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1. NICKEL

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CONTENTS

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INTRODUCTION

As part of an ongoing series, this article attempts to review the coordination chemistry of nickel appearing in 1984, including volumes 100 and 101 of Chemical Abstracts. The format of the previous review [1] has been adopted, and the material has been arranged by oxidation state, with further subdivision in terms of ligand donor type. In addition, complexes with mixed ligands have been classified, wherever possible, according to the fundamental theme of the article in which they appeared.

Some articles of general interest have appeared in the literature. These include a review of Fe, Co and Ni which covers 1982 and contains 401 references [2], as well as a study of the dynamic stereochemistry of nickel compounds in which the principle of structure correlation is applied to 78 different pentacoordinate nickel complexes [3].

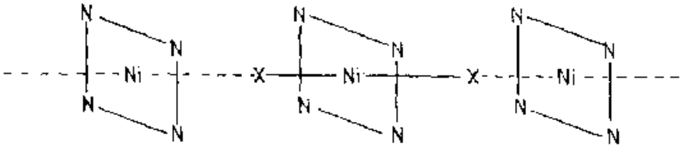
1.1 NICKEL(IV)

Interest in the +4 oxidation state of nickel has centred predominantly on the redox chemistry of nickel(IV) oxime complexes. However, some unusual compounds containing nickel in this oxidation state have been synthesised and are worthy of mention.

The metathetical process previously developed for $(NF_4)_2NiF_6$ has been successfully transferred to the synthesis of the new compound $(ClF_2O)_2NiF_6$. The complex was isolated as a deep purple crystalline solid that is stable at 60°C under a dynamic vacuum. In addition, it is the first example of ClF_2O^+ having been coupled successfully to a highly energetic anion in the form of a stable salt [4].

A new heteropolymolybdate of nickel(IV) of composition $K_2H_8NiMo_7O_{28}\cdot 6H_2O$ with a 1:7 (Ni:Mo) stoichiometry has been reported. The electronic spectrum indicates that the Ni(IV) ions are present in an octahedral array of oxygen atoms which is consistent with the structures available for the heteropolymolybdates [5].

Ni(II)-Ni(IV) mixed-valence complexes continue to attract interest. X-Ray photoelectron spectroscopy has been used to characterise the one dimensional Ni(II)-Ni(IV) mixed valence complexes $Ni(pn)_2Cl_3$ (pn = 1,2-propanediamine) and $NiLBr(ClO_4)_2$ (L= 1,4,8,11-tetraazacyclotetradecane). Square-planar divalent complexes and tervalent six-coordinate complexes of the trans dihalogeno type are alternately arranged as shown below (1) [6].



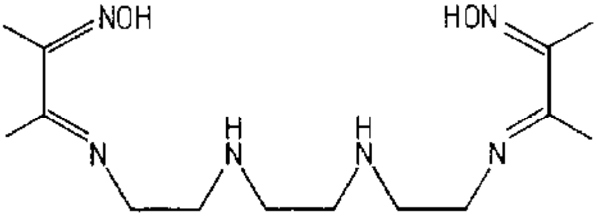
(1)

Of particular interest is the extended partially oxidised linear-chain compound $[NiL_2Br]Br_{1.77}$ (L=1R,2R-cyclohexanediamine). Whereas all reported halogen-oxidised nickel amine complexes have been formulated as stoichiometric compounds with a nickel to halogen ratio of 3, the chemical analysis of the above compound shows a deficiency of 7.7% in the bromide content. It is concluded that this compound, unlike its chloro analogue $[NiL_2Cl]Cl_2$, is not a mixed valence Ni(II)-Ni(IV) system, but rather a mono valent partially oxidised Ni(II) system [7].

1.1.1 Nitrogen-donor ligands

The kinetics of electron transfer in the redox system containing tris(dimethylglyoximato)nickelate(IV) and hydroxylamine have been studied in aqueous medium in the pH range 8.04 - 11.81. A probable mechanism is proposed in which the Ni(IV) complex does not appear to have any kinetic role in the redox system and is involved only in rapid product formation steps [8]. In addition, the acid decomposition of this tervalent nickel complex in the presence of a series of nucleophiles has been investigated [9].

In a continuation of their earlier work, Macartney and McAuley have investigated the kinetics of the reduction of the nickel(IV) oxime complex, $[NiL]^{2+}$ (H_2L=3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dioxime(2)). However, in this work catechol, hydroquinone and 2-methylhydroquinone have been used a reductants in aqueous perchlorate media in the pH range 3.5-6 [10]. The above tervalent complex has also been used as an oxidant in the reduction of <u>bis</u>(2,9-dimethyl-4,7-bis(sulfonatophenyl)-1,10-phenanthrolinato)copper(II) [11].



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1.1.2 Sulphur-donor ligands

Dipropyl- and diisopropyldithiocarbamate have been used as ligands in the synthesis of the complexes $[Ni(S_2CNR_2)_3]I_5$ and $[Ni(S_2CNR_2)_3]Br$ (R=propyl, isopropyl). Both series of complexes are octahedral and diamagnetic [12].

1.2 NICKEL(III)

Multidentate cyclic ligands with nitrogen donor atoms and bidentate sulphur donor ligands have been predominantly utilised in the isolation of nickel in its trivalent oxidation state. Apart from the isolation and characterisation of a few Ni(III) complexes, the main focus of attention as èxpected has been the Ni(III/II) redox couple.

1.2.1 Nitrogen-donor ligands

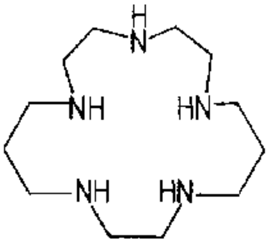
The structure of $[Ni(2,2'\text{-}bipy)_3](ClO_4)_3 \cdot 2CH_3CN \cdot \frac{1}{2}CH_2Cl_2$ has been determined. The coordination sphere consists of the six nitrogen atoms of the three bipyridine ligands in a tetragonally distorted octahedral arrangement with two pairs of longer equatorial bonds [2.022(6) and 2.000(5)A] and a pair of shorter axial bonds [1.924(6)A] [13]. In addition, the kinetics of the oxidation of L-ascorbic acid in acidic aqueous media, using $[Ni(2,2'\text{-}bipy)_3]^{3+}$ as oxidant, have been investigated [14].

Molecular chlorine has been used to oxidise the complex $[Ni(en)_2]^{2+}$ which is located within zeolite Y, to a complex containing nickel in the tervalent oxidation state. EPR confirms the presence of $[Ni(en)_2Cl_2]^+$ which is located within the supercage of the zeolite [15].

The preparation, characterisation and outer-sphere electron-transfer reactions of the macrocyclic complex ion $[NiL_2]^{3+}$ (L= 1,4,7-triazacyclononane) have been described [16,17]. The Ni(III) complex is prepared via oxidation of the corresponding Ni(II) complex and is unusual in that octahedral symmetry around the metal centre is retained upon electron transfer. A self-exchange rate for the Ni(III/II) couple of 6.0 x 10^3 $dm^3mol^{-1}s^{-1}$ has been determined using a Marcus correlation.

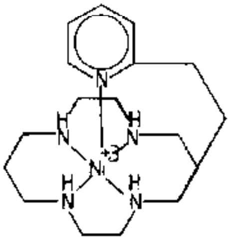
Ti(III) has been used as a reductant in a kinetic and mechanistic study of the reduction of several nickel(III)-macrocyclic complexes. These range from $[NiL]^{3+}$ (L= 1,4,8,11-tetraazacyclotetradecane, C-rac-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, C-meso-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane, 5,12-dimethyl-1,4,8,11-tetraazacyclo-tetradeca-4,11-diene) to $[NiL_2]^{3+}$ (L= 1,4,7-triazacyclononane). Rate constants for the reduction vary from 2.6×10^5 to 2.7×10^6 $dm^3mol^{-1}s^{-1}$ depending on the macrocycle used [18].

The preparation of the pentadentate macrocyclic ligand 1,4,7,11,14-pentaazacycloheptadecane (3) and its complexation with nickel has been reported. The oxidation of $[NiL](ClO_4)_2$ [L=(3)] to the corresponding Ni(III) complex in acetonitrile has been investigated. Cyclic voltammetry indicates an essentially reversible Ni(II)/Ni(III) redox couple with somewhat sluggish electron transfer [19].



