} [153], square planar $[NiL_2]$ {HL = 1-phenylazo-2-naphthylamine} [154], and distorted square planar $[NiL_2](ClO_4)_2$ {L = 4-methyl-2-(pyridylazo)resorcinol} [155]. In addition, the complexation of 4-(2-pyridylazo)resorcinol [156] and pyridine-2-azo-*para*-dimethylaniline [157] with Ni(II), have been investigated in solution. In the above complexes, coordination was found to generally occur via the nitrogen atoms of the azo group and the appended heterocyclic fragment.

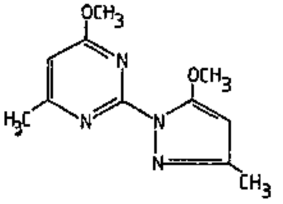
A number of variously-substituted pyridine ligands have been complexed with

Ni(II). Di-2-pyridyl ketone (L), 2-pyridyl *N*-methyl-2-imidazolyl ketone (L^1) and di(*N*-methyl-2-imidazolyl) ketone (L^2) reacted with $Ni(NO_3)_2$, yielding the octahedral complexes $[Ni(L)(H_2O)_2(NO_3)_2]\cdot 1/2H_2O$, $[Ni(L^1)_2(NO_3)_2]\cdot 1/2H_2O$ and $[NiL^2_2(NO_3)_2]\cdot 3/2MeOH$, respectively. The former complex is of interest as the ligand has been hydrated during complexation forming a geminal diol [158].

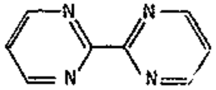
TGA and DTA have been used to study the thermal behaviour of the nickel complexes of a series of pyridyl substituted sulfonamides. Of particular interest is the complex $[NiL_2(H_2O)_2]$ ($HL = C_5H_5NCH_2NHSO_2Ph$) which exhibits reversible transition of coordinated H_2O to lattice H_2O. Apparently, this is the first example of isomerism of the Lifschitz-type in the field of neutral chelates [159].

Complex formation of 2-amino-3-aminomethyl-4,6-di-methylpyridine and 2-amino-3-aminomethyl-4-methyl-6-methoxymethylpyridine with Ni(II) has been studied potentiometrically. Both 1:1 and 2:1 (ligand:metal) complexes were observed in solution [160]. Similarly, the stability constants of the mixed-ligand complexes of Ni(II) with 2,2′-bipyridine, 1,10-phenanthroline, and thioformohydroxamic acid [161], as well as with 1,10-phenanthroline and a series of *N*-(*para*-substituted-phenyl)glycines [162], have been determined in aqueous solution.

4-Methoxy-2-(5-methoxy-3-methylpyrazol-1-yl)-6-methyl pyrimidine (**33**), when reacted with Ni(II), yielded the octahedral complex, $[NiL_3](ClO_4)_2$ {L = (**33**)} [163]. 2,2′-Bipyrimidine (**34**) reacted in a similar fashion, yielding the analogous complex, $[NiL_3](ClO_4)_2$ {L = (**34**)}, which has been studied spectroscopically [164].



(**33**)



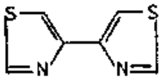
(**34**)

2-Methyl- and 2-phenyl-3-(2′-pyridyl)-quinazolin-(3*H*)-4-one reacted with $NiCl_2$ yielding octahedral complexes of the type, $[NiL_2Cl_2]$. The related ligands 2-methyl- and 2-phenyl-3-hydroxyquinazolin-(3*H*)-4-one reacted with deprotonation, yielding square planar complexes of the type, $[NiL_2]$ [165].

The new pyrazolone ligands, bis-methylaminoantipyrylpropane and bis-methylaminoantipyrylbutane (L), have been prepared and reacted with $Ni(NCS)_2$. The resultant complexes, $[NiL(NCS)_2]$, are square planar, with the ligands functioning in a didentate fashion [166].

The nickel(II) complexes of 4,4′-bithiazole (**35**) [167] and (4-pyridine-2-yl)thiazole (**36**) [168] have been prepared. Crystal and molecular structures of both complexes, $[NiL_3]^{2+}$ {L = (**35**) or (**36**)}, isolated as their perchlorate salts, have been determined. Both complexes are essentially octahedral with average Ni–N bond lengths of 2.082(2) Å and 2.088(5) Å, respectively.

The poly(2-mercaptobenzothiazolyl)borate ligands ($L = BH_{4-x}R_x$, R =



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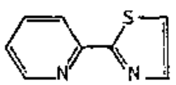
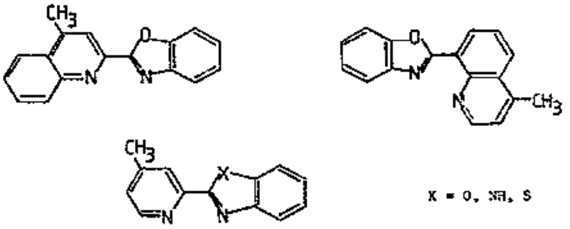


(36)

2-mercapto-benzothiazolyl; $x=2, 3, 4$), have been reacted with Ni(II). Spectroscopic evidence indicates that the complexes, $[NiL_2]$ ($x=2, 4$), are square planar whereas the complex, $[NiL_2]$ ($x=3$), is octahedral [169].

A series of 2-(4′-methyl-2′-pyridyl and 2′- or 8′-quinolyl)-benz-X-azoles (X=O, NH, S) (**37**) have been prepared and reacted with $NiCl_2$. All of the ligands function in a didentate fashion coordinating via the pyridine and isoxazole nitrogen atoms. The stereochemistry of the nickel atom varies from distorted octahedral to pentacoordinate [170].

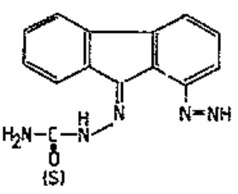


(37)

Turning to Schiff bases, the ligands 4-RC_6H_4N:CHCH:C(C_6H_4R'-4)NHC_6H_4R-4 (HL; R=H, Me, MeO, EtO, Br; R′=H, Br) have been reacted with Ni(II). The resultant complexes, NiL_2, are tetrahedral with coordination occurring via both N atoms [171]. In addition, the interaction of Ni(II) with the Schiff base sulfadimethoxine salicylaldimine has been investigated potentiometrically in dioxane–water. Both 1:1 and 1:2 (metal:ligand) complexes were observed [172].

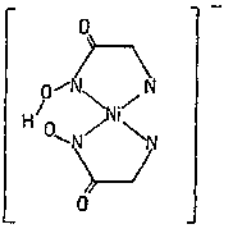
1-Azafluorenone semicarbazone and thiosemicarbazone (L) (**38**), when reacted with NiX_2 (X=Cl, NO_3), yielded the hexacoordinate complexes, $[NiL_2X_2]$. L is coordinated via the imino N and azofluorenone N atoms [173].

The crystal and molecular structure of sodium bis(aminoaceto-



(38)

hydroxamate)nickel(II) have been reported. The complex is essentially square planar, but is unusual in that one of the ligands is doubly-deprotonated, whereas the other is only singly-deprotonated (**39**) [174].



(**39**)

1,2,3-Triamino-2-methylpropane L functions in a tridentate fashion when complexed with Ni(II), yielding the complex, $[NiL_2](ClO_4)_2$. The ligand field of L is significantly stronger than that of ethylenediamine [175].

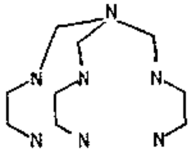
Another tridentate ligand that has elicited interest is terpyridine (L). The crystallographic data of the octahedral complexes, $[NiL(H_2O)_3]Cl_2$, $[NiL(H_2O)(NO_3)_2]$, and $[NiL(H_2O)(CN)_2]$ have been reported [176]. Similarly, the complex formation reactions of Ni(II) with 2,2′:6′,2″-terpyridine have been studied in aqueous solution [177].

The structure of the *cis*-facial isomer of bis[2,2′-iminodi(acetamide oxime)-*N*,*N*′,*N*″]nickel(II) dichloride has been reported. The two terdentate ligands are attached to opposite faces of a distorted Ni(II) octahedron. Coordination occurs via the amino nitrogen and two oxime nitrogen atoms [178].

Polydentate tripod ligands and their metal complexes continue to attract interest. The crystal and molecular structure of the compound, $[NiL(NO_3)](NO_3)$, where L is the tripodal tetradentate ligand, tris(3,5-dimethylpyrazol-1-ylmethyl)amine, have been reported. The complex has a distorted octahedral structure with the nitrate ion functioning in a symmetrically didentate fashion [179]. In a separate article, the same ligand has been reacted with a number of nickel salts. Reaction with NiX_2 (X = Cl, NCS) resulted in complexes of the type $[NiLX_2]\cdot 3/2H_2O$, whereas reaction with $Ni(BF_4)_2$ resulted in complexes of type $[Ni_2L_3](BF_4)$ and $[Ni_2L_2F_2](BF_4)_2$ [180]. Other tripodal ligands that have been reacted with Ni(II) are the tetradentate ligand, 2,4,8-trimethyl-5-(3-methyl-3-azabutyl)-2,5,8-triaza-4(*S*)-nonane [181] and the pentadentate ligand, *N*,*N*,*N*′-tris((3,5-dimethylpyrazol-1-yl)-methyl)-1,3-diaminopropane) [182].

The preparation and characterization of the Ni(II) complex of tris(((aminoethyl)amino)methyl)amine (L) (**40**), isolated as its perchlorate salt, $[NiL](ClO_4)_2$, has been reported. The complex was assigned pseudooctahedral geometry [183].

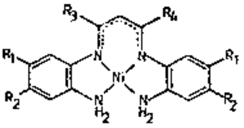
The reaction of triethylenetetramine (trien) with the nickel complexes, nickel(II) *N*,*N*′-bis(2-aminoethyl)malonamidate [184] and nickel(II) *N*,*N*′-bis(2-aminoethyl)oxaldiamide [185] has been investigated. Transfer of the Ni(II) ion to trien, to form $Ni(trien)^{2+}$, proceeds via three general pathways.



(40)

Condensation of phenylbiguanide and benzil yields the tetradentate Schiff base, [PhNHC(:NH)NHC(:NH)N:C(C_6H_5)]$_2$ (H_2L), which has the ability to function in neutral, uninegative, or binegative form, depending on the pH. Reaction with Ni(II) yielded complexes of the type, [Ni(H_2L)Cl_2], [NiLX_2] (X=py, α-, β-, γ-picoline) and [NiL] [186].

Continuing with Schiff bases, the synthesis and characterization of a series of Ni(II) complexes of linear tetradentate ligands, derived from *N,N″*-(1,3-propanediylidene)bis(1,2-benzenediamine) (**41**), have been reported [187]. Similarly, a series of tetradentate bis-imine nickel(II) complexes, formed from various 7-formylindoles and 1,2-diaminobenzene (**42**), has been prepared [188].



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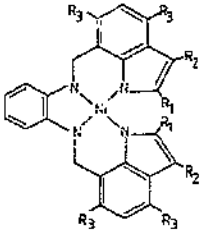

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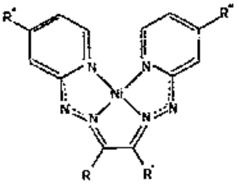
The tetradentate hydrazone ligands, prepared by the condensation of 2 mol of 2-pyridylhydrazine with an α-diketone (**43**). have been complexed with Ni(II), yielding both monomeric and dimeric species [189]. In addition, diacetylbis(2-pyridyl)-hydrazone has been utilized as an extracting agent for Ni(II) [190].



(43)

The crystal and molecular structure of [2,4-pentanedione bis-*S*-methylthiosemicarbazonato (2-)]nickel(II) iodide has been determined. Coordination occurs via the four N atoms of the thiosemicarbazide ligand with the stereochemistry of the Ni(II) ion being essentially square planar [191].

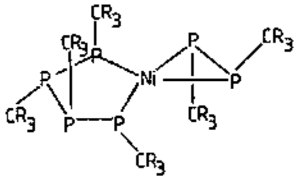
4.5. Complexes with phosphorus donor ligands

The ability of phosphine ligands to stabilise complexes containing Ni–C σ-bonds has been known for some time. A series of compounds of the type *trans*-[NiR(R′)L_2] (L = PMe_2Ph, PEt_3; R and R′ = variously-substituted benzene or ethylene ligands) has been prepared, and the structure of one of these complexes, [$Ni(C_2Cl_3)(C_6H_2Me_3$-2,4,6)$(PMe_2Ph)_2$], has been determined [192]. In a separate study, photoreactions of the complexes, *trans*-[Ni{2,6-$(MeO)_2C_6H_3$}$_2L_2$] (L = Me_3, PMe_2Ph), have been studied in order to investigate the excitation effects on the Ni–L and Ni–C bonds [193].

$(Ph_3P)_2NiBr_2$ when reacted with *nido*-2,3-$Et_2C_2B_4H_5{}^-$ in THF, yielded the unusual complex 1-Br-1,5-$(Ph_3P)_2$-1,2,3-Ni$(Et_2C_2B_4H_3)$. The crystal structure of this complex reveals that the phosphino ligands are attached to the nickel and boron atoms, respectively. In addition, it is the first metallacarbaborane of Ni(II) containing a Ni–Br bond to be reported [194]. Similarly, 6,6′-$(B_{10}H_{13})_2O$ has been reacted with *cis*-[$NiCl_2(PMe_2Ph)_2$] yielding a variety of known phosphine-boranes, as well as a low yield of the metallaborane, *closo*-[$(PhMe_2P)_2NiB_9H_7Cl_2$], the crystal and molecular structure of which have been determined. In this complex, the chlorine atoms are attached to boron atoms, as is usually the case [195].

The complex, [Ni(P{NEt_2}$_3$)Br_2], has been prepared from $NiBr_2$ and $P(NEt_2)_3$. IR and NMR data indicate that the phosphorus acid amides are P-bonded [196].

The synthesis and X-ray crystal structure of the nickel phosphametallocyclopentane complex, [(*t*-BuPP-*t*-Bu)Ni(*t*-BuP-*t*-BuP-*t*-BuP-*t*-BuP)] (**44**), have been reported. The complex is unique for two reasons. Firstly, it contains the phosphametallocyclopentane unit which demonstrates the first example of a coupling reaction between two P=P units at a metal centre and, secondly, it is the first example of a mononuclear η^2-bonded diphosphane transition metal complex that does not have Cp, CO or PR_3 as stabilizing ligands [197].



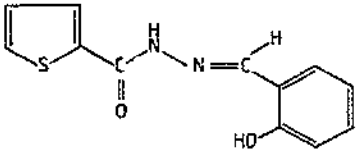
(44)

The crystal and molecular structure of the biphosphalene complex, dichloro[2,2′-bi(1-phenyl-3,4-dimethyl-2,5-dihydro-1*H*-phosphole)]nickel(II), have been determined. The coordination geometry is essentially square planar with both the Ni–P bonds (2.236 Å) being noticeably short [198].