(3)

Electrochemical and potentiometric methods have been used to study the structure and oxidation behaviour of a series of square-planar macrocyclic tetraamine complexes of Ni(II) containing a variety of ring sizes, number of imide ions, and extraplanar phenyl, pyridyl and pyridine N-oxide substituents. Of particular interest is the oxidation of the Ni(II) complexes with an appended pyridyl donor. The neutral N_4 species yields a five-coordinate Ni(III) complex (4), while the dianionic N_4 species yields a four-coordinate Ni(III) complex (5) [20]. A novel complex related to (5) in which O_2 bonds directly to nickel and formally exists as $Ni^{3+}-O_2^-$ has been discovered (6) and forms part of a new model reaction for biological mono-oxygenases [21].



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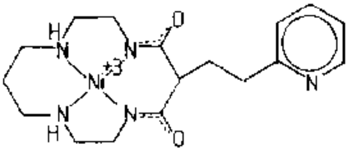

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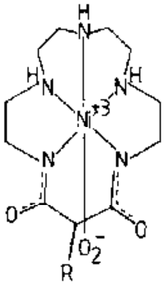


(6)

1.2.2 Sulphur-donor ligands

Bidentate sulphur-donor ligands and in particular dithiolate and dithiocarbamate ligands continue to be utilised in the synthesis of Ni(III) complexes. The crystal and molecular structure of tetra-n-butylammoniumbis(stilbene dithiolato)-

nickelate(III) has been reported. The nickel atom has an approximate square-planar configuration with a mean Ni-S bond length of 2.137(2)A, which is significantly longer than that found in corresponding neutral complexes [22].

A series of Ni(III) dithiocarbamate complexes, $[NiL_2]X$ (L = morpholine dithiocarbamate, X = Cl^-,Br^-,I^- [23]; L = dipropyl- and diisopropyldithiocarbamate, X = I_3^- [12]) have been prepared by oxidation of the corresponding Ni(II) complex using halogen as oxidant. Square-planar geometry is assigned to all the complexes.

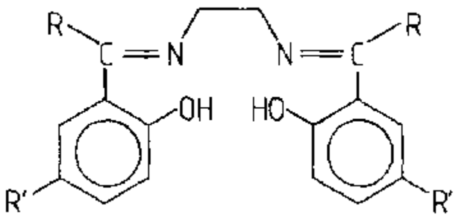
ESR has been used to characterise the Ni(III) complexes of N-mercaptoacetylglycyl-L-histidine and N-mercaptoacetyl-glycyl-glycyl-glycine. Results indicate a structure similar to that found for the Ni(III) chromophore of hydrogenases, in which the metal exhibits tetragonal symmetry with coordination occurring via the sulphur atom of the cysteine moiety [24].

1.2.3 Phosphorus- and Arsenic-donor ligands

In an ongoing study, the five-coordinate nickel(III) complexes $[NiLX_3]$ (L= $Ph_2PCH_2CH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, $Ph_2PCHCHPPh_2$, $o\text{-}C_6H_4(PPh_2)_2$ and $Me_2PCH_2CH_2PMe_2$; X = Cl^-,Br^-) have been prepared by oxidation of $[NiLX_2]$ using X_2 as oxidant. The crystal and molecular structure of $[Ni(Ph_2PCH_2CH_2PPh_2)Br_3]\cdot C_6H_5Me$ reveals an approximately square-pyramidal environment for the metal ion which lies above the P_2Br_2 plane towards the apical bromine atom (Ni-Br = 2.346(3), 2.417(3) and 2.363(3); Ni-P = 2.223(5) and 2.236(5) A) [25].

1.2.4 N,O-donor ligands

A series of dibasic Schiff base ligands H_2L (7) has been complexed with nickel. Depending on the Schiff base and oxidant used, a variety of structures are obtained for the trivalent nickel complexes. Square-planar complexes of the type [NiL]X are obtained when R= R' = H and X= Cl^-,Br^- [26], whereas square-based pyramidal complexes of the type [NiLX] are obtained when R= CH_3, CH_2CH_3; R'= CH_3, Cl and X= I^- [27].



(7)

R = H; R' = H [26]
R = CH_3, CH_2CH_3; R' = CH_3, Cl [27]

The solution properties of a series of bis(dipeptide)-nickelate(III) complexes of GlyGly, AlaGly, AlaAla, GlyAla and AibGly (Gly = glycyl, Ala = alanyl, Aib = α-aminoisobutyryl) have been investigated. EPR indicates that oxidation of the Ni(II) complexes yields Ni(III) species in which the metal ion occupies a compressed octahedral geometry. These complexes undergo an irreversible intramolecular rearrangement in the presence of acid, yielding a yellow transient Ni(III) complex with tetragonally elongated octahedral geometry. The rate of interconversion depends on the peptide [28]. In addition, the electron-transfer kinetics for a series of deprotonated peptide complexes of Ni(III/II) and Cu(III/II) have been measured [29].

1.3 NICKEL(II)

1.3.1 Halide ligands

A novel route for the synthesis of tetrafluoronickelate(II) complexes from aqueous media has been reported. The method allows complexes of the type $A_2[NiF_4]$ (A = NH_4^+,K^+,Rb^+) to be synthesised directly from the corresponding metal acetylacetonate in very high yields [30].

The tetrachloronickelate(II) anion has been isolated with tetraphenylstibonium [31] and 3-acetylpyridinium [32] as cations. Analytical data indicates a tetrahedral environment for the metal ion in both cases, although a polymeric structure is proposed for the latter. In addition, the pentachloronickelate anion $[NiCl_5]^{3-}$ has been isolated as a 4-acetylpyridinium salt. A polymeric structure is proposed for this complex as well [32].

The reaction of I_2 with a series of nickel(II) iodo-complexes has been investigated. Complexes that have been isolated include diamagnetic $[NiL_2][I_3]_2$ (L= en, o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(PMe_2)(PAs_2)$, o-$C_6H_4(PAs_2)_2$), paramagnetic $[NiL_2(I_3)_2]$ (L = $MeSCH_2CH_2SMe$, $MeSeCH_2CH_2SeMe$), $[NiL_2I_4]$ (L= o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(AsPh_2)_2$) and $[Ni(Ph_2PCH_2CH_2PPh_2)I_6]$ [33].

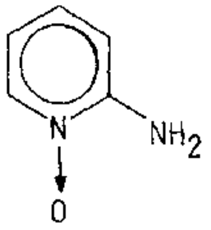
1.3.2 Oxygen-donor ligands

1.3.2.1 Monodentate ligands

Not unexpectedly, H_2O features prominently in this category. The crystal and molecular structure of the hexaaqua-nickel(II) cation, isolated as $[H_3NCH_2CH_2NH_3][Ni(H_2O)_6][SO_4]_2$, has been reported. In the $[Ni(H_2O)_6]^{2+}$ species, the Ni-O distances are very similar {2.060(2), 2.064(2), 2.066(2)A}, while rather unexpectedly, there is a significant departure from octahedral symmetry in the angles [34].

Various tetraaqua-nickel(II) complexes of the type $[Ni(H_2O)_4(HL)_2]$ (H_2L= 4-carboxyphenoxyacetic acid [35], maleic acid [36], salicylic acid [37]) and $[Ni(H_2O)_4L_2]$ (HL= nicotinic acid N-oxide) [38] have been reported. The carboxylic acid ligands function in a unidentate fashion with trans octahedral coordination occurring in all cases. In addition, salicylic acid, apart from functioning in a mondentate fashion, was also found to function as a bidentate ligand and the tetraaquo complex $[Ni(H_2O)_4(HL)]$ was also isolated [37].

2-Aminopyridine N-oxide (8) has the capability of coordinating as a bidentate liquid, or a unidentate O or N ligand. The reaction of (8) with various nickel(II) salts has been investigated. The neutral ligand appears to be an O-donor in most cases, as exemplified by the octahedral complexes $[NiL_6]X_2$ (X= ClO_4^-, BF_4^-, NO_3^-). An N-oxide bridged species $[NiL_2Br_2]_2$ (9) has also been isolated [39].



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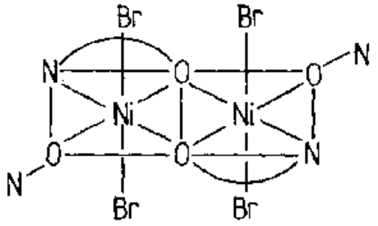


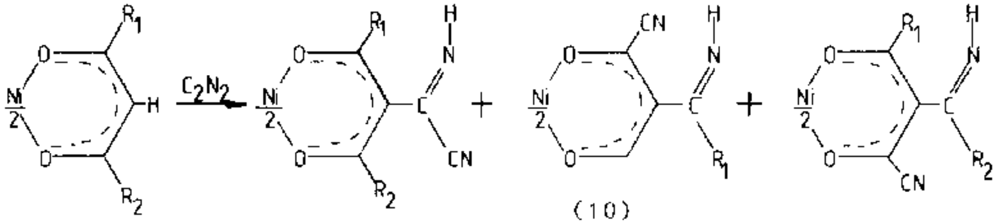
(9)

2-Pyrrolidone, which possesses two possible sites for coordination (NH and CO groups), has been used as a ligand in the synthesis of some mixed ligand Ni(II) complexes. Analysis of the complexes $[NiL_2L'_2]$ (HL= pyrrolidone; L'= heterocyclic diamine) reveals that 2-pyrrolidone functions as a unidentate O-donor ligand [40]. In addition, a study of the magnetic properties of the cyano complexes of Ni(II) with oxygen-donor organic ligands, $[Ni(CN)_2L]$ (L= dimethylsulphoxide, dimethylformamide, dimethylacetamide), has been undertaken [41].

The complexation of 1-hydroxyethane-1,1-diphosphonic acid (H_5L) with Ni(II) has been studied in aqueous solution. Equilibrium and stability constants for a large number of complexes have been determined using nuclear magnetic relaxation methods [42].

1.3.2.2 Bidentate ligands

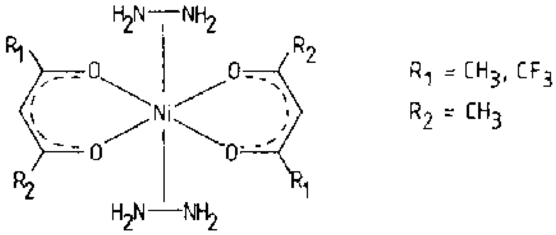
β-Diketonato complexes of Ni(II) continue to attract interest, although the emphasis seems to have shifted to their reactions rather than synthesis. A series of bis(β-carbonylenolato)nickel(II) complexes have been found to be reactive towards C_2N_2. Reaction occurs at the active carbon of the chelate ring and gives rise to square-planar isomers (10) [43,44]. The mass spectrometric behaviour of these complexes has also been investigated [45].



(10)

Various adducts of Ni(II) β-diketonate complexes have been synthesised and studied. Nuclear magnetic resonance has been used to study the effect of axial ligand strength on the proton isotropic contact shifts of the β-diketone ligand in the complexes $[NiL_2L'_2]$ (HL= 2,2,6,6-tetramethyl-3,5-heptanedione; L'= triethylamine, pyridine, piperidine, tetrahydrofuran, dimethylsulphide, dimethylformamide, dimethylsulphoxide, hexamethylphosphorictriamide) [46]. The thermal behaviour of the adducts of nickel(II) β-diketonates with hydrazine has been studied. Data obtained from thermal analysis and infrared spectroscopy indicate that the hydrazine is bonded side-on (11) [47].

(11)



While on the subject of β-diketonate complexes, several new ternary complexes of the types $[NiLL'(H_2O)]$, $[NiL_2(HL')]$ and $[NiLL'(pyridine)_2]$ (HL= acetylacetone, HL'= 1-nitroso-2-naphthol) have been prepared and characterised. The latter two complexes are octahedral while magnetic data indicate the possibility of an overall antiferromagnetic interaction between nickel atoms in the aquo complex and its anhydrous analogue [48].

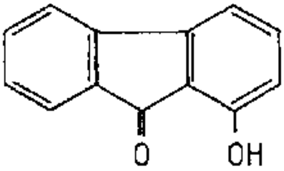
Biuret, structurally similar to acetylacetone, has been reacted with various nickel(II) salts. Infrared and magnetic data indicate that the resultant complexes $[NiL_2X_2]$ (L= biuret; X= Cl^-, Br^-,I^-) are octahedral with a trans configuration [49].

Salicylaldehyde, salicylic acid and their substituted analogues have been the subject of some study. Complexes that have been isolated in the solid state consist of $[Ni(HL)_2]$ (H_2L= salicylic acid) [50], $[Ni(HL)_2(H_2O)_2]$ (H_2L= $(3\text{-}HO_2C\text{-}4\text{-}HO\text{-}C_6H_3)\text{-}C(O)(CH_2)_4CO_2H)$) [51] and [NiLCl] (HL = $RC_6H_4N{:}NC_6H_3$-m-CHO-p-OH; R= o-, m-, p-OMe and o-, m-, p-NO_2) [52]. In all cases coordination occurs via the deprotonated α-hydroxy and carbonyl (aldehyde) or carboxylate (acid) groups. In addition, the stability constants of the nickel(II) complexes of a series of substituted salicylic acid ligands [53] as well as the binary complexes of other substituted salicylic acid ligands with 1,10-phenanthroline [54], have been determined potentiometrically.

Oxalic acid complexes of Ni(II), and in particular their hydrazine adducts, have attracted considerable interest. The oxalate ligand has the capability of coordinating in a bidentate fashion as found in $[Ni(C_2O_4)(N_2H_4)]\cdot H_2O$ [55] and $[Ni(C_2O_4)_2(N_2H_4)_2]$ [56], or in a tetradentate manner as in $[Ni(C_2O_4)(N_2H_4)_2]$ [56]. The equilibrium constants of the oxalato-hydrazine-Ni(II) system have also been determined, and it is found that there is a decrease in the stability of the complexes as the number of coordinated hydrazine molecules is increased [57].

Various carboxylic acid ligands have been reacted with Ni(II). The sodium salt of 2-ethylhexanoic acid reacts metathetically with $NiSO_4$ and $Ni(NO_3)_2$ yielding [Ni(OH)L] and $[NiL_2]$ [58]. The interaction of Ni(II) with dithiodipropionic acid has been investigated. Two chelates having 1:1 and 1:2 molar ratios of metal to ligand are formed [59]. Other acids that have been complexed with Ni(II) are variously-substituted benzoic acids [60], phthalic acid [61] and succinic acid [62]. The ester, ethyl α-ketocyclopentylcarboxylate (L), reacts with divalent nickel yielding the octahedral complex $[NiL_2(H_2O)_2]$ [63].

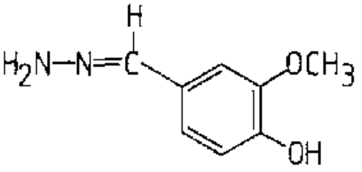
1-Hydroxy-9-fluorenone (HL) (12), a β-ketoenolate ligand, has been shown to react with Ni(II) in its deprotonated form. The resultant complex $[NiL_2(H_2O)_2]$ is octahedral [64].



(12)

Vanillin-hydrazone (HL) (13) has the capability of coordinating via a number of donor atoms. In addition, the possibility of forming dimeric as well as monomeric complexes exists. Reaction of the sodium salt of (13) with $Ni(SO_4)\cdot 7H_2O$ yields a monomeric trans octahedral complex $[NiL_2(H_2O)_2]$ in which coordination occurs via the two oxygen donor atoms [65].

(13)



Tris octahedral complexes of the type $[NiL_3]^{2+}$ are obtained when the ligands Rac- and Meso-1,2-bis(phenylsulphinyl)ethane [66] and 2,2'-biquinoline 1,1'-dioxide [67] are complexed with Ni(II).

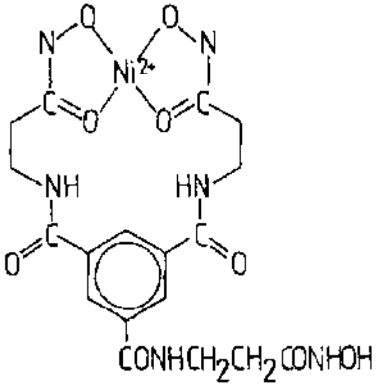
The complex $[Ni(triphos)(\eta^2\text{-}CS_2)]$ reacts with CO_2 yielding CO and the square-planar complex $[NiL(CO_3)]$ $\{L = O{=}PPh_2CH_2C(CH_3)\text{-}(CH_2PPh_2)_2\}$ of which the X-ray crystal structure has been determined. This reaction is unusual since it is an example of a metal-promoted reduction of CO_2 in which both the ligand and CO_2 function as oxygen sinks [68].