4.6. Complexes with nitrogen–oxygen donor ligands

Ligands derived from the condensation of aldehydes and ketones with amines and diamines, such as Schiff bases, hydrazones, oximes, azines, carbazones, and semicarbazones, continue to dominate this category. As in previous years, the main thrust is still on Schiff base, and to a lesser degree, hydrazone ligands.

A variety of *N*,*O*-donor Schiff base ligands are listed in Table 3 [199–237]. The didentate ligands tend to coordinate via a deprotonated hydroxyl group and an imino nitrogen atom, yielding neutral square planar complexes of the type [NiL_2], or their bis aquo analogues, [$NiL_2(H_2O)_2$], which are usually octahedral. Of particular interest is *N*-(thiophene-2-carboxamido) salicylaldimine (**45**) which functions as a didentate or tridentate ligand, giving rise to a number of Ni(II) complexes, depending on the reaction conditions employed [202].



(45)

A number of coordination possibilities are available to tridentate Schiff base ligands, of which N,N,O [209,210], N,O,N [211] and O,N,O [212–214] have been reported. Complexes are generally of the form [NiLX] (H_2L = tridentate Schiff base; X = monodentate ligand). Noticeable exceptions are the Ni(II) complexes of the Schiff bases formed from 4-acetyl-3′-methyl-1-(3′-chlorophenyl)-2-pyrazolin-5-one and a series of amines. In these complexes, the stereochemistry was found to be strongly dependent on the substituted amine used [211].

Turning to tetradentate Schiff base ligands, the predominant mode of coordination is O,N,N,O and square planar complexes of the type [NiL] (H_2L = dibasic tetradentate Schiff base ligand) are widely encountered [215–245]. An encouraging development is the appearance of a large number of asymmetric tetradentate azomethine ligands [226–231]. Of particular interest is a report in which optically pure α-methyl-α-amino acids have been prepared via alkylation of the asymmetric Ni(II) Schiff base complex formed by the reaction of (*R*,*S*)-alanine with (*S*)-2-*N*-(*N*′-benzylprolyl)aminobenzaldehyde (**46**) [228].

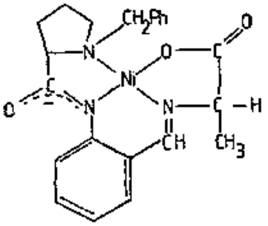
The Schiff bases derived from 2-acetyl-1,8-dihydroxy-3,6-dimethylnaphthalene and a series of diamines [232], as well as those prepared from 2-hydroxy-3-carboxy-1-naphthaldehyde and a series of substituted 1,2-diaminobenzenes [233], have the potential to form dinuclear complexes. Reaction with Ni(II) yielded only mononuclear complexes, with the nickel ion preferring N_2O_2 coordination, as opposed to O_4 coordination.

The asymmetrical Schiff base complex, *N*-salicylaldehyde-*N*′-acetylacetoneethylenediaminonickel(II), has been reacted with *p*-nitrobenzenediazonium tetrafluoroborate, yielding the substituted *p*-nitrophenylazo complex (**47**). The coor-

Table 3
Nitrogen–oxygen donor Schiff base ligands and their Ni(II) complexes

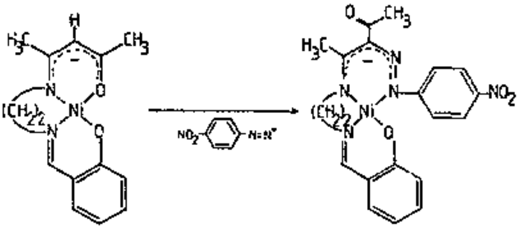
Ligand	Complex	Comments	Ref.
Didentate			
4-Salicylideneamino-1,2,4-triazole (HL)	[NiL_2]	Photochemical study	[199]
4-(2-Methoxybenzylidene) amino-1,2,4-triazole (HL)	[NiL_2]	Photochemical study	[199]
N-Alkylsalicylaldimine (HL),*N*-Alkylbenzoylacetoneimine (HL)*N*,*N*′-Disalicylideneethylenediamine (HL)	[NiL_2][NiL_2][NiL_2]	Study on the reactivity of planar and tetrahedral configurational isomers and a variety of octahedral adducts	[200]
(*N*-Salicylideneacetylhydrazino pyridinium) chloride		Potentiometric study	[201]
N-(Thiophene-2-carboxamido)salicylaldimine (H_2L)	[$Ni(H_2L)_2Cl_2$]	Octahedral	[202]
	[Ni(HL)Cl]	Pseudo-octahedral polymeric	[202]
	[$NiLX_2$]	Octahedral; ($X = H_2O$, pyridine)	[202]
	[$Ni(HL)_2$]	Octahedral; ligand functions as O,O,N donor	[202]
2-Salicylideneamino-5-phenyl-1,3,4-thiadiazole (HL)	[NiL_2]	Solution study	[203]
2-Salicylideneimino-5-(*p*-anisyl)-1,3,4-thiadiazole (HL)	[$NiL_2(H_2O)_2$]	Octahedral stereochemistry	[204]
2-(2′-Hydroxyacetophenoneimino)-5-(*p*-anisyl)-1,3,4-thiadiazole (HL)	[$NiL_2(H_2O)_2$]	Octahedral stereochemistry	[204]
N-(2,5-Dihydroxyacetophenoneimino)-2,5-dichloroaniline (H_2L)	[$NiL_2(H_2O)_2$]	Coordination occurs via azomethine N and phenolic O atoms	[205]
N-(2-Hydroxy-1-naphthylidene)benzylamine (HL)	[$NiL_2(H_2O)_2$]	Potentiometric study	[206]
o-Hydroxynaphthaldimine (HL)	[NiL_2]	^{13}C-NMR study in solution	[207]
N-(*o*-Hydroxyacetophenoneimine)-l-tyrosine hydrazide (H_2L)	[$Ni(H_2L)_2Cl_2$]	H_2L functions as a neutral didentate ligand	[208]
Tridentate			
N-(*o*-Hydroxyacetophenoneimine)-l-tyrosine hydrazide (H_2L)	[$NiL(H_2O)$]	H_2L functions as a binegative tridentate species	[208]
7-Amino-4-methyl-5-aza-3-heptene-2-one (HL)	[NiL(py)]ClO_4	Square planar	[209]
N-(Pyrrole-2-carboxaldimine)ethanolamine (H_2L)	[$NiL(H_2O)$]	Template synthesis of L^{2-}	[210]
N-(4-Acetyl-3-methyl-1-(3′-chlorophenyl)-2-pyrazolin-5-oneimine)-R (HL)	[$NiL_2(H_2O)_2$]	($R = o$-, m-$H_3CC_6H_4NH_2$, m-$ClC_6H_4NH_2$)	[211]
	[$NiL(OAc)(H_2O)_2$]	($R = p$-$ClC_6H_4NH_2$)	
	[Ni_2]	($R = HOCH_2CH_2NH_2$, glycine)	
Pyridoxylideneglycine (H_3L)	[$Ni(H_2L)_2$]$\cdot 6H_2O$	Octahedral; crystal structure	[212]
N-(Acetylacetoneimino)-R (R = amino acid) (H_2L)	[$NiL(H_2O)_2$]	Octahedral	[213]
O-(α-Benzoylmethylbenzylideneimino)benzoic acid (H_2L)	[Ni(L)X]	($X = H_2O$, pyridine)	[214]

Tetradentate			
Bis(acetylacetone)ethylenediimine (H_2L)	[NiL]	Kinetic and mechanistic study	[215]
Bis(2-thienylglyoxal)-1,2-benzyldiimine (L)	[NiLCl$_2$]	Octahedral	[216]
Disodium *N*,*N*′-propane-1,3-diylbis-(salicylideneimine-5′-sulfanato) $Na_2(H_2L)$	Na_2[NiL]·2H_2O	Square planar	[217]
Disodium *N*,*N*′-ethylenebis(5-sulfosalicylideneimine) $Na_2(H_2L)$	Na_2[NiL]·2H_2O	$^1O_2$ quenching study in aqueous solution	[218]
N,*N*′-Ethylenebis(acetylacetoneimine) (H_2L)	[NiL]·*n*H_2O	TGA/DTA study	[219]
N,*N*′-1,2-Diphenylethylenebis(benzoylacetonateimine) (H_2L)	[NiL]		[220]
N,*N*′-1,2-Phenylbis(salicylaldimine) (H_2L)	[NiL]	Template synthesis of L^{2-}; crystal structure	[221,222]
N,*N*′-Ethylenebis(dehydroacetic acid imine) (H_2L)	[NiL(H_2O)]		[223]
N,*N*′-1,2-Phenylbis(salicylaldimine) (H_2L)	[NiL(H_2O)$_2$]	Octahedral; other Schiff base ligands	[224]
N,*N*′-Ethylenebis(5′-R′-2′-hydroxyacetophenoneimine) (R = CH_3, Cl) (H_2L)	[NiLB]	(B = 2,2′-bipyridine; 1,10-phenanthroline)	[225]
N-R-[(*S*)-*o*-(*N*-Benzylprolyl)aminoacetophenoneimine] (R = various amino acids) (H_2L)	[NiL]	Crystal structure for R = (*S*)-valine has been determined	[226,227]
N-(*R*,*S*)-Alanine (*S*)-2-*N*-(*N*′-benzylprolyl)amino-benzaldehydimine (H_2L)	[NiL]	Used as a synthon for the preparation of optically pure α-methyl-α-amino acids	[228]
N,*N*′-1,5-3-Azapentane(R-imine)(R′-imine) (R = salicylaldehyde, R′ = 2′-hydroxyacetophenone) (H_2L)	[NiL]	Template synthesis of asymmetric Schiff base ligand	[229]
N,*N*′-1,2-Benzyl(R-imine)(R′-imine) (R = 1-methoxy-1-butene-3-one; R′ = 3-ethoxymethylpentane-2,4-dione) (H_2L)	[NiL]	Asymmetric Schiff base ligand	[230]
N,*N*′-Ethylene (pentane-2,4-dioneimine)(2-pyrrole-carboxaldimine) (H_2L)	[NiL]	Square planar; crystal structure	[231]
N,*N*′-R-Bis(1,8-dihydroxy-3,6-dimethyl-2-acetyl-naphthalene) (R = ethyl; 1,2-propyl) (H_4L)	[Ni(H_2L)]	C_2 symmetry	[232]
N,*N*′-1,2-Benzyl bis(2-hydroxy-3-carboxyl-1-naphthaldimine) (H_4L)	[Ni(HL)]	Potentially dinucleating ligand	[233]
N,*N*′-1,2-R-Benzyl(2-hydroxy-3-carboxy-1-naphthaldimine)(2-hydroxy-5-methyl isonaphthaldimine) (H_3L)	[Ni(HL)]	Potentially dinucleating ligand	[233]
Polydentate			
Bis(2-hydroxy-1-naphthylideneimine-3-propyl)amine (H_2L)	[NiL]	Electrochemical investigation	[237]



(46)

dination sphere changes from O,N,N,O to N,N,N,O via a rearrangement of part of the chelate ring [234].

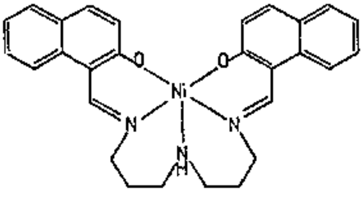


(47)

The equilibrium of the species, formed by adding $NaBPh_4$ to solutions of *N*,*N*′-ethlenebis(salicylideneaminato)nickel(II) and *N*,*N*′-*o*-phenylenediaminebis-(salicylideneaminato)nickel(II). has been studied spectrophotometrically. Comparison with other cations revealed that the complexes exhibit a preference for Na^+ [235].

$SiCl_4$ when reacted with NiL (H_2L = bis-Schiff bases derived from 5-(R-substituted)salicylaldehyde {R = H, Cl, CH_3} or 2-hydroxynaphthaldehyde and $H_2N(CH_2)_nNH_2$ {$n = 2, 3$} or *o*-phenylenediamine) yielded complexes of the type $[LNi(\mu\text{-}Cl)_2SiCl_2]$ [236].

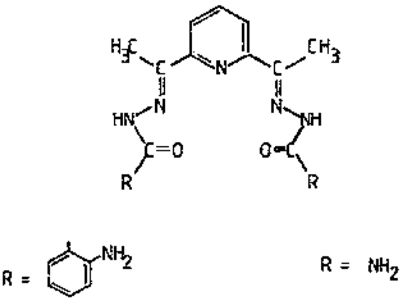
The electrochemical behaviour of the penta-coordinated nickel complex, bis(2-hydroxy-1-naphthylideneimine-3-propyl)aminonickel(II) (**48**), has been investigated in aprotic solvent [237].



(48)

A variety of hydrazone ligands have been complexed with Ni(II) (see Table 4). Complexes containing didentate [238–242], tridentate [243–247] and pentadentate ligands [249], have been reported. In addition to the complexes listed in Table 4, a series of mononuclear and dinuclear complexes of Ni(II) with the aroylhydrazones of a number of β-dicarbonyl compounds have been prepared [248].

Of particular interest are the structurally related ligands 2,6-diacetylpyridinebis(2-aminobenzoylhydrazone) (**49**) and 2,6-diacetylpyridinebis(semicarbazone) (**50**). The former ligand was reacted with nickel chloride, yielding $[Ni(H_2L)_2Cl_2]$ $\{H_2L=(\mathbf{40})\}$ [249], while reaction of the latter with $Ni(NCS)_2$ yielded $[Ni(H_2L)_2(NCS)_2]$ $\{H_2L=(\mathbf{50})\}$ [250]. Both ligands function in a pentadentate fashion (O,N,N,N,O) and were assigned pentagonal bipyramidal structures, of which the latter has been verified via a single crystal X-ray determination.



(49) **(50)**

Continuing with semicarbazones, the aminoguanizones of pyruvic acid (H_2L) and salicylaldehyde (HQ) have been complexed with Ni(II). The resultant complexes, $[Ni(HL)_2]$ and $[NiQ(H_2O)]$, were octahedral and square planar, respectively, with both ligands functioning as O,N,N donors [251]. In addition, the complexation of *p*-chlorobenzaldehydesemicarbazone with Ni(II) has been studied in solution. Both 1:1 and 1:2 complex species were observed [252].

Turning to carbazones, the stability constants for the complexation of Ni(II) with a variety of substituted diphenylcarbazones have been determined. Electron withdrawing groups and, in particular, NO_2, had a profound effect on the stability constants [253].