The interaction of Ni(II) with a selection of hydroxyanthraquinone ligands has been investigated. 1,2-Dihydroxyanthraquinone (H_2L) and 1,2-dihydroxy-3-sodium sulphonate anthraquinone (Na^+H_2L) produce complexes of the type $[Ni(HL)_2]$ and $[Ni(HL)_2]^{2-}$ respectively. However, 1-hydroxyanthraquinone (HL) yields the mixed-ligand complex $[NiL(H_2O)(CH_3COO)]$. In addition, 1,2-dihydroxyanthraquinone also yields the complex $[NiL(H_2O)]$ in which the ligand functions as a tridentate O-donor ligand [69].

1.3.2.3 Polydentate ligands

The synthesis of a new tris-bidentate ligand N,N',N" tris[2-(N-hydroxycarbamoyl)ethyl]-1,3,5-benzenetricarboxamide has been described. Solution studies indicate that only two arms of the ligand are utilised for coordination, and that the ligand coordinates as a tetradentate oxygen donor (14) [70].

(14)

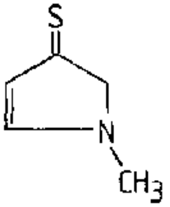


1.3.3 Sulphur- and Selenium-donor ligands

1.3.3.1 Monodentate ligands

A series of diarylthiolatonickel(II) complexes, formulated as $[Ni(ArS)_2L_2]$ (ArS= C_6H_5S, p-Cl-C_6H_4S, p-CH_3-C_6H_4S, p-NO_2-C_6H_4S; L= 2,2'-bipyridine, PEt_3) has been prepared. These complexes are formed by the oxidative addition of the corresponding diarylsulphide and basic ligands to $Ni(cod)_2$ [71].

The crystal and molecular structure of the tetrakis complex $[NiL_4]Br_2$ (L= 1-methylimidazoline-2(3H)-thione (15)) has been reported. The structure consists of distorted square-planar cations (Ni-S= 2.207(2) and 2.217(2)A) and bromide ions held together by a combination of H-bonds and van der Waal's forces [72].



(15)

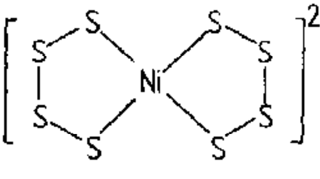
Acetophenone thiosemicarbazone has the capability of coordinating via a number of donor atoms. A single crystal X-ray analysis reveals that Ni(II) coordinates to the sulphur atoms alone, yielding the tetrahedral complex [NiL_2Cl_2] (L= acetophenone thiosemicarbazone) [73].

1.3.3.2 Bidentate ligands

Dithiocarbamate ligands and their complexation with nickel continue to attract interest as can be seen in table 1. Complexes are mostly square-planar with the S_4-coordination sphere predominating even in the presence of other donor atoms. The ligands generally function in a bidentate fashion with the exception of ethyl N-phenyldithiocarbamate which coordinates as a monodentate sulphur-donor ligand [83]. In addition, the crystal and molecular structure of the mixed-ligand complex [NiLL']$^-$ (L=diethyl-di-selenocarbamate, L'= maleonitrile-dithiolate) has been determined as its tetra-n-butylammonium salt. The anion is essentially planar but has low symmetry with the metal-donor atom bond distances varying considerably (Ni-S = 2.15(3) and 2.08(4)A; Ni-Se = 2.37(2) and 2.31(2)A) [84].

Turning to dithiolate Ni(II) complexes, the olive-green anionic precursor to Hieber's nickel(IV) dithiolate [$Ni(S_2CC_6H_5)$-$(S_3CC_6H_5)$], originally thought to be [$Ni(IV)S(S_2CC_6H_5)_2$], has been identified as [$Ni(S_2CC_6H_5)_3$]$^-$. The structure of this anion has been determined using [K(2,2,2-crypt)]$^+$ as a cation. The coordination geometry is that of a distorted NiS_6 octahedron with an average Ni-S bond length of 2.4A [85].

A rather unusual "binary nickel-sulphur" complex [$Ni(S_4)_2$]$^{2-}$ has been isolated as a tetraethylammonium salt. A single-crystal X-ray analysis reveals a planar configuration with the $S_4{}^{2-}$ ligands coordinating in a bidentate fashion similar to that found in dithiolate complexes (16) (Ni-S = 2.185(2)A) [86].



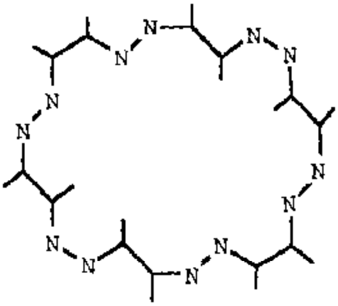
(16)

EPR spectroscopy has been used to study the ligand exchange of [NiL_2] (HL= 1,1-diethyl-3-thiobenzoyl-thiourea, 1,1-diethyl-3-

TABLE 1. Dithio(seleno)carbamate ligands and their Ni(II) complexes

LIGAND (L)	COMPLEX	COMMENTS	REF.
$[(CH_3CH_2CH_2CH_2)_2NCS_2]^-$	$[NiL_2]$	Square-planar: Crystal structure	[74]
$[\overline{CH_2CH_2XCH_2CH_2N}CS_2]^-$ ($X=CH_2,NH,NCH_3,O,S$)	$[NiL_2]$	Square-planar, XPS study	[75]
$[\overline{CH_2CH_2XCH_2CH_2N}CS_2]^-$ ($X=C_6H_5CH,C_6H_5N$)	$[NiL_2]$	Square-planar	[76]
$[X(H)NCS_2]^-$ (X=$\underline{o}$,$\underline{m}$ or $\underline{p}$-ClC_6H_4)	$[NiL_2]$	Square-planar, Thermal analysis	[77]
$[H_2NCS_2]^-$	$[NiL_2]$	Normal Coordinate Analysis	[78]
$[(CH_3CH_2CH_2)_2NCS_2]^-$	$[NiL_2]$	Photoelectron study	[78,79]
$[HS(CH_2)_3(H)NCS_2]^-$	$[NiL_2]$	Square-planar, Novel synthesis	[80]
$[(CH_3CH_2)_2NCS_2]^-$	$[NiLL']$	L'= γ-picoline, isoquinoline	[81]
$[\overline{CH_2CH_2CH_2CH_2N}CS_2]^-$	$[NiLL']$	L'= dimethylglyoxime, 8-hydroxyquinoline	[81]
$[(CH_3CH_2)_2NCSSe]^-$	$[NiL_2]$	Thermal study	[82]

planar geometry is proposed on the basis of infra red and ^1H n.m.r. spectroscopic results [555].



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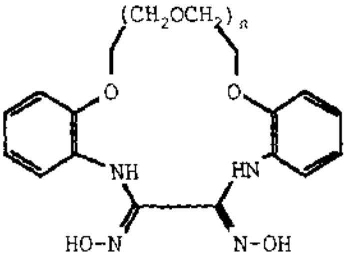


(158)

Improved syntheses to metal, including cobalt(II), complexes containing quadridentate, macrocyclic ligands have been described; individual ligands are too numerous to list here, but are related to **(42)** or **(129)** [556, 557].

Cobalt(II) complexes invoking porphyrin or phthalocyanine ligands are detailed below. Any non-standard abbreviations used have previously been defined in Section 2.2.7.7. The catalytic properties of [Co(TPP)] and [Co(Pc)], with respect to quadricyclane isomerisation, have been studied [558]. During the course of electrochemical investigations, species of the type $[Co(TPP)(NO)L]^+$ have been observed; formation constants, log *K*, for the complexes are 3.1±0.1, 3.3±0.1, and 5.3±0.2 for L = dmf, dmso, and py respectively [559]. An interesting bridged, heterometallic complex has been characterised and exhibits a nickel(II) Schiff base complex coordinated *via* an imidazole residue to the axial site of [Co(TPP)] [560]. Stopped flow techniques have been used to monitor the complex formation between Co(II) ions and *N*-methylated-$TPPH_2$; the reaction is second order, depending on each reagent, and a value of $\Delta V^{\ddagger} = 8.0 \pm 0.3$ cm^3 mol^{-1} has been determined [561]. In experiments designed to provide models for coenzyme B_{12}, e.p.r. spectra of complexes with spin-labelled py coordinated to [Co(TFPP)], ($TFPPH_2$ = tetra(*p*-trifluoromethyl)porphyrin), have been analysed [562]. Alkoxy-derivatives of $TPPH_2$ have been the subjects for both preparative, [563], and catalytic, [564], investigations. A rather exotic ligand sporting a crown ether-substituted tri(*p*-chloro)porphyrin has been prepared; reaction with cobalt(II

The electron-electron spin-spin interaction is shown to decrease rapidly as the number of CH_2 groups is increased [91].

1.3.4 Nitrogen-donor ligands

1.3.4.1 Monodentate ligands

The most widely studied monodentate N-donor ligand is still pyridine and its substituted analogues. However, as can be seen in table 2, the emphasis has shifted towards the variously-substituted pyridine ligands and the effect that the substituent has on coordination geometry. Tetrahedral [92,93], square-planar [92,93] and octahedral complexes [92-97] have been isolated with the stereochemistry depending on nature and position of substituent, as well as the type of anion, if present.

The interaction of Ni(II) with benzimidazole and its substituted analogues has been studied using dimethylsulphoxide as solvent. Both 1:1 and 1:2 (metal:ligand) complexes are formed in solution, while it is observed that the alkyl substituents (Me,Et,Bu) in the 1-position exert very little effect on the stabilities of the complexes [99]. In addition, the formation constants of the nickel complexes of 4-methyl-, 2-(2'-hydroxyphenyl)-, 2-(2'-hydroxy-5'-bromophenyl)-, 2-(2'-hydroxy-3-methoxy)- and 2-(1'-hydroxyethyl)benzimidazole have been determined potentiometrically. Results indicate that the metal ion reacts with the neutral ligand initially and with the anionic ligand in the latter stage [100].

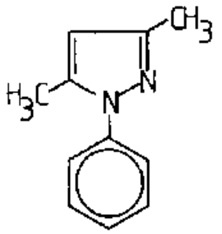
Turning to the solid state, complexes of the type $[NiLX_2]$, $[NiL_2X_2]$, $[NiL_4X_2]$ (L= 6-methyl-2-aminobenzothiazole; X= I^-, NCS^-, OAc^-) and $[NiL_2L'_2X_2]$ (L'= 2-methylbenzimidazole; X= Cl^-, Br^-, I^-, NCS^-) have been prepared. Coordination of L occurs via the amino group whereas coordination of L' occurs via the tertiary nitrogen atom [101].

1-Phenyl-3,5-dimethylpyrazole (19) has been reacted with various Ni(II) salts yielding square-planar complexes $[NiL_2X_2]$ (X= Br^-, NCS^-) and the octahedral complex $[NiL_2(NO_3)_2]$ in which NO_3^- functions as a bidentate ligand. Coordination of the ligand occurs via N(2) in each case [102]. The related ligand, isothiazole (20), and its 3-, 4- and 5-methyl substituted analogues

TABLE 2. Some pyridine and substituted pyridine complexes of Ni(II)

LIGAND (L)	COMPLEX	COMMENTS	REF.
2-,3-,4-R-pyridine ($R=CH_3,CH_2CH_3,Cl,Br,CN$)	$[NiX_2L_2]$ (X=NCS,Cl,Br,I)	Various stereochemistries depending on position and nature of substituent as well as anion used.	[92,93]
3-,4-methylpyridine	$[NiX_2L_4]$ (X=Cl,Br)	Mixed-complex combinations of Ni(II) with picolines, Characterised thermogravimetrically.	[94]
2-,3-aminopyridine	$[Ni(OAc)_2L_2]$	Acetate group coordinates in a bidentate fashion when L=2-aminopyridine and in a monodentate fashion when L=3-aminopyridine.	[95]
2-,3-,4-hydroxypyridine or 2-,3-,4-aminopyridine	$[Ni(OAc)_2L_2]$	*Trans*-octahedral with acetate group coordinating in a bidentate fashion.	[96]
4-hydroxypyridine	$[Ni(OAc)_2L_4]$	*Trans*-octahedral with acetate group coordinating in a monodentate fashion.	[96]
pyridine	$[Ni(A\text{-}A)L_2]$	Pyridine exchange monitored using ^{14}N-n.m.r. (A-A=dithiocarbamate,xanthate dithiophosphate and monothioacetylacetonate ligands).	[97]
pyridine	$[NiX_2L_2]$ (X=Cl,Br,I)	Catalyst for the oxidative coupling of CO with alkali alkoxides to give oxalic acid derivatives.	[98]

have been complexed with various nickel(II) salts. Complexes of the type [NiL_2X_2] (L= 3-methyl- and 5-methylisothiazole; X= Cl^-, Br^-), [NiL_4X_2] (L= 4-methyl- and 5-methylisothiazole; X= Cl^-, Br^-) and [NiL_6]$(ClO_4)_2$ (L= 4-methyl- and 5-methylisothiazole) were isolated. All the complexes are coordinated via the nitrogen atom [103]. In addition, 3-amino-5-methylisoxazole (21) coordinates via the heterocyclic nitrogen atom yielding the complex [NiL_2Cl_2] which has been studied using ^1H-n.m.r. [104].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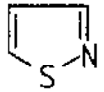
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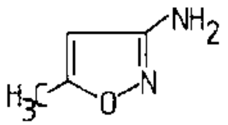
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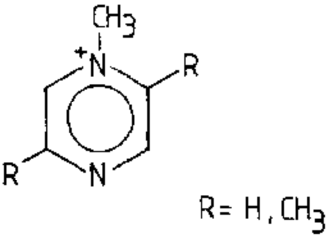
The crystal and molecular structure of [NiL_2Cl_2] (L= 3,4-dihydro-1-phenyl-1H-[1,4]-oxazino [4,3-a]benzimidazole) has been reported. Coordination of the ligand occurs via the secondary nitrogen atom while the stereochemistry adopted by the metal ion is essentially distorted tetrahedral (Ni-N = 1.992(4) and 2.002(5)A; Ni-Cl = 2.213(2) and 2.240(2)A) [105].

In an ongoing structural investigation of Ni(II) complexes, the crystal and molecular structure of the complex compound [$NiL_4(NCS)_2$] (L= piperidine) has been reported. The complex has a trans-octahedral structure, coordinated by two N atoms from the NCS groups (Ni-N = 2.00(1)A) and by four N atoms from the piperidine molecules (Ni-N = 2.28(2) and 2.36(3)A) [106]. As part of this series, the crystal and molecular structure of [NiL_2(pyridine)$(NCS)_2(H_2O)$]·2L (L= piperidine) has also been determined. The Ni(II) atom exhibits octahedral coordination with the thiocyanate groups occupying the trans-axial positions. Some relevant data are Ni-N(NCS)= 2.064(6), Ni-N(piperidine)= 2.208(6), Ni-N(pyridine)= 2.148(9) and Ni-O(H_2O)= 2.165(7)A [107].

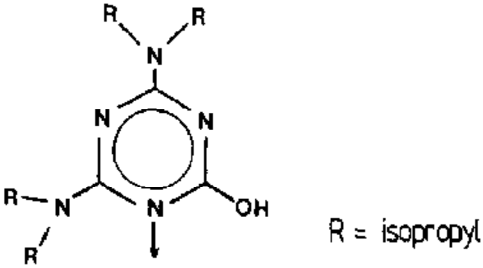
Structurally related morpholine has been complexed with various nickel(II) salts. Apart from [NiL_3Br_2] (L= morpholine), which appears to contain bridging morpholine, all the other complexes have the neutral ligand acting in a monodentate fashion identical to piperidine. Other complexes that have been isolated are square-planar [$NiL_2(C_6F_5)_2$], psuedo-octahedral [NiL_2Br_2], and octahedral [NiL_4I_2] [108].