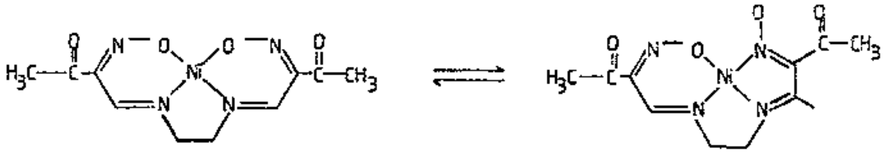
The synthesis of 1,3-diphenyl-4,4-bis(hydroximino)imidazolidine (H_2L), and its complexation with Ni(II), have been reported. The resultant complex, $[Ni(HL)_2]$, has a tetrahedral structure, as verified by a range of spectroscopic techniques [254]. In addition, the extractive properties of a series of α-amino oximes towards Ni(II) have been investigated [255].

The vicinal oxime-imine ligand, *N*,*N*-ethylenebis(*iso*-nitrosoacetylacetoneimine) (H_2L), is of interest, since a number of coordination modes are possible. Reaction with Ni(II) acetate yielded the neutral complex, [NiL], in which both oximato groups are coordinated to Ni(II) via the oximino-oxygen atoms (**51**). The linkage

Table 4
Some hydrazone ligands and their Ni(II) complexes

Ligand	Complex	Comments	Ref.
Didentate			
3-Bromo-2-hydroxy-5-methylacetophenone hydrazone (HL)	$[NiL_2(H_2O)_2]$	Coordinates via hydroxy O and imino N atoms	[238]
o-Hydroxyacetophenone (*N*-benzoyl)glycylhydrazone (H_2L)	$[Ni(H_2L)_2Cl_2]$	Octahedral	[239]
	$[NiL(H_2O)_3]$	Octahedral; ligand functions in tridentate fashion	
Acetone (*N*-benzoyl)glycylhydrazone (H_2L)	$[Ni(H_2L)_2Cl_2]$	Octahedral	[240]
	$[NiL(H_2O)_3]$	Octahedral; ligand functions in tridentate fashion	
o-Carboxyphenylhydrazoethylacetoacetate (H_2L)		Potentiometric study	[241]
Vanillin hydrazone (HL)		Potentiometric study	[242]
Tridentate			
3-Hydroxyamino-2-butanone-1-benzoylhydrazone (H_2L)	$[Ni(H_2L)_2]X_2 \cdot 2H_2O$	Octahedral; ($X = Cl, Br, NO_3, ClO_4$)	[243]
	$[NiL]$	Diamagnetic	
	$[NiL(py)_3]$	Octahedral	
Pyridine-2-carboxaldehyde isonicotinoylhydrazone (HL)	$[Ni(HL)X_2]$	Octahedral; ($X = Cl, NCS$)	[244]
	$[Ni(HL)Br_2]$	Trigonal bipyramidal	
	$[NiL_2]$	Octahedral	
α-Hydroxy-β-naphthaldehydepyridylhydrazone (HL)	$[NiL_2]$	Octahedral	[245]
α-[(2-Hydroxyphenyl)azo]-α-acetoacetonitrile	$[NiL]$	Kinetic and mechanistic study	[246]
α-(8-Quinolylazo)-α-acetoacetonitrile	$[NiL]$	Kinetic and mechanistic study	[246]
	$[NiL_2]$	Determination of formation constants	[247]
Polydentate			
2,6-Diacetylpyridine bis-(2-aminobenzoylhydrazone) (H_2L)	$[Ni(H_2L)Cl_2] \cdot H_2O$	Ligand coordinates in a quinquedentate fashion	[249]
	$[NiL]$		

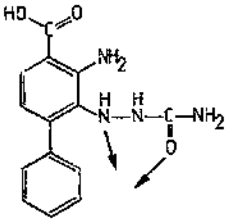
isomer (**52**), in which one group is coordinated via the oximino-nitrogen atom, has been prepared from (**51**). Both complexes were assigned square planar stereochemistry [256].



(51) **(52)**

Phenylacetylhydrazine (L) has been reacted with a variety of nickel salts. The resultant complexes, $[NiL_3]X_2$ ($X = Cl, NO_3, 1/2SO_4$) and $[NiL_2(NCS)_2]$, are octahedral with L coordinating via the nitrogen atom of the primary amino group and the oxygen atom of the carbonyl group. $[NiL_2(NCS)_2]$ was assigned a *trans* configuration on the basis of its infrared spectrum [257].

The preparation and characterization of the nickel(II) complexes of 1-anthranyl-4-phenyl-3-semicarbazide (**53**) and 1-anthranyl-4-phenyl-3-thiosemicarbazide (**54**) have been reported. The resultant complexes, $[NiL_2]$ {HL = (**53**) or (**54**)}, are tetrahedral, with both ligands functioning in a didentate fashion, but with different coordination sites as shown below [258].



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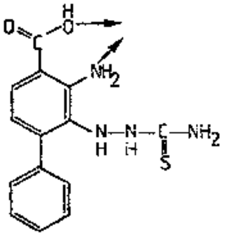


(54)

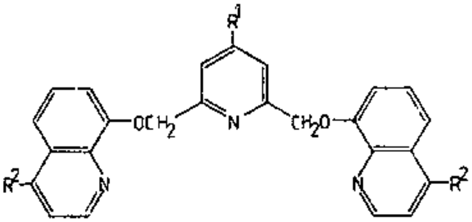
While on the subject of semicarbazide ligands, 4-phenyl-1-cyanoacyl-3-semicarbazide (HL), has been reacted with $NiCl_2$ yielding the octahedral complex, $[NiL(H_2O)_3Cl]H_2O$. Coordination was found to occur via a secondary amine and the enolic carbonyl oxygen of the hydrazide moiety [259].

Carbohydrazide (L), when reacted with $Ni(NCS)_2$, yielded the octahedral complex, $[NiL_2(NCS)_2]$. The complex was assigned a *cis* configuration with the NCS groups adjacent to each other [260]. The related ligand, *N*-benzylidene-5(3)-methylpyrazole-3(5)-carbohydrazide (L) has been reacted with various nickel(II) salts. The resultant complexes, $[NiL_2]X_2$ ($X = Cl, Br, I, NO_3, BF_4, ClO_4$, SCN, $1/2SO_4$), are octahedral, with L coordinating via the tertiary N of the pyrazole ring and the ketonic O and azomethine N of the hydrazine component [261].

A number of variously-substituted azine ligands have been complexed with nickel.

These include 2-hydroxy-5-methyl-azobenzene, 2-hydroxy-5-methyl-2′-carboxyazobenzene, 2,4-dihydroxy-2′-carboxyazobenzene [262], *o*-carboxybenzeneazodimethylaniline [263,264], a series of phenylazo-β-naphthols [265], 1-(2-pyridylazo)-2-naphthol [266], and 3-hydroxy-1,3-diphenyltriazine [267]. Coordination usually occurs via one of the azine nitrogen atoms and one or more deprotonated hydroxyl groups, depending on the pH employed during reaction.

Various aspects of the Ni(II)-8-hydroxyquinoline interaction have been investigated, both in solution and in the solid state. Complexes that have been isolated in the solid state include distorted square planar $[NiL_2]$ (HL = 2-, 5-, and 7-methyl-8-quinolinol) [268], tetrahedral $[NiL_2]Cl_2$, and octahedral $[NiL_2](ClO_4)_2$ (L = biacetalmonoquinolylhydrazone) [269]. Complexes that have been studied in solution include those of 8-hydroxyquinoline [270], 2-methyl-8-hydroxyquinoline [271], 8-quinolinyl monoethyl orthophosphate [272], 7-(dicyclohexylaminomethyl)-8-hydroxyquinoline [273], and 4-(dimethylamino)-8-hydroxyquinoline [274]. Of interest is the last ligand, which has been used as a donor group in the podand ligands (**55**).



(R^1=HeO, Cl, Me_2N; R^2=H, Cl, MeO)

(**55**)

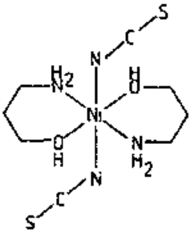
Another facet of 8-hydroxyquinoline ligands that has been examined, is their ability to extract metals into various solvents. 5,7-Dichloro-2-methyl-8-hydroxyquinoline [275] and a variety of alkyl and alkoxy-substituted quinoline-2-carboxylic acids [276] have been examined as selective extractants for Ni(II). In addition, benzeneazo-8-hydroxyquinoline, immobilized on a SiO_2 surface, has been shown to form 1:1 complexes with Ni(II) [277].

The interaction of Ni(II) with substituted-pyridine ligands has been studied in solution. Ligands that have been investigated include 5-butylpyridine-2-carboxylic acid [278], 6-methylpyridine-2-phosphoric acid [279], 3-(2′-thiazolylazo)-2,6-dihydroxypyridine, and 3-(4′,5′- dimethyl-2′-thiazolylazo)-2,6-dihydroxypyridine [280].

The stability constants of the nickel(II) complexes of various hydroxy-substituted 2-arylbenzazoles and 2-arylimidazopyridines have been determined in aqueous dioxane. The stabilities were found to be influenced by the various substituents [281].

Mixed-ligand complexes of the type $[NiL_2X_2]$ (HL = 1-hydroxymethyl-5(3)-methylpyrazole-3(5)-carboxylic acid; X = H_2O, NH_3, pyridine, α-, β-, γ-picoline) and $[NiL_2Y]$ (Y = *o*-phenanthroline and 2,2′-bipyridine) have been isolated. The geometry about nickel was found to be pseudooctahedral, with L coordinating via the pyrazolyl ring N and carboxylic acid O atoms [282].

A number of novel nickel complexes of aminoalcohols have been prepared. The crystal and molecular structure of bis(3-aminopropanol-*O*,*N*)bis(isothiocyanato)-nickel(II) have been reported. The complex is centrosymmetric with Ni(II) octahedrally coordinated by N of the NCS ions and by O and N of the 3-aminopropanol didentate ligands (**56**) (Ni–O = 2.06(1) Å, Ni–NH_2 = 2.085(1) Å, Ni–NCS = 2.062(1) Å) [283].



(**56**)

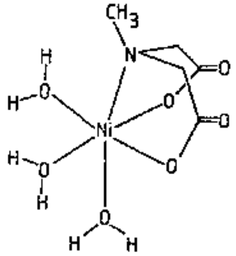
Other aminoalcohols that have been complexed with Ni(II) are α-phenyl-4-(5′-chloro-2′-hydroxybenzalamino)benzenesulfonamide, α-phenyl-4-(5′-chloro-2′-hydroxybenzalamino)benzenesulfonamido-2′-thiazole, α-phenyl-4-(5′-chloro-2′-hydroxybenzalamino)benzenesulfonamido-4′,6′-dimethyl-2′-pyrimidine [284], and monoethanolamine [285]. In addition, a kinetic study of the complexation of 2-aminophenol and its 4-sulfonic acid derivative with Ni(II) has been undertaken [286]. Similarly, the kinetics of the formation and dissociation of a variety of nitrosonaphtholsulfonate complexes of Ni(II) have been studied in 0.10 M $LiClO_4$ [287].

X-ray K-absorption edge analysis has been used to study the bonding in a variety of nickel complexes of isonitrosoketones. Results indicated that the nickel ions in $[NiL_2]$ (HL = 2-hydroxy-5-methyl-acetophenoneoxime) have a square planar structure, whereas the nickel ions in $[NiL_2]$ (HL = thioglycolic acid aniline) have a tetrahedral structure. On the other hand, both of the complexes, $[NiL_2]$ (HL = ethyl-α-isonitrosoacetylacetone and isonitrosoaceto-*p*-carboxyaniline), were assigned octahedral structures [288].

The structure and thermal behaviour of bis(acetylacetonemonoiminato)nickel(II) have been studied in the gas phase. Magnetic measurements indicated that the complex is low spin, while spectral data indicated that it has a planar configuration. Of particular interest is the fact that H-bonding was found to be absent in the gaseous phase, but present in the solid phase, as confirmed by IR [289].

Turning to tridentate ligands, the complex formation equilibria of Ni(II) with ethylenediamine-*N*-acetic acid have been investigated potentiometrically. Both 1:1 and 1:2 (Ni:ligand) complexes were observed [290]. A structurally similar ligand, *N*-methyliminodiacetic acid (H_2L), when complexed with Ni(II) in D_2O yielded the 1:1 complex, $[NiL(D_2O)_3]\cdot D_2O$, the crystal structure of which has been determined.

L coordinates in a tridentate, facial arrangement, with the three water molecules completing a near-octahedral coordination sphere (57) [291].



(57)

Bis(2-pyridyl)phenylcarbinol (HL), when reacted with nickel(II), yielded $[Ni(HL)_2](ClO_4)_2$ and $[Ni(HL)L]ClO_4$. The ligand functions in a tridentate N,N,O mode, regardless of whether the carbinol group remains protonated or not [292].

Moving on to tetradentate ligands, the structure of {diaqua[*N*,*N*′-bis(β-carbamoyl)-2-hydroxytrimethylenediamine]}nickel(II) dichloride has been determined. The coordination geometry about the nickel atom is pseudo-octahedral, with the water molecules occupying *trans* apical positions. Relevant crystal data are Ni–O = 2.056(2) Å, Ni–N = 2.085(2) Å, and Ni–OH_2 = 2.100(3) and 2.159(2) Å [293]. *N*,*N*′-Bis(1-hydroxymethylpropyl)ethylenediamine (L), when reacted with $NiSO_4$, yielded the 1:1 complex, $[NiL]SO_4$. L functions in a tetradentate fashion, with coordination occurring via a O,N,N,O set of donor atoms [294].

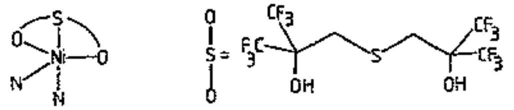
To conclude, the kinetics of formation and dissociation of the Ni(II) complexes of a number of diaminodiamide ligands have been studied, using the stopped flow technique. Ligands investigated include, *N*,*N*′-bis(β-carbamoylethyl)ethylenediamine, *N*,*N*′-bis(β-carbamoylethyl)trimethylenediamine, *N*,*N*′-bis(β-carbamoylethyl)-1,2-propylenediamine and *N*,*N*′-bis(β-carbamoylethyl)-2-hydroxytrimethylenediamine. All of the ligands function as tetradentate O,N,N,O donors [295].

4.7. Complexes with sulfur–oxygen donor ligands

The crystal and molecular structure of bis[*N*-(diethylaminothiocarbonyl)-*N*′-phenylbenzamidinato]nickel(II) have been reported. The nickel atom occupies a distorted tetrahedral coordination environment, with the ligands in a *cis* configuration. Deviation of the chelate rings from planarity was also observed [296]. In addition, the stability constants of the nickel(II) complexes of a series of substituted acetoacetylthioamides have been determined potentiometrically. The stability constants of the complexes were related to the Hammett substituent constants [297].

2,2′-[Thiobis(methylene)]bis[1,1,1,3,3,3-hexafluoro-2-propanol] (H_2L) has the potential to coordinate as a tridentate, dibasic, ligand. Reaction of H_2L with Ni(II) in the presence of base (base = pyridine or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine {TMED}) resulted in formation of the penta-coordinate complexes, $[NiL(py)_2]$ and

[NiL (TMED)], respectively. The complexes were assigned trigonal-bipyramidal geometry (**58**) [298].



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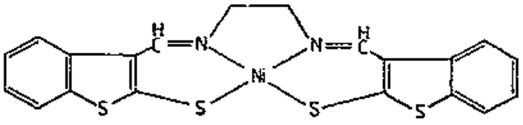
4.8. *Complexes with nitrogen–sulfur donor ligands*

Ligands derived from the condensation of carbonyl-containing compounds and amines, as in previous years, tend to dominate this section. However, unlike the analogous N,O-donor counterparts, it is the thiosemicarbazone ligands rather than the Schiff base or hydrazone ligands that have attracted the most interest. Table 5 lists a variety of didentate [299–304], tridentate [305–308], and tetradentate [309,310] thiosemicarbazone ligands and their Ni(II) complexes. Coordination usually occurs via the azomethine nitrogen atom and a thiol or deprotonated thiol group, depending on whether the ligand is functioning in a neutral or uninegative fashion. In addition, the structurally related ligands, 4-(*o*-methoxyphenyl) thiosemicarbazide [311] and benzamidothiosemicarbazide [312] have been complexed with Ni(II).

Turning to Schiff bases, a number of variously-substituted *N*-(thiocarbamoyl) benzamidines $\{HL = R'_2NC(S)N{:}C(C_6H_5)NH_2;\ R' = Et,\ Bu;\ NR'_2 = \text{morpholino}\}$ have been complexed with Ni(II). The ligands function in a didentate fashion, coordinating via the primary amine N and thione S atoms [313]. Other Schiff bases that have been coordinated to Ni(II) include 2-picolylphenylketone hydrazine-*S*-benzyl dithiocarbazate, which functions as a tridentate N,N,S donor ligand [314], and the imines of 2- and 3-benzo[*b*]thiophenecarboxaldehyde, which function as tetradentate S,N,N,S donor ligands (**59**) [315].



(59)

A number of monophosphazenes $\{L = RNHPPhNPhC(S)NHPh,\ RNHPRNRC(S)NHR;\ R = o\text{-tolyl}\}$ have been reacted with $NiCl_2$. L coordinates via the phosphazene N and thiocarbonyl S atoms, yielding complexes of the type, $[NiLCl_2]$. In addition, the stability constants of these complexes have been determined [316].

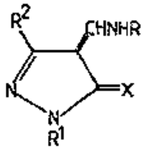
N^1-Benzoyl-N^2-(5-phenyl-1,3,4-oxadiazole-2-yl)thiocarbamide (L) and N^1-benzoyl-N^2-(5-*p*-anisyl-1,3,4-oxadiazole-2-yl)thiocarbamide (L^1) have been prepared

Table 5
Thiosemicarbazone ligands and their Ni(II) complexes

Ligand	Complex	Comments	Ref.
Didentate			
N-(Dimethylaminomethyl)isatin-β-thiosemicarbazone (HL)	$[NiL_2]$	Tetrahedral structure	[299]
Diethylketone and methyl-*n*-propyl thiosemicarbazones (HL)	$[NiL_2]$ $[NiL_2(py)_2]$	Square planar Octahedral adducts	[300]
Vanillin thiosemicarbazone (L)	$[NiL_2(H_2O)_2]Cl_2$	*Trans*-octahedral	[301]
p-Anisaldehydethiosemicarbazone (HL)	$[NiL_2(H_2O)_2]$	*Trans*-octahedral	[302]
2-Methylcyclohexanonethiosemicarbazone (HL)	$[Ni(HL)_2X_2]$ $[Ni(HL)_2]X_2$	High spin; ($X=Cl$, Br, I, NCS) Low spin; ($X=NO_3$, $1/2SO_4$)	[303]
Acetone and ethylmethylketone thiosemicarbazone (HL)	$[NiL_2]$	Reaction with acetyl and benzyl chloride	[304]
Tridentate			
3-Azabicyclo[3.2.2]nonane-3-thiocarboxylic acid	$[Ni(HL)_2](ClO_4)$	Tetrahedral	[305]
2-[1-(6-Methyl-2-pyridinyl)ethylidene]hydrazide (HL)	$[NiLCl]$	Square planar	
5(3)-Methylpyrazole-3(5)-aldehydo-4-phenylthiosemicarbazone (HL)	$[Ni(HL)]X_2$ $[NiL(NCS)]$	Octahedral Square planar	[306]
1-Formylisoquinoline thiosemicarbazone (L)	$[NiLCl_2]$	Distorted trigonal-bipyramidal structure	[307]
4-Methyl-5-amino-1-formylisoquinoline thiosemicarbazone (L)	$[NiLCl_2]$	Distorted trigonal-bipyramidal structure	[308]
Tetradentate			
Acetylacetone bis(thiosemicarbazone) (H_2L)	$[NiL]$	Planar	[309]
1,3-Cyclohexanedione bis(thiosemicarbazone) (H_2L)	$[NiL]$	Planar	[310]

and reacted with a variety of nickel salts. The resultant complexes, $[NiL_2X_2]$ (X = Cl, Br, NO_3) and $[Ni_2L_2^1X_4]$, are octahedral and distorted octahedral, respectively, whereas $[NiL_2](ClO_4)_2$ has been assigned square planar geometry [317]. The related ligand, *N*-(*p*-tolyl)-*N'*-benzoylthiocarbamide (HL), in its deprotonated form, reacted with $NiCl_2$, yielding the neutral complex $[NiL_2(H_2O)_2]$ [318].

Dynamic NMR spectroscopy has been used to study the enantiomerization of $[NiL_2]$ {HL = (**60**)} in a number of solvents. The kinetic and activation parameters indicate that enantiomerization occurs via a diagonal twist mechanism [319,320].



(X=S, Se; R=alkyl, aryl; R^1=*iso*-Pr, $PhCH_2$, Ph; R^2= Me, *iso*-Pr)

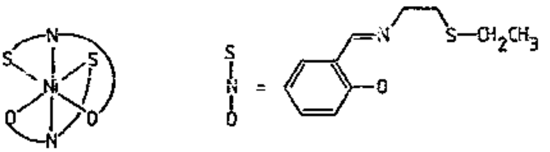
(60)

While on the subject of NMR spectroscopy, the first application of 2D-NMR to the spectral analysis of a paramagnetic complex, bis[R-(+)-*P*,*P*-diethylthiophosphonic acid–*N*-α-methylbenzylamido]nickel(II), has been reported. The complex was assigned a pseudo-tetrahedral configuration [321].

The crystal and molecular structure of bis(β-mercaptoethylamine)nickel(II) has been determined and shows that the complex, contrary to earlier belief, has a *trans* configuration. Some relevant crystal data are Ni–S = 2.159(1) Å and Ni–N = 1.868(3) Å [322].

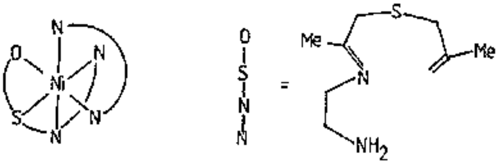
4.9. *Complexes with nitrogen–oxygen–sulfur donor ligands*

The tridentate Schiff base ligand *N*-(3-thia-*n*-pentyl)salicylaldimine (H_2L) and its nickel(II) complex, $[NiL_2]$, have been prepared. The crystal structure reveals a distorted octahedron for Ni with two oxygen atoms in *cis* positions, two nitrogen atoms in *trans* positions, and two sulfur atoms in *cis* positions (**61**). Relevant crystal data are Ni–O = 1.978(3) Å and 1.981(3) Å, Ni–N = 2.006(3) Å, Ni–S = 2.720(2) and 2.663(2) Å [324].



(61)

A single crystal X-ray investigation of the nickel(II) complex, $[NiL(en)](NO_3)_2$ {$L = NH_2(CH_2)_2N{=}C(CH_3)CH_2SCH_2COCH_3$}, has been undertaken. L functions in a tetradentate fashion, with the N, N and S atoms arranged meridionally and the coordination sphere completed by the O atom of L and the nitrogen atoms of 1,2-diaminoethane (en) (**62**)[323]. Relevant crystal data are Ni–O = 2.16 Å, Ni–S = 2.45 Å, Ni–NH_2 = 2.10 Å, Ni–N=C = 2.05 Å and Ni–N(en) = 2.08(av) Å [325].



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5. Nickel(II) macrocycle complexes

As in previous years, a substantial amount of interest has centred on Ni(II)–macrocyclic complexes. While the field still tends to be dominated by nitrogen donor and, in particular, tetraaza ligands, a significant number of mixed-donor macrocyclic complexes have been reported. In order to facilitate clarity, complexes have been, as far as possible, dealt with in order of increasing number of donor atoms and ring size.

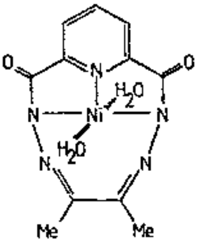
5.1. *Macrocycles with nitrogen donor atoms*

By way of introduction, a number of articles have reported trends within a series of macrocyclic complexes relating to ring size and its effect on stability and axial bond formation. XPS has been used to study the Ni($2p^{3/2,1/2}$), N(1s) and Cl(2p) core levels of seven Ni(II) tetraaza macrocyclic complexes. The binding energy data for the core levels were interpreted in terms of the structural features of these complexes [326]. Similarly, the stability constants for the Ni(II) complexes of a series of 12- to 16-membered ring tetraaza macrocycle ligands have been determined. The variation of log K_2 as a function of metal ion was discussed [327].

The Ni(II) complex (**63**) has been prepared via the in situ reaction of Ni^{2+}, 2,6-dipicolinic acid hydrazide, and 2,3-butanedione. The complex was assigned a trigonal-bipyramidal structure on the basis of spectroscopic and electromagnetic evidence [328].

1,4,7,11-Tetraazacyclotridecane (L) has been reacted with $Ni(ClO_4)_2$ yielding the square planar complex, $[NiL](ClO_4)_2$. Reaction of this complex with ethylendiamine (en) yielded the octahedral complex, *cis*-$[NiL(en)](ClO_4)_2$. In addition, the isomerisation of *cis*-$[NiL(H_2O)_2]^{2+}$ has been studied kinetically [329].

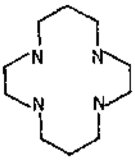
The molecular structures of the *trans*-dichloro and *trans*-bis(isothiocyanato)nickel(II) complexes of 1,4,8,11-tetraazacyclotetradecane (**64**), 1,4,8,12-



(63)

tetraazacyclopentadecane **(65)**, and 1,5,9,13-tetraazacyclohexadecane **(66)**, have been determined by single crystal X-ray analysis. The average in-plane Ni–N distance increased 0.05–0.06 Å for each ring member added, on going from **(64)** to **(66)**, while the mean axial bond length (Ni–X, X = Cl or NCS) was found to decrease as the average in-plane Ni–N distance increased [330].

Similarly, the reaction of **(64)** and Ni(II), in the presence of a series of ligands, has been studied in solution using pH-static and spectrophotometric methods [331].



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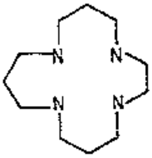

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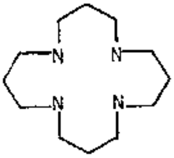


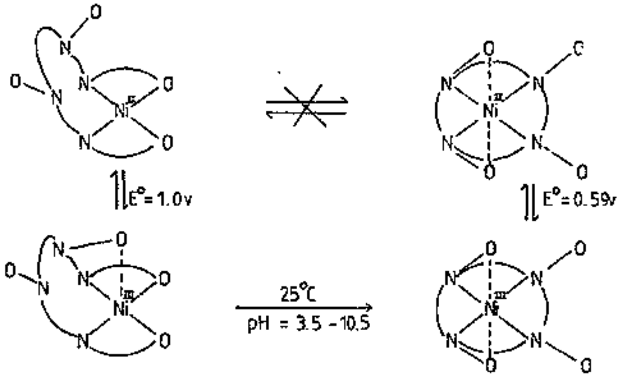
(66)

Tetramethylcyclam complexes of nickel(II) continue to attract interest. An ultrasonic relaxation and variable-pressure spectrophotometric study of the planar⇆octahedral equilibrium in aqueous solutions of [(1*R*,4*S*,8*S*,11*R*)-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane]nickel(II), has been reported [332]. In addition, the solvation of (*R*,*S*,*R*,*S*)(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)-nickel(II) in aqueous solution has been investigated. The effect of added salts was found to be quite pronounced [333].

The previously unknown "Ni(II)-in" complex of cyclamtetraacetate has been prepared from the "Ni(II)-out" isomer. The high kinetic barrier for metal insertion has been circumvented by oxidation of the metal in the "Ni(II)-out" complex **(67)** [334].

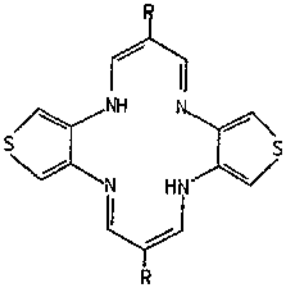
The structure of the fully conjugated macrocyclic complex, (1,4,8,11-tetraazacyclotetradeca-2,4,6,9,11,13-hexaene-2,3,9,10-tetracarbonitrilato)nickel(II) has been reported. The complex is essentially planar, with Ni–N = 1.851(1) Å [335].

A number of variously-substituted dibenzotetraaza[14]annulene–nickel(II) complexes have been prepared. Synthetic procedures used involve preparation of the ligand followed by complexation [336], facile template synthesis [337,338], and the introduction of substituents onto the macrocyclic complex [339]. Similarly, a number



(67)

of variously-substituted nickel(II) complexes of (4*H*,12*H*)-[1,4,8,11]tetraazacyclotetradecino[2,3-c:9,10-c^1]dithiophene **(68)** have been prepared via metal template cyclocondensation reactions [340].



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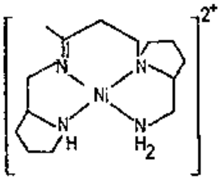
Reaction of $[NiL_3]^{2+}$ {L=(2*S*)-2-(aminomethyl)pyrrolidine} with but-3-en-2-one yielded two complexes, one of which is an open-chain complex **(69)**, while the other is the optically active tetraaza macrocyclic complex **(70)**. Both complexes were isolated as their tetraphenylborate salts [341].



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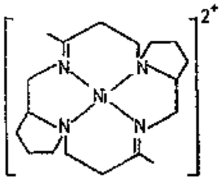
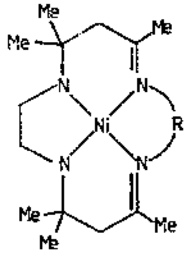


(70)

^{13}C-NMR spectroscopy has been used as a probe to study the effects of ligand superstructure on the binding constants of lacunar macrobicyclic complexes with O_2. The binding constants appear to be directly related to the bridge length [342].