Monoquaternised pyrazinium cations (22) have been utilised as "non-basic" nitrogen donor ligands. N-methylpyrazinium (L^+) forms zwitterionic complexes of the type [$Ni(L^+)_2X_4$] ($X= Cl^-, Br^-$), while mono-hindered N(1)-methyl-2,5-dimethyl-pyrazinium yields square-planar complexes of the type [$Ni(L^+)X_3$] [109].



(22)

Considering the number of available coordination sites, it is somewhat surprising that 6-hydroxy-2,4-bis(isopropylamino)-1,3,5-triazine (23) functions as a monodentate ligand when reacted with $NiCl_2$. The resultant complex [NiL_2Cl_2] has a tetrahedral configuration, with coordination occurring via N(1) as shown below [110]



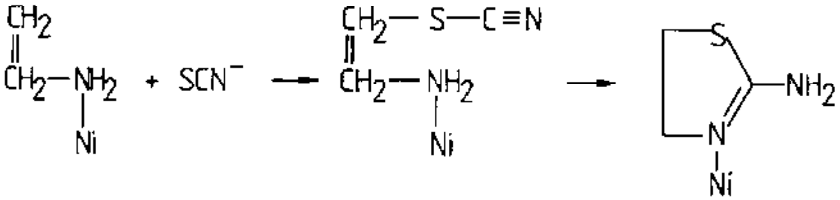
(23)

Four Schiff bases, viz. vanillideneaniline, vanillidene-o-toluidene, vanillidene-m-toluidene and vanilledene-p-toluidene have been complexed with $NiSO_4$. The resultant complexes [$NiL_2(H_2O)_4$] (L= Schiff base) are octahedral and are unusual in that the Schiff bases function as monodentate ligands coordinating only through their azomethine nitrogen atoms [111].

The complex formation reactions of a series of Ni(II) salts with 1-(2-pyridylazo)-2-naphthol in acetic acid to form the 1:1 complex have been studied using a stopped-flow technique. The second-order rate constants and activation parameters were determined and a dissociative mode of activation is suggested [112]. In addition, the effect of substituents on structural isomerism in the 1:1 nickel chelates of various asymmetrical O,O'-dihydroxyazo compounds has been investigated [113].

Turning to primary amine ligands, the crystal and molecular structure of $[NiL_4(Cl_3CCOO)_2]\cdot 2L$ (L= para-chloroaniline) has been reported. The Ni atom exhibits distorted trans-octahedral coordination in which the apical positions are occupied by the acetate moieties (Ni-O = 2.03(2)A) while the remaining coordination sites are occupied by aniline molecules (Ni-N= 2.20(4) and 2.25(4)A) [114]. The complex cation $[Ni(NH_3)_6]^{2+}$ has been isolated as a nitro-formate salt and its crystal structure determined. As expected, the cation is an almost regular octahedron with Ni-N varying from 2.12(1) to 2.18(1)A [115].

The complex formation of (thiocyanato)nickel(II) in dimethylformamide has been studied as a function of temperature and pressure. The kinetic parameters indicate that a dissociative activation mode is prevalent [116]. Finally, while on the subject of thiocyanate ligands, the reaction of NH_4SCN with tetrakis-(ethylenimine)nickel(II) thiocyanate has been reported. The reaction is interesting in that the ethylenimine ligands are converted to 2-aminothiazoline ligands via an inner-sphere mechanism (24) [117]



(24)

1.3.4.2 Bidentate ligands

Diamines, and in particular ethylenediamine, still constitute the most widely studied ligands in this category. Surprisingly a substantial amount of work has been done on the fundamental tris and bis nickel(II) complexes, with relatively few mixed-ligand complexes being reported (see table 3). Of particular interest is a study of the conformational changes of nickel(II) diamine complexes in the solid state. Various conformers of $[NiL_3]X_2$ (L= ethylenediamine, 1,3-propane-diamine; X= NCS^-,Br^-) and $[NiL_2(NCS)_2]$ are reported [118]. Also of interest is the fact

TABLE 3. Ethylenediamine and related-ligand complexes of Ni(II)

LIGAND (L)	COMPLEX	COMMENTS	REF.
$H_2NCH_2CH_2NH_2$	$[NiL_3](NCS)_2$	Isolation of conformational isomers and a study of the solid state phase transitions.	[118]
	$[NiL_2](NCS)_2$	*Trans*-chelated monomer obtained from $[NiL_4(NCS)_4]$.	[118]
	$[NiL_3]X_2$ (X=various sulphanilamides)	Estimation of the ligand field parameters of outer sphere ions.	[119]
	$[NiL_3]^{2+}$	Cation in various mixed-metal complexes.	[120]
	$[NiL_2(H_2O)_2](C_2Cl_3O_2)_2$	*Trans*-octahedral; Crystal structure	[121]
	$[NiL(H_2O)_4]SO_4$	Octahedral; Crystal structure	[122]
	$[NiL_2(H_2O)_2B_2]\cdot 2H_2O$ (HB=pyrrolidine)	Distorted octahedral	[123]
$RHNCH_2CH_2NHR$ (R=2,4-dinitrophenyl)	$[NiL_2]X_2$ ($X=CH_3COO^-$, 1/2 SO_4^{2-}, 1/2 $C_4H_4O_4^{2-}$, $C_7H_6NO_2^-$)	Square-planar	[124]
$H_2NCH_2CH_2CH_2NH_2$	$[NiL_3]Br_2\cdot H_2O$	Isolation of conformational isomers	[118]
	$[NiL_2(NCS)_2]$	Isolation of conformational isomers	[118]
	$[NiL_2B_2]$ (HB=trichloroacetic acid)	*Trans*-octahedral; Crystal structure	[125]
	$[NiL_2B_2]$ (HB=*o*-methylbenzoic acid)	*Trans*-octahedral; Crystal structure	[126]
	$[NiL(H_2O)_2B_2]$ (HB=pyrrolidine)	Distorted octahedral	[123]

that all of the complexes listed in table 3 are hexacoordinate, with the exception of the N,N'-bis(2,4-dinitrophenyl)ethylenediamine complex, which is square-planar. This is probably due to the steric nature of the ligand [124].

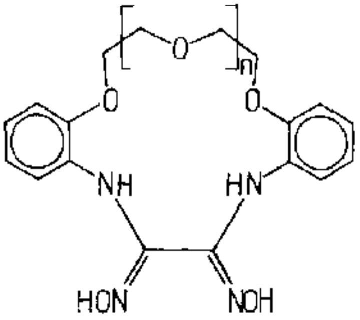
Turning away from the solid state, the formation rates of the 1:1 and 1:2 nickel(II) ethylenediamine complexes with 1,10-phenanthroline have been studied using a stopped-flow technique [127]. In addition, the kinetics of the substitution of cyanide ion with $[Ni(en)_2]^{2+}$ in aqueous solution have been studied spectrophotometrically [128]. Rate expressions have been determined in both of the above cases.

The stability constants of the Ni(II) complexes with 2,2'-bipyridine and 1,10-phenanthroline as primary ligands and N-thiobenzoylhydroxylamine as secondary ligand have been determined potentiometrically in dioxane-H_2O. Formation of the 1:1:1 mixed-ligand complex was observed [129]. The same ligands have been used to synthesise complexes of the type $[NiL_3][H_2PO_4]_2{\cdot}H_3PO_4$ and $[NiL_2][H_2PO_4]_2$ (L= 2,2'-bipy and 1,10-phen). The former complex is octahedral while the latter has been assigned a pseudo-tetrahedral stereochemistry. Phosphate does not coordinate in either of the complexes [130].

The unusual conformational features of 1,5-diazocyclooctane complexed with nickel(II), still continues to generate interest. Empirical force-field methods have been used to reinterpret the published X-ray diffraction data of $[NiL_2](ClO_4)_2$ (L= 1,5-diazocyclooctane). A new molecular disorder is revealed and the refined molecular structure approximates more closely the model expected on chemical grounds [131]. The crystal structure of the nickel(II)tetraphenylborate complex of 1,5-diazocyclooctane and dimethylsulphoxide, $[Ph_4B]_2[NiL_2]{\cdot}(dmso)_2$, has been reported. Coordination is square-planar with the mean angle subtended at the nickel atom by cis nitrogen donors being 90°, and 175° for trans nitrogen ligand atoms [132]. In addition, the dissociation kinetics of bis(1,5-diazocyclooctane)nickel(II) have been studied electrochemically in acidic and basic solution [133].