The interaction between the nickel(II) complexes of 3-acetyl-, 3-benzoyl-, and 3-ethoxycarbonyl-9-methyl-5,8-diazadodeca-3,9-diene-2,11-dione and a variety of aliphatic diamines has been investigated. Reaction with 1,2-diaminoethane yielded asymmetric 14-membered tetraaza macrocycles, whereas reaction with 1,3-diaminopropane yielded an acyclic complex [343]. In a similar study, the transamination reactions of **(71)** {$R=(CH_2)_4$} with a number of diamines {$H_2N\text{-}(CH_2)_n\text{-}NH_2$, $n=2,3,4,5$; 1,2-diaminobenzene}, have been investigated. It is interesting to note that the transamination reaction only occurred with a decrease in the size of the macrocyclic ring [344].



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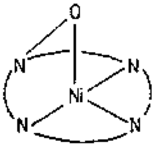
A number of naturally-occurring porphyrins, isolated from oil shale as their Ni(II) complexes have been reported. These include etioporphyrins [345], polar porphyrins [346], and bacteriopetroporphyrins [347]. The complexes have been identified by nuclear Overhauser effect studies.

Proton nuclear magnetic resonance has been used to study the structure of nickel(II) octaethylpyrrocorphinate in the solid state and in solution. An inversion barrier between the saddle conformers of the complex was observed in solution [348]. Similarly, proton NMR studies have been used to characterise chloro(*N*-methyl-5,10,15,20-tetraphenylporphyrinato)nickel(II) and chloro(*N*-methyl-octaethylporphyrinato)nickel(II) [349].

The structure of octaethylporphyrin *N*-oxide and its complexation with Ni(II) have been reported [350]. The X-ray crystal and molecular structure of the Ni(II) complex of octaethylporphyrin N-oxide dianion reveals an unusual mode of bonding. The Ni(II) ion is bound to three of the four N atoms and a bridging O atom as shown below **(72)**. Relevant crystal data are Ni–N = 1.922(4), 1.929(5) and 1.900(4) Å; Ni–O = 1.788(4) Å [351].

Turning to synthesis, a series of nickel(II)–isobacteriochlorin complexes have been prepared by the reaction of Raney Ni with the corresponding nickel(II)–chlorophyll-derivative complexes. Isomers were separated and characterized using HPLC and high-field NMR spectroscopy, respectively [352]. In addi-



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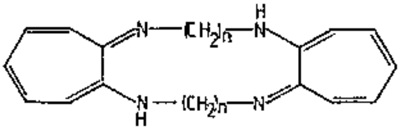
tion, the first chemical partial synthesis of the nickel complex of a cobyrinic acid derivative from its seco-corrinods complex, has been reported [353].

High-temperature electrocrystallization has been used to prepare a phthalocyanine "molecular metal" complex, Ni(L) $(BF_4)_{0.33}$ (L = phthalocyanine) [354], while the kinetics of complexation of tetrabenzoporphyrintetrasulfonic acid with nickel acetate have been determined spectrophotometrically in pyridine [355].

The relationship between the structures and electronic spin states of six Ni(II) complexes, [NiL], of the tropocoronand ligands $\{H_2L = $ **(73)**$\}$, has been investigated by single-crystal X-ray diffraction and magnetic methods. The complexes having $n,n = 3,3$; 4,4; 4,5 are distorted planar molecules, whereas those with $n,n = 5,5$; 6,6 have distorted tetrahedral geometry [356].



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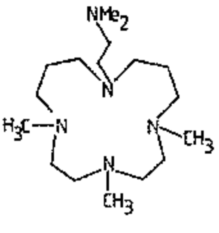
A new 14-membered, pendant-arm macrocyclic ligand, 11-(2′-dimethylaminoethyl)-1,4,7-trimethyl-1,4,7,11-tetraazacyclotetradecane **(74)**, has been prepared and reacted with Ni(II). The resultant complex, $[NiL](ClO_4)_2$ $\{L = $ **(74)**$\}$, is penta-coordinate and was assigned a distorted trigonal bipyramidal geometry [357]. Similarly, the quinquedentate macrocycle **(75)** has the possibility of coordinating in an analogous fashion. However, spectroscopic evidence indicates that the pendant arm is not coordinated in the complex $[NiL](ClO_4)_2$ $\{L = $ **(75)**$\}$ [358].



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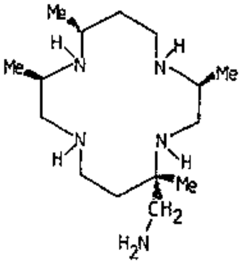
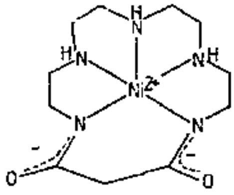


(75)

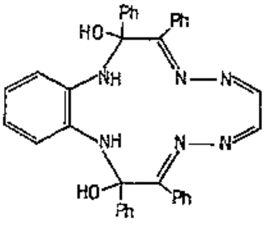
The crystal and molecular structure of the nickel(II) 16-membered dioxopentaamine macrocyclic complex (76) have been determined. The complex has a square-pyramidal structure with the following relevant data: Ni–N(amide) = 1.978(4) Å and Ni–N(amino) = 2.095(4) Å. Of particular interest, is the fact that the structural and electronic parameters are favourable for its interaction with O_2 [359].



(76)

1,8,9,20-Tetrahydro-3,6-dimethyl-1,8-diphenyldibenzo[c,m]dipyrazolo[3,4-f:4′,3′-j]-[1,2,5,8,9,12]hexaazacyclotetradecine (H_2L) when reacted with Ni(II), yielded two linkage isomers of formula [NiL]. ^1H- and ^{13}C-NMR indicate that coordination occurs via N(1), N(5), N(8) and N(12) in one isomer and via N(2), N(5), N(8) and N(12) in the other [360].

The neutral macrocyclic complex, [NiL] {H_2L (77)}, has been prepared by the template condensation of the open chain ligand, 1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione with *o*-phenylenediamine, in the presence of nickel(II) acetate. The presence of the dicarbinolamine moiety in the complex was established spectroscopically [361].



(77)

A number of macrocycles derived from 2,6-diacetylpyridine have been reported. $[NiL(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ (L = 2,5,11,14-tetramethyl-3,4,12,13,19,20-hexaazatricyclo [13.3.1.1^{6,10}]eicosa-1(19),2,4,6,8,10(20),11,13,15,17-decaene) has been prepared by the reaction of 2,6-diacetylpyridine with hydrazine in the presence of $Ni(ClO_4)_2$ [362]. Similarly, a number of 28-atom membered macrocycles, derived from 2,6-diacetylpyridine and the amines, 3,3′-diamino dipropylamine or 3,3′-diamino-*N*-methyl dipropylamine, have been complexed with Ni^{2+}. Both mononuclear and dinuclear complexes were isolated [363].

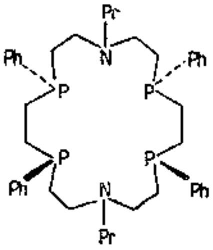
Some interesting reactions have been carried out on tetraaza macrocyclic nickel(II) complexes. The complexes, $[NiL](ClO_4)_2$ {L = (7*RS*, 14*RS*)-5,5,7,12,12,14-

hexamethyl-1,4,8,11-tetraazacyclotetradecane or 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane}, take up CO_2 as R_2NCO_2, yielding the carbamato complexes, $[Ni(O_2CNR_2)(L)]^+$ [364]. In addition, $[NiL](ClO_4)_2$ reacted with nitroalkanes ($RR'CHNO_2$, $R=R'=H,Me$; $R=H,R'=CH_3$) in the presence of NEt_3, yielding the nitro–alkanoato complex cations $[NiL(O_2NCRR')]^+$ [365].

To conclude, $Ni([14]ane\ N_4)^{2+}$ and $Ni(Me_6[14]4,11\text{-diene}\ N_4)^{2+}$ have been used as reductants in a kinetic study of the reduction of $[Mn(H_2O)_6]^{3+}$ in acidic perchlorate media [366].

5.2. *Macrocycles with phosphorus donor atoms*

In a continuing study of macrocyclic polyphosphane ligands, (4*RS*,7*RS*,13*SR*,16*SR*)-tetraphenyl-1,10-dipropyl-1,10-diaza-4,7,13,16-tetraphosphacyclooctadecane (**78**) has been complexed with Ni(II). The X-ray crystal structure of the resultant complex, $[NiL](BPh_4)_2$ {L=(**78**)}, has been determined, revealing a square planar environment for the nickel atom which is coordinated to the four phosphoros atoms of the macrocycle [367].



(78)

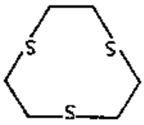
In addition, the related macrocycle, (5*RS*,8*RS*,16*RS*,19*RS*)-tetraphenyl-5,8,16,19-tetraphospha-1,12-dithiacyclodocosane has been reacted with a variety of nickel salts. Various stoichiometric complexes were obtained, depending on the nickel salt used [368].

5.3. *Macrocycles with sulfur donor atoms*

1,4,7-Trithiacyclonane (**79**) when reacted with $Ni(ClO_4)^2$ yielded the hexacoordinate complex $[NiL](ClO_4)_2$ {L=(**79**)}. Magnetic susceptibility measurements indicate that the complex is paramagnetic with two unpaired electrons per Ni(II) [369].

5.4. *Macrocycles with nitrogen–oxygen donor atoms*

The crystal and molecular structure of $[NiL(H_2O)](ClO_4)_2$ {(L=(**80**)} have been determined as part of a study, in which the relative thermodynamic stabilities of the nickel complexes of related O_2N_3-donor macrocyclic ligands have been modelled.



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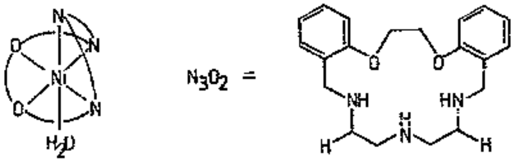
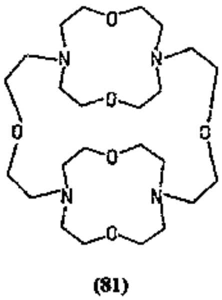
The study predicts a facial coordination arrangement, which was confirmed by the crystal structure [370].



(80)

Two new endocyclic dihydroxamate macrocycles, 5,14-dihydroxy-4,15-dioxo-1,5,14,18-tetraaza-8,11,21,24-tetraoxacyclohexacosane and its 1,18-diacetic acid derivative, have been synthesized and their affinities for Ni(II) investigated. The results show stability enhancement over analogous complexes having exocyclic hydroxamate donor groups [371].

Potentiometry and UV spectrophotometry have been used to study the complexing properties of the cylindrical macrotricycle, 1,7,13,19-tetraaza-4,16-dioxa-10,22,27,32-tetraoxatricyclo-[17.5.5.5]tetratriacontane (**81**), and of its constitutive monocyclic subunit, 1,7-diaza-4,10-dioxacyclodecane (**82**), with Ni(II). Only mononuclear complexes were observed [372].



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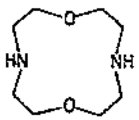
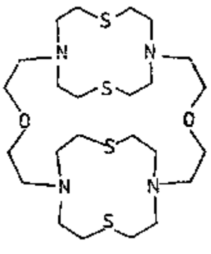


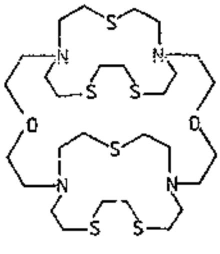
(82)

5.5. *Macrocycles with nitrogen–sulfur donor atoms*

The sulfur analogue of (**81**), 4,16-dioxa-10,22,27,32-tetrathia-1,7,13,19-tetraazatricyclo-[$17.5.5.5^{7,13}$]tetratriacontane (**83**), as well as the related ligand, 4,19-dioxa-10,13,25,28,33,38-hexathia-1,7,16,22-tetraazatricyclo-[20.8.5.5^{7,16}]tetracontane (**84**), have been prepared and complexed with Ni(II). However, unlike (**81**), (**83**) and (**84**) form dinuclear complexes with Ni(II) [373].



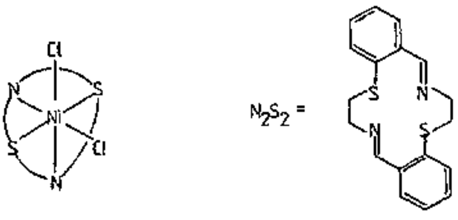
(**83**)



(**84**)

The nickel(II) complexes of 1-oxa-4,7-diazacyclonane and 1-thia-4,7-diazacyclononane have been isolated as their perchlorate salts, $[NiL_2](ClO_4)_2$. The ligands function in a terdentate fashion, with the heteroatoms introducing increased flexibility to the chelate rings [374].

The crystal and molecular structure of *cis*-$[Ni(L)Cl_2]$ {L=(**85**)} have been reported. Two conformations of the molecule are possible, (λδ) and (λλ or δδ), and both were observed in the unit cell of the triclinic crystals [375].

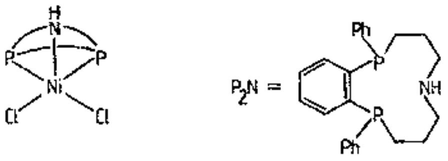


(**85**)

5.6. *Macrocycles with nitrogen–phosphorus donor atoms*

Reaction of *meso*-*cis*-2,10-diphenyl-6-aza-K*N*-2,10-diphospha-K^2*P*-bicyclo-[9.4.0]pentadeca-11(1),12,14-triene (**86**) with $NiCl_2$, yielded $[NiLCl_2]$ {L(**86**)}, the crystal structure of which had been determined. The coordination geometry about Ni(II) is square-pyramidal with the NH moiety occupying the apical position [376].

The crystal and molecular structure of [NiL], where H_2L is the new P_2N_2 macrocyclic ligand (**87**), has been reported. [NiL], formed during the template synthesis of (**87**), contains Ni coordinated to the ligand in a *meso*-configuration [377].



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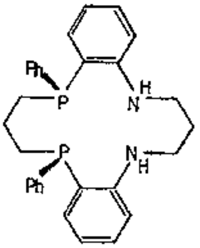

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6. Nickel(II) complexes with biological ligands

A wide variety of ligands of a biological nature have been complexed with Ni(II). These include amino acids (including their derivatives as well as peptides and proteins), polyheterocyclic bases, carbohydrates and organic acids. Once again it is the amino acids and their derivatives that have attracted considerable attention. Table 6 lists some of these ligands which include glycine [378–385], variously-substituted glycines [386–393], proline [394], cysteine [395], lysine [396], methionine and ethionine [397], variously substituted histidines [399–401], histamine [402], and substituted α- and β-alanines [403].

While on the subject of amino acids, a general method for the diastereoselective and enantioselective synthesis of β-hydroxy-α-amino acids has been reported. The synthesis involves the condensation of formaldehyde with a Ni(II) complex of glycine Schiff base with (*S*)-2-[*N*-(benzylprolyl)amino]acetophenone or its benzophenone analogue (**88**) [407]. A similar system, which utilizes the Schiff bases of a variety of α-amino acids, has been investigated and contributes to the understanding of the Akabori reaction [408].

Turning to peptides, the stability constants of the complexation of Ni(II) with the cyclic dipeptides, cyclo(glycyl-L-histidyl) and cyclo(L-methionyl-L-histidyl), have been determined. In addition, ^{1}H-NMR data indicate that the metal ion links exclusively to the N atom of the imidazolyl group of cyclo-(L-methionyl-L-histidyl) [409]. Similarly, CD spectroscopy has been used to study the interaction of prolyl-(glycyl)$_n$ ($n = 1, 2, 3$) with Ni(II) [410].

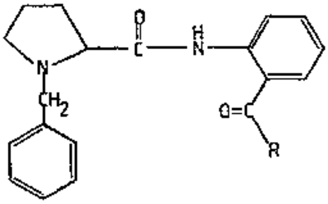
Aminoguanizone pyruvate $\{H_2L = HN{:}C(NH_2)NHN{:}C(CH_3)CO_2H\}$ when reacted with Ni(II) yielded $[Ni(HL)_2]\cdot 1/2H_2O$. This complex was assigned octahe-

Table 6
Some amino acids and amino acid derivatives that have been complexed with Ni(II)

Ligand	Comments	Ref.
Glycine (HL)	Stability constants of NiL^+ and NiL_2 have been determined	[378]
	EXAFS study of NiL_2 in solution indicates that two water molecules bind to complete the octahedral structure	[379,380]
	Preparation of mixed-ligand complexes with uracil or 2-thiouracil. Results show that glycine is didentate in all cases	[381]
	Kinetic study of ternary complex formation between [NiA] (H_2A = ethylenediamine-*N*,*N′*-diacetic acid) and HL	[382]
	Potentiometric study of the mixed-ligand complexes with benzimidazole	[383]
	Spectrophotometric study of the mixed-ligand complexes with amethopterin	[384]
	Formation constants of complexes of the type [NiAL] where, A = 2,2′-bipyridine, 1,10-phenanthroline, 2-(2′-pyridyl)benzimidazole	[385]
N,*N*-Dimethylglycine (HL)	Solution study in H_2O/MeOH; NiL and NiL_2 species observed	[386]
N-Methylglycine (HL)	Solution study in H_2O/MeOH; NiL and NiL_2 species observed	[387,388]
N-Phenylglycine (HL)	Solution study in H_2O/MeOH; NiL and NiL_2 species observed	[387,388]
N-substituted phenylglycine (HL)	[NiL_2] have been prepared and characterised spectroscopically	[389]
N-(2-Mercapto propionyl)glycine	Potentiometric study; mono- and polynuclear species observed	[390]
N-Benzoylglycine hydrazide (H_2L)	$Ni(H_2L)_2Cl_2$, $Ni(HL)_2 \cdot 2H_2O$ and $NiL \cdot 3H_2O$ were prepared	[391]
N,*N′*-Diglycylethylenediamine (H_2L)	Kinetic study of the reaction of NiL with triethylenetetramine	[392]
N′-Diglycylpropylenediamine (L)	Octahedral$\rightleftharpoons$square planar rates of conversion for NiL^{2+}	[393]
DL-Proline (HL)	Synthesis and characterisation of $NiL_2 \cdot 2H_2O$, $K[NiL_3] \cdot 3H_2O$, $K_2[NiL_3](CO_3)_{0.5} \cdot 2H_2O$ and $K_3[NiL_3] \cdot CO_3 \cdot 5H_2O$	[394]
Cysteine (H_2L)	Individual complexes of Ni(II) with H_2L and L^{2-} have been isolated and studied	[395]
L-Lysine · HCl	Solution study; NiL_2 was isolated as a diamagnetic solid	[396]
DL-Methionine	Potentiometric investigation of mixed-ligand complexes with taurine	[397]
α-Aminoisobutyric acid (H_2L)	Kinetic study of the acid dissociation of NiL^-	[398]
Histidine (HL)	Isolation of $NiL_2 \cdot H_2O$. Ligand functions in a tridentate fashion	[399]
	Polarographic study. 1:2 complexes were observed in solution	[400]
N-Benzenesulfonyl-L-histidine	Potentiometric study. 1:1 and 1:2 complexes were observed	[401]

Table 6
Some amino acids and amino acid derivatives that have been complexed with Ni(II)

Ligand	Comments	Ref.
Histamine (L)	Kinetic study of the reaction of $Ni(OH_2)_6^{2+}$ with tautomeric forms of L	[402]
N-Tosyl-α-alanine (HL)	Isolation of $[NiL_2(H_2O)_4]$. Distorted octahedral structure	[403]
Iminodiacetic acid (H_2L)	Thermogravimetric study	[404]
N-Hydroxyimino-di-α-propionic acid	Solution study. Stability constants have been determined	[405]
o-Phenylene biuret (H_4L)	Isolation of $Na_2[NiL]\cdot 4Me_2SO$. Square planar structure	[406].

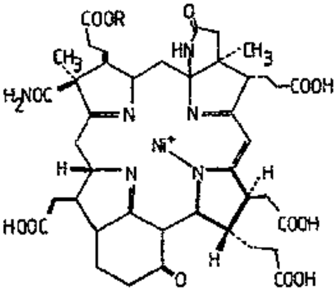


($R=CH_3$, C_6H_5)
(88)

dral stereochemistry with the uninegative ligand functioning in a tridentate fashion [411].

The complexation of Ni(II) with the proteins, gliadin, glutenin, and gluten has been studied by NMR in DMSO solution. Of particular interest is the fact that complexation can induce a U-shape deformation of these globular proteins [412,413].

The metalloenzyme, factor F430 (**89**), isolated from methanogenic bacteria, was found to isomerize in aqueous solution when heated. Three isomers have been identified and characterised using a number of spectroscopic techniques [414].

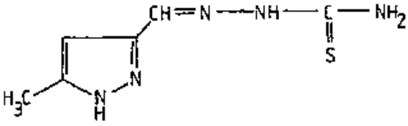


(89)

A number of ligands that are structurally related to imidazole have been complexed with Ni(II). Apart from those described earlier, the complexing properties of 1-*n*-propyl-2-α-hydroxybenzylbenzimidazole [415], *N*-cyano-*N*′-methyl-*N*″-(2-[(5-methyl-1*H*-imidazol-4-yl)methylthio]ethyl) guanidine [416] and a series of *N*-alkylimidazoles (alkyl = ethyl, propyl) [417] with Ni(II), have been investigated. In addition, the inhibitory activity of the latter complexes on Ca,Mg-dependent ATPase has been reported [417].

Continuing with biologically important heterocycles, 4-acetyl-2-(acetylamino)-5-dimethyl-D^2-1,3,4-thiadiazole (L) when reacted with Ni(II), yielded the hexacoordinate complex, $[NiL_2(H_2O)_2]Cl_2$ [418], while 2,5-bis(3′,5′-dimethylpyrazol-1′-ylmethyl)-2,5-diazahexane (L^1) yielded hexacoordinate complexes of the type $[NiL^1X_2]$ (X = NCS, N_3). The crystal structure of $[NiL^1(N_3)_2]$ reveals that the Ni(II) ion is octahedrally surrounded by four nitrogen atoms of L^1, and that the azide anions occupy *cis*-positions [419].

The synthesis, characterization and coordination properties of the new pyrazole-derived thiosemicarbazone, 5(3)-methyl-pyrazole-3(5)-aldehydrothiosemicarbazone (**90**), have been reported. Reaction with a variety of Ni(II) salts yielded octahedral complexes of the type $Ni(HL)_2X_2$ {HL = (**90**); X = Cl, Br, ClO_4, $1/2SO_4$, NO_3, BF_4}, in which the mode of coordination is dependent on the anion present [420].



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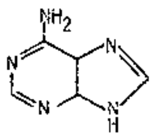
The complexation of 2-pyrrolidinone with Ni(II) has been studied polarographically. The stability constants have been determined, and were shown to increase with increasing ligand concentration [421].

Bromazepan (L = 7-bromo-1,3-dihydro-5-(2-pyridyl)-2*H*-1,4-benzodiazepine-2-one), an anxiolytic drug, has been reacted with $NiCl_2$, yielding $[NiL_2Cl_2]$. The complex was assigned a pseudo-octahedral structure with the two α-diimine groups occupying the equatorial plane, while the Cl atoms occupy *trans*-axial positions [422]. In a continuation of the above work, the thermal decomposition of a series of bromazepan complexes of Ni(II) has been studied using TG/DTA [423].

A number of nucleobase moieties, which form an integral part of the chemistry of nucleic acids, have been complexed with Ni(II). These include adenine (**91**) [424], guanine (**92**) [425], xanthine (**93**) [426], a series of 9-substituted purines (**94**) [427], 5-fluorouracil (**95**) [428], and 2-guanidino-4,6-dimethyl pyrimidine (**96**) [429].

Of particular interest are the complexes of adenine, guanine, and xanthine, which have been assigned a polymeric structure in which the deprotonated base functions in a bridging role [424–426]. In addition, the formation constants of the ternary complexes, [NiL(ATP)] (L = 2,2′-bipyridine or 1,10-phenanthroline), have been



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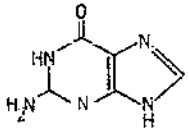

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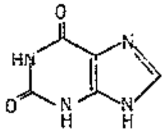

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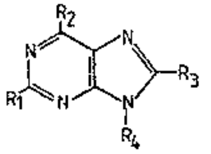

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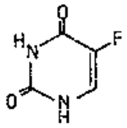

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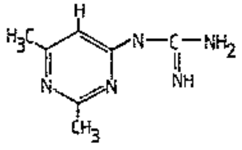

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determined. Intramolecular stacking between the heteroatoms of the didentate ligands and the adenine moiety of the ATh was observed [430].

The complexing properties of barbituric acid and its derivatives have been investigated potentiometrically. Both 1:1 and 1:2 (Ni:ligand) complexes were observed [431]. Similarly, 5,5-diethylbarbituric acid (HL) when reacted with Ni(II), yielded the tetracoordinate complex, $[NiL_2(H_2O)]$. L functions in a monodentate fashion with coordination occurring via the deprotonated N atom [432].

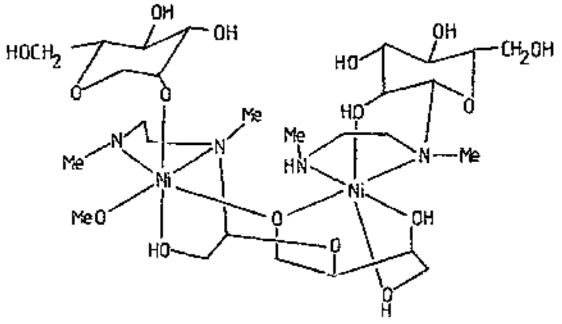
Citric acid and its complexation with Ni(II) have been studied in some detail. The relative stability of the citrato complexes of Ni(II) have been determined electrophoretically. Both mono- and bis-complexes were observed [433]. In addition to the homonuclear system, the heterodinuclear systems Ni–Cd–citrate [434] and Ni–Cu–citrate [435], have been investigated potentiometrically.

Continuing with organic acids, the interaction of L-ascorbic acid (H_2L) with Ni(II) has been investigated, both in solution [436], and in the solid state [437]. Reaction occurred with deprotonation of H_2L, yielding the hexacoordinate complex, $[Ni(HL)_2(H_2O)_4]$. Other organic acids that have been complexed with Ni(II) include thiolactic acid [438], 1-amino-1-cyclopropanecarboxylic acid [439], and propanediaminetetraacetic acid [440].

A number of ligands containing the isonicotinoyl moiety have been investigated. These include isonicotinic acid amide [441], isonicotinoylhydrazine, *N*-acetyl-*N'*-isonicotinoylhydrazine [442], and pyridine-4-carboxaldehydeisonicotinoylhydrazone [443]. Some of the complexes have been tested for their effect on tuberculosis [442] and their antibacterial activity [443].

The interaction of 3-methyl-2-thio-2,4(1*H*,3*H*)-quinazolinedione with Ni(II) has been investigated potentiometrically. The stability constants were determined in 75 vol.% aqueous dioxane [444].

Carbohydrates and their derivatives continue to attract interest. In particular, the reaction of amino sugars with tris(diamine)nickel(II) complexes has received much attention, as manifested by a number of crystal structures [445,446]. Of particular interest is the dinuclear nickel(II) complex, **(97)**, obtained from the reaction of D-mannose with $[Ni(MeNHCH_2CH_2NHMe)_2(H_2O)_2]Cl_2$. The crystal and molecular structure of **(97)** has been determined, revealing two essentially octahedrally coordinated nickel atoms linked by a mannose residue [447,448].



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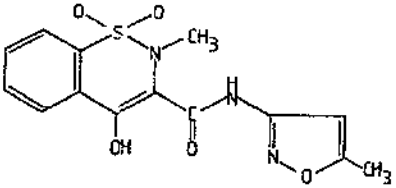
Turning to solution studies, the complex-forming properties of dextran carboxymethyl ether [449] and glucose oxime [450], have been investigated potentiometrically.

To conclude, the preparation, spectroscopic and magnetic properties of the nickel(II) complex of the anti-inflammatory drug, 4-hydroxy-3-(5-methyl-3-isoxazolocarbamyl)-2-methyl-2*H*-1,2-benzothiazine-1,1-dioxide **(98)**, have been reported. The complex $[NiL_2(H_2O)_2]\cdot 3H_2O$ {HL=**(98)**} is octahedral with L coordinating via the enolate oxygen atom and the carbonyl oxygen atom of tile amide group [451].