Dioxime ligands have been used extensively to complex with Ni(II). This is substantiated by the publication of a review, containing 156 references, on the configuration and reactivity of the complexes of Ni(II) with dimethylglyoxime and salicylaldoxime [134].

The synthesis and complex formation of four new macrocyclic vic-dioximes {H_2L = (25)}, having an anti structure, have been reported. The resultant complexes [$Ni(HL)_2$] are square-planar with coordination occurring via the dioxime moiety. This emphasises the stability of nickel-dioxime complexation which in this case prevails over the possibility of macrocyclic coordination [135].

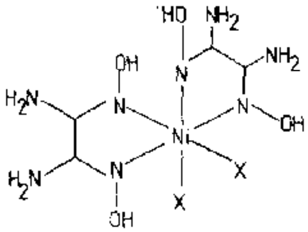


(25)

Oxamide oxime has the capability of coordinating via its amino or oxime functional groups. The crystal and molecular structures of the squaric acid salts of bis(oxamide oxime)-nickel(II) have been reported. Coordination occurs via the oxime nitrogen atoms in both the 1:1 salt $[C_4O_4][Ni(C_2H_6N_4O_2)_2]$ and the 1:2 salt $[C_4O_4]\cdot 2[Ni(C_2H_5N_4O_2)(C_2H_6N_4O_2)]$. As expected, the coordination geometry around Ni(II) is square-planar in both cases with an average Ni-N bond length of 1.87A [136].

Various acids have been added to the square-planar neutral nickel(II) complex of oxamide oxime. Addition of the acid leads to a molecular rearrangement with the resultant complexes adopting an octahedral configuration in which the neutral oxamide oxime ligands coordinate in a bidentate fashion, while the acid anions occupy cis-positions (26). The crystal and molecular structures of [NiL_2X_2] (L= oxamide oxime; HX = hydrochloric acid, sulphanilic acid, phthalic acid [137] and propiolic acid [138]) have been reported.

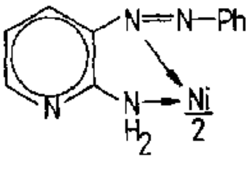
The complex formation equilibria of nickel(II) with 2-amino-acetamidoxime and its variously N-methylated derivatives have been studied potentiometrically. Both octahedral and square-planar complexes are observed in solution [139].



(26)

In addition, the crystal and molecular structures of $[Ni(HL)_2(H_2O)_2]Cl_2$, $[Ni(HL)L]Cl\cdot 1\frac{1}{2}H_2O$ (HL= 2-amino-acetamidoxime) and $[Ni(HL)_2-(H_2O)_2]Cl_2\cdot H_2O$ (HL= 2-(dimethylamino)-acetamidoxime) have been reported. In all three structures the bidentate ligand is coordinated to the nickel atom via its amino and oxime nitrogen atoms. The first and last complexes exhibit octahedral symmetry while the second complex is essentially square-planar [140].

Variously-substituted pyridine ligands have been complexed with Ni(II) yielding a variety of coordination geometries. Ligands used include α-aminopyridine and its methyl derivatives [141], 2-, 3- and 4-pyridinecarboxylic acid hydrazide [142], N-2-picolyl-N'-phenylthiourea [143] and the Schiff bases, picolinethioanilide [144] and o-(N-3,5-di-chloro-α-pyridoneimino)benzene sulphonate [145]. The ligands generally behave in a bidentate fashion coordinating to the metal ion via the pyridine nitrogen atom and a nitrogen atom contained in a pendant side chain. Notable exceptions are 2-pyridinecarboxylic acid hydrazide which coordinates via the pyridine nitrogen atom and the carbonyl oxygen atom [142], and 3-phenylazo-2,6-diaminopyridine [146] which does not utilise the pyridine nitrogen atom at all, and coordinates via the α-amino and azine moieties yielding the more stable 5-membered chelate ring as shown below (27).



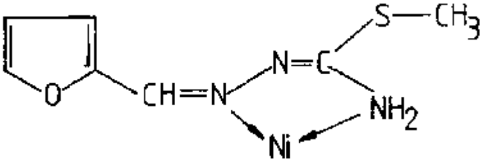
(27)

Finally, the effect of added cations on rate enhancements for the Ni(II)-PADA (PADA= pyridine-2-azo-p-dimethylaniline) reaction in micellar solutions has been examined. Kinetic analyses reveal that the principal effect leading to a decrease in rate enhancement with salt present was a lowering of the surface potential which is manifested by an increase in reaction volume [147].

3-Amino-1-phenylpyrazol-5-one (L) and its Schiff base with salicylaldehyde (HL') have been reacted with $NiCl_2$ yielding $[NiL_2Cl_2]$ and $[NiL'_2]$ respectively. Both complexes are hexacoordinate, with coordination occurring via the two amino groups in the former case, while in the latter case the Schiff base ligand coordinates in a tridentate fashion via the endocyclic amino, imino and phenolic oxygen groups [148].

A new bidentate ligand, [(1-(1H-pyrrole-2-yl)ethylidene)-amino]benzene (HL), synthesised from 2-acetylpyrrole and aniline, has been complexed with Ni(II). The resultant complex, $[NiL_2]$, has square-planar geometry with coordination occurring via the pyrrole and imino nitrogen atoms respectively. In addition, the solution thermodynamic parameters of the complexation have been determined [149].

S-methylthiosemicarbazone (HL) reacts with $Ni(ClO_4)_2 \cdot 6H_2O$ in ethanol yielding the octahedral complex $[Ni(HL)_2(H_2O)_2](ClO_4)_2$ which has a trans-(H_2O)-trans-(HL) configuration. HL functions as a bidentate ligand coordinating via its amino and imine nitrogen atoms as shown (28). Heating of $[Ni(HL)_2(H_2O)_2](ClO_4)_2$ gives the complex $[Ni(HL)_2(ClO_4)_2]$ which also exhibits octahedral coordination [150].



(28)

Acetonecarbodihydrazone, $Me_2C{:}NN(H)C(O)N(H){:}CMe_2$, has a multitude of sites available for coordination. However, the ligand coordinates in a bidentate fashion via its two imino moieties yielding the octahedral complex $[NiL_2Cl_2] \cdot H_2O$ (L= acetonecarbodihydrazone) [151].

The structure and synthesis of bis(N^1-acetimidoylacetamidine-N^1,N^3)nickel(II) chloride trihydrate have been reported. The nickel atom is coordinated by an almost perfect square-planar arrangement of four imino nitrogen atoms (Ni-N ranges from 1.849 to 1.873(4)A). Of particular interest is the fact that the N^1-acetimidoylacetamidine ligand may be prepared by a selfcondensation reaction of acetamidine [152]. In addition, the single-crystal and molecular structure of the related compound, bis-(diiminosuccinonitrilo)nickel(II), has been determined. The complex is essentially square-planar with an average Ni-N distance of 1.827(4)A [153].

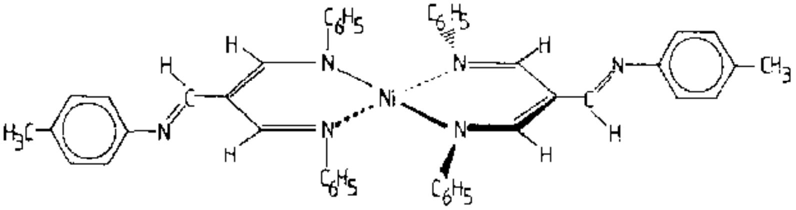
Compounds of formulae $[NiL_2][Cu(acac)_2X]_2$ and $[NiL'_2]$-$[Cu(acac)_2Cl_2]$ (acac= acetylacetonate, X= Cl^-, Br^-, I^-; L = biguanide, L'= N-alkylbiguanide) have been prepared. It is suggested that the nickel complex ions exist as discrete square-planar moieties, with coordination occurring via the imine nitrogen atoms of the biguanide ligands [154].

A spectrophotometric study of the complexation of 2- and 8-diethylaminomethylquinoline with Ni(II) in propylene carbonate has been undertaken. Stability constants and extinction coefficients were calculated and it is shown that the five-membered chelate ring complexes formed by 2-diethylaminomethylquinoline are more stable than the six-membered ring complexes formed by 8-diethylaminomethylquinoline [155].