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7. Nickel(II) polynuclear complexes

Polynuclear nickel complexes continue to generate considerable interest. While a diversity of complexes have been reported, the main thrust of research has centred on clusters (complexes that contain a nickel–nickel or nickel–metal interaction have been classified as a cluster), complexes containing Schiff base and related ligands, sulfur-bridged complexes, and complexes containing halide or pseudo-halide bridging

Table 7
Crystallographic data of some homonuclear and heteronuclear nickel-containing cluster complexes

Complex	Structural data (Å)	Comments	Ref.
Homonuclear			
$[(Ni(NPh_2)_2)_2]$	Ni–Ni = 2.327(2)	This complex and $[Ni(NPh_2)_3]^-$ appear to be the first three coordinate Ni complexes that have been reported	[452]
$[\{NiCl(L)(EtOH)\}_4]$	Ni–Ni(av.) = 3.18	L = 3,5-dimethyl-1-oxymethyl-pyrazolate. No significant Ni–Ni interaction	[455]
$[Ni_8(CO)_{16}C]^{2-}$	Ni–Ni = 2.477(2), 2.627(2)	Isolated as Bu_4N^+ salt	[456]
$[Ni_9(CO)_{17}C]^{2-}$	Ni–Ni(av.) = 2.55	Isolated as Bu_4N^+ salt	[456]
$[Ni_{10}(CO)_{16}C_2]^{2-}$	Ni–Ni(av.) = 2.618	Isolated as Ph_4As^+ salt	[457]
$[Ni_{16}(CO)_{23}C_4]^{4-}$	Ni–Ni(av.) = 2.604	Isolated as Me_4N^+ salt	[458]
Heteronuclear			
$[NiMo(CO)_2\{\mu\text{-}\eta^2,\eta^2\text{-}C\text{-}(Me)C(Me)C(O)\}(\eta\text{-}C_5H_5)\text{-}(\eta\text{-}C_5H_4Me)]$	Ni–Mo = 2.5859(2)	Significant Ni–Mo single bond	[459]
$[Th(\eta\text{-}C_5(CH_3)_5)_2(\mu\text{-}PPh_2)_2\text{-}Ni(CO)_2]$	Ni–Th = 3.206(2)	First reported interaction between an actinide and transition metal	[460]
$[Ni_{38}Pt_6(CO)_{48}H_2]^{4-}[Ni_{38}Pt_6(CO)_{48}H]^{5-}$	$\left\{\begin{array}{l}\text{Ni–Ni (av.)} = 2.580\text{Ni–Pt} = 2.510,\\ 2.764\text{Pt–Pt (av.)} = 2.719\end{array}\right.$	Highest nuclearity carbonyl clusters whose structures have been determined by X-ray crystallography	[462]

groups. To facilitate clarity, complexes have been divided into clusters, and those that do not contain metal–metal interactions. In addition, it should be noted that some polynuclear complexes have been reported in preceding sections.

7.1. Cluster complexes

A variety of homonuclear [452–458] and heteronuclear [459–462] nickel-containing clusters have been prepared and isolated in the solid state. Due to the complex nature of these compounds, single-crystal X-ray crystallography continues to be the preferred method of characterisation and Table 7 lists some relevant structural data.

Homonuclear clusters vary from those containing the Ni_2 single bond to one containing a Ni_{16} framework. Of particular interest is the complex, $[\{Ni(NPh_2)_2\}_2]$, which has been prepared from $[Ni(NPh_2)_3]^-$. These appear to be the first three-coordinate Ni complexes that have been reported [452]. Apart from the homonuclear complexes listed in Table 7, the EPR spectra and structures of $Ni_2(CO)_8^+$, $Ni_2(CO)_7^-$, and $Ni_2(CO)_6^+$, have been reported [453], while a comprehensive molecular orbital study of triangular nickel clusters has been undertaken [454].

Heteronuclear clusters that have been isolated include those containing nickel and molybdenum [459], nickel and thorium [460], nickel and hafnium [461], and nickel and platinum [462]. The complexes, $[AsPh_4]_4[Ni_{38}Pt_6(CO)_{48}H_2]$ and $[AsPh_4]_2[NBu_4]_3[Ni_{38}Pt_6(CO)_{48}H]$, deserve special mention, as they appear to be the highest nuclearity carbonyl clusters whose structures have been determined using X-ray crystallography [462].

7.2. General polynuclear complexes

Schiff base [463–465,469–473] and related ligands, such as hydrazones [467,468,474] and oximes [466], continue to be utilized extensively in the synthesis of polynuclear nickel complexes (see Table 8). Apart from a series of homonuclear complexes [463–468], a number of heteronuclear complexes containing Ni and Zn [469], Ni and Cd [469], Ni and Sn [470], Ni and Cu [471,474], and Ni and a variety of lanthanides [472,473], have been reported. Of interest is a group of dinuclear Schiff base complexes that contain flexible bridging moieties. The first group (**99**)

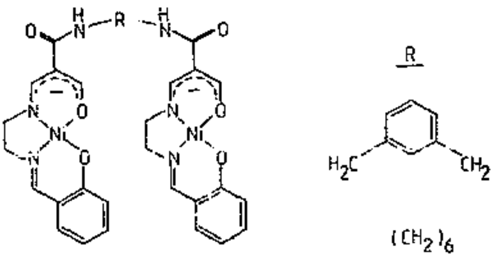

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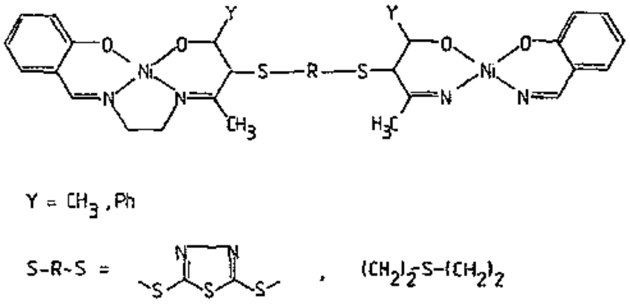
Table 8
Homo- and hetero-polynuclear Ni(II)-Schiff base and related complexes

Ligand	Complex	Comments	Ref.
Homonuclear			
N-(3-Hydroxycarboxylsalicylidene)-X-hydroxyphenylamine (X = 2 or 3) (H_2L)	$Ni_2L_2 \cdot 5H_2O$	Octahedral geometry for both Ni atoms	[463]
4-Hydroxybenzylidene-2-(2-aminophenyl)-benzimidazole (L)	$NiLX_2$	Octahedral geometry; X = Cl, Br, NCS	[464]
Tetradentate Schiff base derived from 2/2 condensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol (H_2L)	$Ni_2LCl_2 \cdot 2H_2O$	Square-pyramidal geometry for Ni(II)	[465]
4,4′-(4,4′-Biphenylylenebisazo)bis(2-hydroxyacetophenone oxime) (H_2L)	$Ni_2L_3 \cdot 4H_2O$	Octahedral geometry for Ni(II)	[466]
Benzyldihydrazone (L)	NiX_2L_2	Octahedral structure; X = Br, I, NCS, NO_3	[467]
1,2-Dimethylethane-1,2-dione dihydrazone (L)	$NiLX_2$	*Trans*-octahedral: X = Cl, Br, I	[468]
Heteronuclear			
1,2-Bis(salicylidene)phenylenediamine (H_2L)	$[NiLMX_2]$	Square planar geometry for Ni(II); M = Zn, Cd; X = Cl, NO_3, ClO_4	[469]
Bis(salicylidene)ethylenediamine) (H_2L)	$[NiLSnX_2]$	X = Cl, Br, NCS	[470]
N,*N*′-Ethylenebis(oxosalicyldiimine) (H_2L)	$[CuLNiB_2]$	Crystal structure; HB = hexafluoroacetylacetone	[471]
N,*N*′-Ethylenebis(2-propiono-acetylphenol) (H_4L)	$[NiLa(L)]NO_3$	The propylene analogue has also been prepared	[472]
N,*N*′-Propylene bis(salicylideneimine) (H_2L)	$Ln(NO_3)_3[NiLB]_2 \cdot 2H_2O$	Ln = Ce, Nd, Sm, Eu, Dy; B = 1,3-diaminopropane	[473]
2-Hydroxy-5-R-phenylthio-carbohydrazone (H_2L)	$NiLCuCl_2$	Square planar geometry for Ni(II)	[474]

have alkylamine bridging groups [475], while the latter (**100**) contain dithiols as bridging groups [476].



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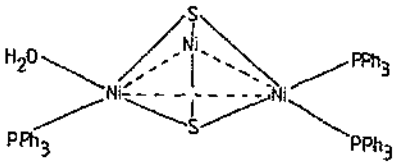
Thiol and related ligands have been used with great effect in the synthesis of sulfur-bridged polynuclear nickel complexes. Table 9 lists a variety of these complexes, which range from dimers to polymers [477–484]. Single-crystal X-ray methods, which have been used to a large degree in the elucidation of the structures of these complexes [477–481], reveal fairly strong Ni–Ni interactions in some cases. The crystal structure of $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5][PF_6]_2$ reveals a triangle of nickel atoms capped above and below by two triply-bridging sulfur atoms. Two nickel atoms are coordinated to two PPh_3 ligands, while the third is bonded to a PPh_3 and H_2O ligand as shown below (**101**) [479].



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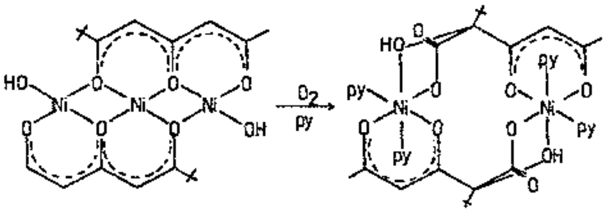
The acetylacetonate complex of nickel(II), $[Ni(acac)_2]_3$, has been used to prepare a number of bimetallic complexes. Reaction of $[Ni(acac)_2]_3$ with MCl_4 (M = Si, Sn, Se, Te) yielded the 1:1 adducts, $[Ni(acac)_2MCl_4]$. These complexes are biologically active, as demonstrated by bacteriostatic, mammalian acute toxicity and antialgal activity tests [485,486].

Continuing with β-polyketone ligands, the trinuclear Ni(II) complex of 2,2-dimethyl-3,5,7-octanetrione (H_3L) has been prepared and characterised as $[Ni_3L_2(OH)_2]\cdot 4MeOH$ (**102**). Reaction of this complex with O_2 in the presence of pyridine yielded a binuclear complex, $[Ni_2L_2(py)_4]$ (L^{2-} = 2-*tert*-butyl-2-hydroxy-3,5-dioxohexanoate) (**103**), the crystal structure of which has been determined [487].

The complexation of ethylene- and *o*-phenylenediamine-*N*,*N*′-bis(dimethylmethy-



(102) **(103)**

lenephosphonic) acids (L) with Ni(II), has been investigated. The ligands function in a tetradentate fashion with polymeric complexes of the type $Ni_2L \cdot nH_2O$ ($n=2$, 4) being isolated [488]. Similarly, methoxymalonamide (L) when reacted with NiX_2 ($X=Br$, NO_3), yielded the polymeric complexes, $NiBr_2 \cdot 3/2L \cdot 4H_2O$ and $Ni(NO_3)_2 \cdot L \cdot 2H_2O$ [489].

Oxalic acid and its various amino and thio analogues have the ability to function as didentate ligands, as bridging tetradentate ligands, or both. The crystal structure of the anhydrous nickel–oxalate complex, β-$Ni(C_2O_4)$, has been reported. The nickel atom is coordinated to two didentate $C_2O_4^{2-}$ and two bridging $C_2O_4^{2-}$ groups [490].

A series of bimetallic complexes, simultaneously containing oxalate and dithioxalate ligands, and 3d and 4f transition metals, has been reported. The complexes, $NaLa(H_2O)_4(C_2O_4)Ni(S_2C_2O_2)_2 \cdot 4.2H_2O$ and $(H_3O)Yb(C_2O_4)Ni(S_2C_2O_2)_2 \cdot 3/2H_2O$, were prepared from the respective lanthanide maleates and $K_2Ni(S_2C_2O_2)_2$ [491]. In addition, the crystal and molecular structure of $Th(H_2O)_6 \cdot Ni_2(S_2C_2O_2)4 \cdot 13/2H_2O$ has been determined. Short Ni–Ni distances (3.43 Å) were observed [492].

Table 9
Polynuclear nickel(II) complexes with bridging sulfur groups

Ligand	Complex	Comments	Ref.
$CH_3CH_2S^-$ (L)	$[Ni_2L_6]^{2-}$	Crystal structure; systematic study of metal(II) thiolates	[477]
$CH_3CS_2^-$ (L)	$[Ni_2L_4]$ $[Ni_2L_4I]$	Crystal structure; Ni–Ni = 2.564(1) Å Crystal structure; Ni–Ni = 2.514(3) Å	[478]
H_2S (H_2L)	$[Ni_3(\mu\text{-}S)_2(H_2O)(PPh_3)_5](PF_6)_2$	Crystal structure; Ni–Ni = 2.95(5) Å	[479]
$(CH_3)_2N(CH_2)_3SH$ (HL)	$[Ni_6L_{12}]$ $[Ni_6(HL)_{12}]X_{12}$	Crystal structure; X = I, ClO_4; Ni–Ni = 2.840(2), 3.018(2), 2.931(2) Å	[480]
$CH_3CH_2OOCCH_2SH$ (HL)	$[Ni_8L_{16}]$	Crystal structure; Ni–S = 2.19 Å	[481]
$CH_2CH_2)_2N(CH_3)CH_2CHSH$ (HL)	$Ni(HL)_2X_2 \cdot nH_2O$	Polymeric; X = Cl, Br, NO_3, ClO_4	[482]
$CH_2(CH_2)_2N(CH_3)CH_2CHSCH_3$ (L)	$[NiL_2]X_2 \cdot nH_2O$	Polymeric; X = Br, I, ClO_4	[483]
$H_2NCH_2CH_2SH$ (HL)	$[Ni(CoL_3)_2]^{2+}$	Synthesis, spectroscopic and electrochemical study	[484]

Tetraethylammonium tetrathioxalate, $[Et_4N]_2[C_2S_4]$, when reacted with $Ni(NO_3)_2$ yielded the polymeric complex, $[Ni(C_2S_4)]x$. Reaction with $Ni(OAc)_2 \cdot 4H_2O$ yielded $[Et_4N]_2[(C_2S_4Ni_3)C_2S_4]$. These oligomers exhibit high electrical conductivities [493].

Large-angle X-ray scattering has been used to study the nickel complex of dithioxamide, $Ni_4(C_2S_2N_2H_3)_2(C_2S_2N_2H_2)_3(H_2O)_{0.25}$. The structural model indicates square planar geometry for Ni, with the ligand functioning as a planar, bridging moiety [494]. In addition, the mixed ligand complex, $Ni_4L_3L^1_2$ (HL = dithiooxamide, HL^1 = thiosemicarbazide), has been prepared. IR and electronic spectra indicate a *trans* configuration for the complex [495].

Halides and pseudohalides such as NCS^-, N_3^- and NO_2^- have the ability to function both as monodentate or bridging ligands. Table 10 lists complexes in which F^- [496], Cl^- [497,498], NCS^- [499,500], N_3^- [501], and NO_2^- [502] function as bridging moieties. Of particular interest are the dimers, $[LNi(\mu\text{-}N_3)_3NiL](ClO_4)$ and $[L^1_2Ni_2(N_3)_2(\mu\text{-}N_3)_2]$ (L = *N,N′,N″*-trimethyl-1,4,7-triazacyclonane; L^1 = 1,5,9-triazacyclodecane). The former complex contains three end-to-end coordinated μ-azido bridges, whereas the latter contains only two μ-azido bridges and two monodentate N_3^- ligands [501].

Turning to nitrogen donor ligands, the coordination complexes of $NiCl_2$ with tetrazole and benzaldehyde tetrazolylhydrazone have been synthesized and character-

Table 10
Polynuclear nickel(II) complexes that contain halide or pseudohalide bridging moieties

Bridging halide	Complex	Comments	Ref.
F^-	$[Ni_3L_6(NCS)_4F_2](H_2O)_2$ (L = 3,5-diethyl-1,2,4-triazole)	Crystal structure of Co analogue; two fluorine atoms and four triazole ligands bridge, while the NCS ligands and two triazole ligands occupy terminal positions	[496]
Cl^-	$[Ni_2L_2Cl_4]$ (L = 2-(3,5-dimethylpyrazol-1-yl)quinoline)	Crystal structure of Co analogue. Two Cl atoms function as bridging ligands. The coordination environment of the metal ion is approximately trigonal bipyramidal	[497]
	$[NiL(H_2O)X]_4X_4$	X = Br; L = *N,N*-diethylnicotinamide	[498]
	$(\mu^4\text{-}O)[NiL(H_2O)]_4X_6$	X = Cl, Br; L = ethyl nicotinate	[498]
	$[NiCuL(H_2O)X_2]_2Y$	X = Cl, Br; Y = CO_3; L = ethylnicotinate or *N,N*-diethylnicotinamide	[498]
NCS	$NiHg(SCN)_4L$	L = various didentate hydrazide ligands	[499]
	$L_2Ni(NCS)_2(NCSAg)_2$	L = various ureas, amides or acetanilides	[500]
N_3	$[LNi(\mu\text{-}N_3)_3NiL](ClO_4)$	L = *N,N′,N″*-trimethyl-1,4,7-triazacyclonone; crystal structure L′ = 1,5,9-triazacyclodecane	[501]
	$[L'_2Ni_2(N_3)_2]$		
NO_2^-	$[NiL_2(NO_2)](ClO_4)$	L = 1,3-diaminopropane; polymeric structure	[502]
	$[Ni_5L_4(NO_2)_8(OH)_2] \cdot 2H_2O$	L = 1,3-diaminopropane; both chelating and bridging NO_2 moieties present	[502]

ised using spectroscopic, magnetic, and X-ray methods. The compounds, $NiLCl_2 \cdot 1/2H_2O$, have a polynuclear structure with octahedral coordination of Ni(II) [503]. Similarly, the coordination behaviour of the related ligands, 2-halo-1,3,4-thiadiazoles, towards Ni(II) has been investigated [504].

3,6-Bis(2′-pyridyl)pyridazine (**104**) and 2,2 bipyrimidine (**105**) have been utilized in the synthesis of dinuclear metal complexes. The former has been used to prepare the bimetallic heteronuclear species, $[MLNiCl_4]$ {M = Pt, Pd; L = (**104**)} [505], whereas the latter has been used to prepare the homobinuclear complexes, $[L^1_2NiLNiL^1_2]$ (L = (**105**); HL^1 = trifluoro-, hexafluoro-, and phenyltrifluoroacetylacetone) [506]. Both (**104**) and (**105**) function as bridging ligands in these complexes.

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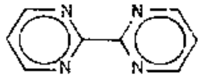


(105)

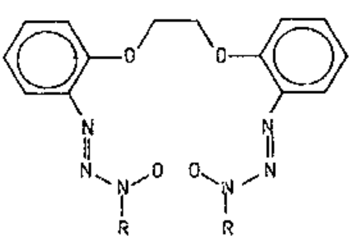
The crystal and molecular structure of tris-1-[bis(8-quinolinato)hydrogen(I)-*N*,*O*]dinickel(II) triiodide has been determined. Each nickel atom is bonded to three didentate quinolinol ligands, with facial conformation, in a distorted octahedral coordination. Three strong hydrogen bonds join two such facial isomers, yielding the dinuclear cation, $[Ni_2\{H(C_9H_6NO)_2\}_3]^+$ [507]. Similarly, the crystal and molecular structure of hexaaquanickel(II) tris(1,8-naphthyridine-2,7-dicarboxylato)dinickelate(II) pentahydrate has been determined, revealing crystals that consist of $Ni(H_2O)_6^{2+}$ and $Ni_2L_3^{2+}$ ions in a hydrogen-bonded network involving five water molecules [508].

Phthivazide (L), when reacted with nickel(II) sulfate, yielded the polymeric complex, $NiL_2SO_4 \cdot 2H_2O$. L coordinates via the heterocyclic N and carbonyl O atoms, while SO_4^{2-} is inner-sphere and bridging didentate. Both water molecules are coordinated as well [509]. In addition, Ni(II) has been complexed with a series of polyurethane-semicarbazides [510], as well as the ionene polymer, poly(ethylenimine) [511].

In a continuing study on polydentate ligands, the hexadentate ligand H_2L (**106**) has been complexed with Ni(II). The resultant complex, NiL, has octahedral geometry, while magnetic moment data suggest a polymeric structure [512].

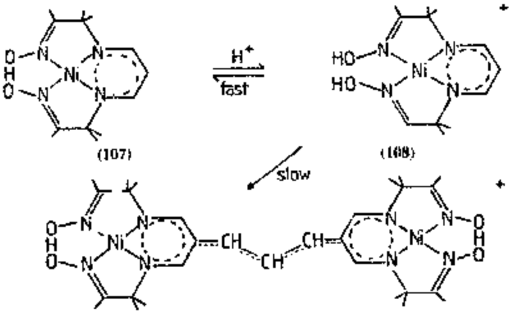
The 20- and 22-membered dinuclear macrocyclic complexes, $[Ni_2LX_4]$ and $[Ni_2L(H_2O)_4](ClO_4)_4$ (X = NCS, NO_2; L = 2,3,6,7,12,13,16,17-octamethyl-1,4,5,8,11,14,15,18-octaazacycloeicosa-1,3,5,7,11,13,17-octaene, 2,3,6,7,13,14,17,18-octamethyl-1,4,5,8,12,15,16,19-octaazacyclodocosa-1,3,5,7,12,14,16,18-octaene), have been prepared by the template condensation of 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione with 1,2-diaminoethane and 1,3-diaminopropane in the presence of Ni(II). Spectroscopic techniques were used to characterize the complexes [513].

2,2,3,9,10,10-Hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene-nickel(II) (**107**) converts, in dilute acid solution, via its oxime-protonated form (**112**), to the expected dinickel complex, [1-[[3,3′-[[(1,1-dimethylacetonyl)amino]methylene]-2-[*N*-(1,1-dimethylacetonyl)formimidoyl]-2,4-



(R=Me, Et)
(106)

heptadienediylidene]dintrilo]bis[3-methyl-2-butanone]tetraoximato](3-)]]dinickel(+1) salt (**109**). The crystal structures of (**107**), (**108**), and (**109**), have been determined [514].



(109)

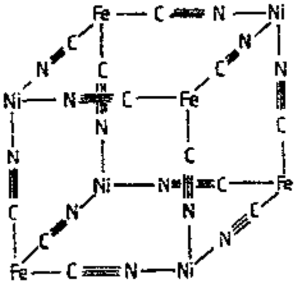
Similarly, the reaction of bis(cycloocta-1,5-diene)nickel with bis(pentamethylcyclopentadienyl)zinc yielded the dinickel complex, $[(C_5Me_5Ni)_2C_{16}H_{24}]$. The reaction is unusual in that it involves an unprecedented coupling between cyclooctadiene ligands that are bound to Ni. A reaction mechanism was proposed, which suggests homolytic cleavage of the Zn–Ni bond in a $(C_5Me_5)Zn$–$Ni(C_5Me_5)(cod)$ intermediate [515].

Various Hoffman-type inclusion compounds have been reported. These include $Cd[NH_2(CH_2)_nNH_2]Ni(CN)_4 \cdot xL$ ($n=4$–8, L = pyrrole, benzene, toluene, aniline, toluidine, xylene, xylidine, dichlorobenzene, trimethylbenzene, ethylbenzene, tetramethylbenzene, styrene, isopropylbenzene) [516]. In addition, the crystal and molecular structure of $Cd[NH_2(CH_2NH_2]Ni(CN)_4 \cdot$ 2.5-xylidene [517], and $Cd[NH_2(CH_2)_6NH_2]Ni(CN)_4 \cdot$ *o*-toluidine [518], have been determined. The structures consist of two-dimensionally extended, but wavy, cyanometal complex layers that are bridged by the diamine to give a 3-dimensional host structure.

A number of other nickel complexes that contain cyanide ligands have been prepared. These include $NiMoO(OH_2)(CN)_4 \cdot nH_2O$ [519], and $Ni[C(CN)_3]_2L_2$ (L =

isonicotinamide) [520]. The latter complex is polymeric with $C(CN)_3^-$ functioning as a tridentate bridging moiety.

The redox behaviour of anodically formed nickel hexacyanoferrate complexes has been examined on electrode surfaces. Cyclic voltammetry indicates a clear size dependence on the ability of metal ions to insert into the lattice (**110**) [521].



(**110**)

8. Nickel(I)

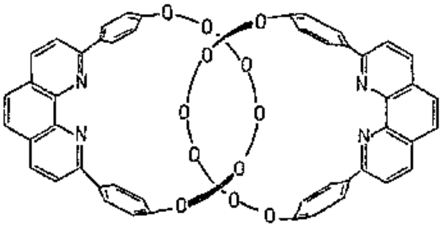
The two principal techniques that have been used in synthesizing Ni(I) complexes are electrochemical reduction of the corresponding Ni(II) complex and, to a lesser degree, oxidation of a suitable Ni(0) precursor.

Electrochemical reduction has been used to great effect in the synthesis of a number of nickel(I)-macrocyclic complexes. This is manifested by a study in which the divalent nickel complexes of 1,4,8,11-tetraazacyotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyotetradecane, *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, and 1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane were reduced to their corresponding Ni(I) complexes in aqueous solution [522]. In addition, the chemical properties of the monovalent nickel complexes, $[NiL]^+$ (L = 1,4,7,10-tetraazacyclotridecane and 1,4,8,11-tetraazacyclopentadecane), have been investigated electrochemically and pulse-radiolytically in aqueous solution [523].

Electroreduction of the nickel(II)–catenand complex, $[NiL]^{2+}$ {L = (**111**)} yielded the corresponding d^9 nickel(I) complex, $[NiL]^+$. This nickel(I) complex displays exceptional redox stability, which is ascribed to the catenand effect [524].

The electrochemical behaviour of a series of BR_2-linked bis(glyoximato)nickel(II) complexes (R = F, C_2H_5) has been investigated in *N*,*N*-dimethylformamide. Results indicate that the electron-withdrawing effect of R affects the electronic states of the nickel complexes [525].

A variety of bis-chelate Ni(I) complexes have been prepared. ESR has been used to study the photoreduction of bis(acetylacetonato)nickel(II) [526], as well as the initial one-electron-reduction products of a series of nickel(II)–bis(1,3-dithio-β-

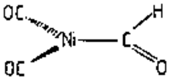


(111)

diketonate) complexes [527]. Similarly, the ESR spectra for dilute solutions of Ni(I) in bis(2-thio-pyridine *N*-oxide)nickel(II) have been studied at 77 K [528].

The electroreduction of a series of complexes of nickel with fluorinated β-aminovinyl ketones and their thio analogues has been reported. Reduction to the Ni(I) species was dependent on ligand used [529].

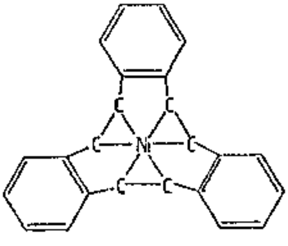
In conclusion, the d^9 species, $(OC)_2NiCHO$ has been prepared by the reaction of H atoms with $Ni(CO)_4$ in a krypton matrix at 77 K. The complex was not thermally interconvertible with its isomer, $HNi(CO)_3$ and, as a result, structure (**112**) was proposed [530].



(112)

9. Nickel(0)

Once again, the bulk of Ni(0) chemistry has centred on phosphine complexes, emphasizing the ability of these ligands to stabilize the lower oxidation states of nickel. By way of introduction to the 0 oxidation state, the synthesis and molecular structure of the Ni(0) complex of 1,2:5,6:9,10-tribenzocyclodeca-1,5,9-tri-

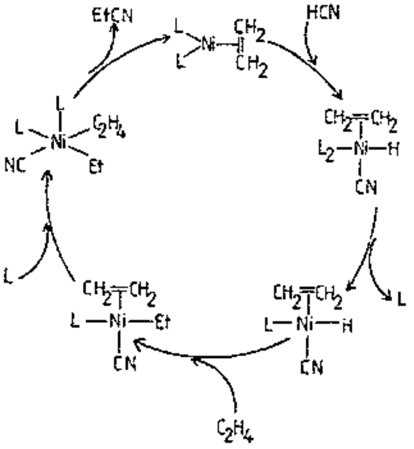


(113)

ene-3,7,11-triyne (**113**) has been reported. The molecule is nearly planar with an average Ni–C distance of 1.958(5) Å [531].

Turning to N-donor ligands, the crystal and molecular structure of 4,6-dimethyl-2,2′-dipyridyldicarbonylnickel(0) has been determined. The coordination geometry about Ni is tetrahedral [532].

The catalytic applications of a number of Ni(0) complexes have been investigated. The reaction of $[Ni(C_2H_4)L_2]$ (L=P{O-*o*-tolyl}$_3$) with C_2H_4 and HCN yielded $[Ni(C_2H_4)L(CN)(C_2H_5)]$ which, when reacted with tri-*o*-tolyl phosphite (L), caused reductive elimination of CH_3CH_2CN and regenerated $[Ni(C_2H_4)L_2]$ (**114**) [533].



(114)

In addition, the reactions of ethylallene, *tert*-butylallene, phenylallene, cyanoallene and methoxyallene with $[Ni(PPh_3)_3]$ have been studied. At low temperatures, both mono- and bis-allene π-complexes have been detected for ethylallene, *tert*-butylallene and dimethylallene [534].

Continuing with compounds that are of catalytic significance, the η^2-(C,C) ketene complex, $[Ni(CH_2=C=O)(PPh_3)_2]$, has been isolated. This complex, which is a model for homogeneous CO reduction, was prepared by carbonylation of nickelacyclobutane complexes, or by the reaction of $[Ni(PPh_3)_4]$ with CH_2Br_2 in the presence of Zn followed by carbonylation [535].

Five new bis(dialkylamino)phosphine nickel complexes of the type $[Ni(CO)_3L]$ (L=Me_2NPF_2, $(Me_2N)_2PF$, $CH_3NCH_2CH_2N(CH_3)PF$, $(Me_2N)_2PH$, $CH_3NCH_2CH_2N(CH_3)PH$) have been prepared in good yield. The complexes were characterised spectroscopically and techniques used included ^{19}F-, ^{31}P- and ^1H-NMR [536].

In conclusion, theoretical studies of the electronic structure, stereochemistry and coordinate bonding in $[Ni(PR_3)_4]$ [537] as well as in the Ni(0)–SO_2 complexes, $[Ni(PH_3)_3SO_2]$ and $[Ni(PH_3)_2SO_2]$ [538] have been undertaken.

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