While on the subject of solution chemistry, the complex formation equilibrium reactions of Ni(II) with the newly synthesised ligand 2-(1'-benzenesulphonylamino-3'-methylmercapto)-propylbenzimidazole have been investigated in 50% (v/v) water-dioxan medium. Various complexes are formed depending on the pH [156].

Potassium dihydrobis(imidazolyl)borate (K^+L^-) has been prepared and reacted with Ni(II) yielding the neutral complex $[NiL_2]$. Spectral and magnetic data indicate an octahedral environment around the Ni(II) ion [157].

It is probably appropriate to conclude this section by referring to work done by Knorr and Ruf in which they have investigated the monomolecular interconversion of tetrahedral and planar isomers of tetracoordinated nickel(II)bis(chelates). They have found that the pseudotetrahedral complex (29) undergoes slow inversion of configuration at 25°C possibly involving transient formation of the planar isomer [158].



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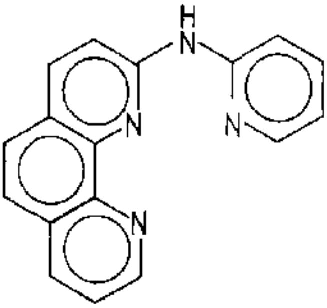
1.3.4.3 Polydentate ligands

The crystal and molecular structure of bis(1,4,7-triazacyclodecane) nickel(II) diperchlorate has been reported. The complex, like its 1,4,7-triazacyclononane counterpart, exhibits nearly trigonal distortion from octahedral symmetry. Ni-N bond lengths vary from 2.102 to 2.143(8)A [159].

1,10-Phenanthrolin-2-yl(pyridin-2-yl)amine (30) has been prepared and reacted with NiX_2 ($X= BF_4^-$, ClO_4^-). The resultant complexes $[Ni(HL)_2]X_2$ (HL= (30)) are octahedral with coordination occurring via the three pyridine nitrogen atoms. Treatment of $[Ni(HL)_2]X_2$ with base yields the octahedral neutral complex $[NiL_2]$ in which the mode of coordination is unchanged [160].



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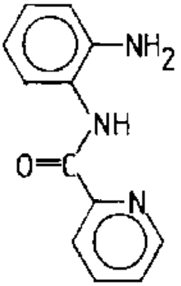
The newly synthesised ligand N,N-bis(3,5-dimethylpyrazol-1-ylmethyl)aminoethane (L) has been complexed with a series of nickel(II) salts yielding complexes of the type $[NiLX_2]$ ($X= Cl^-$, Br^-, NO_3^-) and $[NiL_2](ClO_4)_2$. The bis-adduct exhibits distorted octahedral geometry, while the mono-adducts exhibit pentacoordinate ($X= Cl^-$, Br^-) and hexacoordinate ($X= NO_3^-$) geometry. The tridentate behaviour of the ligand is verified by the single-crystal X-ray structure of $[NiL(NO_3)_2]$, in which one nitrate group is monodentate (Ni-O= 2.052(5)A) while the other is bidentate

(Ni-O= 2.157(5) and 2.145(5)A). Ni-N distances are 2.061(5) and 2.034(5)A for the pyrazole nitrogens and 2.128(5)A for the amine nitrogens [161].

The coordination behaviour of tris(1-pyrazolyl)methane (HL) and 2,2'-bis(1-pyrazolyl)propane (HL') with various Ni(II) salts has been investigated. Tris(1-pyrazolyl)methane yields stable octahedral complexes of the type $[Ni(HL)X_2(H_2O)]\cdot nH_2O$ (X= Cl^-, n=2; X=AcO^-, n=1) and $[Ni(HL)_2]X_2$ (X= Br^-, I^-, NO_3^- or IO_4^-) whilst 2,2'-bis(1-pyrazolyl)propane does not. However, in the presence of poor coordinating polyanions such as BF_4^- or PF_6^-, 2,2'-bis(1-pyrazolyl)propane reacts readily yielding complexes of the type $[Ni(HL')_2X]Y$ (X= Cl^-, NO_3^-, AcO^-; Y= BF_4^-, PF_6^-). An octahedral structure has been proposed for the complex ions $[Ni(HL')_2X]^+$ (X= NO_3^-, OAc^-) with the anion X coordinating in a bidentate fashion, whereas $[Ni(HL')_2Cl]^+$ is considered to have a square-pyramidal structure [162].

N-(2-aminophenyl)pyridine-2-carboxamide (31) has been complexed with Ni(II) in its neutral and deprotonated forms. The deprotonated ligand behaves as a tridentate NNN donor yielding mononuclear complexes of the type $[NiL_2]$ (HL=(31)). The neutral ligand forms dimeric and polymeric complexes in which the ligand coordinates via an NON set of donor atoms [163].



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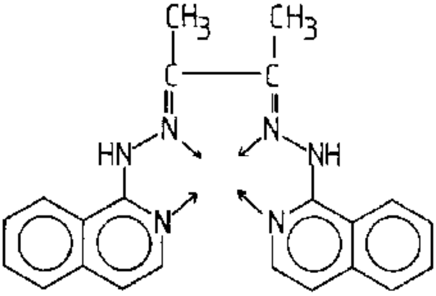
The tridentate ligands diethylenetriamine (dien) and triethylenetetramine (trien) have been utilised in the synthesis of the mixed-ligand complexes $[Ni(dien)L]SO_4$ and $[Ni(trien)L]SO_4$ (L= 3-methyl-4-(p-methylphenylazo)pyrazole-5-one). Spectroscopic and magnetic data indicate distorted octahedral geometry for the nickel(II) ion in these complexes [164].

Tetradentate tripod ligands and their metal complexes continue to attract interest. The nickel(II) complexes of tris-(benzimidazolylmethyl)amine and its methyl-, isobutyl- and isopropyl-substituted derivatives of one of the backbone methylene groups, have been prepared and characterised. The complexes have the general formula $[NiLCl_2]\cdot nH_2O$ (n= 2,4) and are distorted octahedral in structure [165].

Bis-quinolylhydrazone of biacetal (32) has been synthesised and reacted with a selection of nickel(II) salts. Coordination occurs via the imino and aromatic nitrogen atoms and octahedral complexes of the type $[NiLX_2]$ ($X=Cl^-,Br^-,SCN^-$) and $[NiL(ClO_4)]ClO_4$ {L=(32)} have been isolated [166].



(32)

The crystal structure and single-crystal polarised spectrum of $[NiL(L')_2](ClO_4)_2$ (L= 1,4,7,10-tetraazadecane; L'= N-methylimidazole) have been determined. L is bonded via its four nitrogen atoms in such a fashion that the terminal nitrogen atoms occupy trans-positions on the octahedron (Ni-N varies from 2.119(3) to 2.156(3)A), while the remaining coordination sites are occupied by the imidazole ligands (Ni-N= 2.103(3) and 2.110(3)A) [167].

The 1:1 complex of Ni(II) with N,N'-ethylenebis(pyrrol-2-ylmethyleneamine), [NiL] {H_2L = N,N'-ethylenebis(pyrrol-2-ylmethyleneamine)}, has been prepared and characterised by single-crystal X-ray analysis. The complex is essentially planar although the geometry of coordination is highly strained. Ni-N bond lengths vary from 1.822 to 1.906(5)A [168].

N,N,N',N'-tetrakis(pyrazol-1-ylmethyl)-1,2-diaminoethane (L), a new hexadentate N_6 donor ligand, has been reacted with NiX_2 ($X= ClO_4^-$, BF_4^-). The resultant complexes $[NiL]X_2$ exhibit a coordination geometry that is close to octahedral with coordination occurring via all six nitrogen atoms [169].

1.3.5 Phosphorus- and Arsenic-donor ligands

1.3.5.1 Monodentate ligands

The ability of trialkyl- and triarylphosphine ligands to stabilise complexes containing nickel-carbon σ-bonds continues to be utilised a great deal. This is substantiated by Tatsumi et al who describe an associative mechanism for the reductive elimination of a series of complexes $[NiR_2(PR_3)_2]$ (R=alkyl or aryl moiety) [170].

The kinetics and mechanism of the oxidative addition of cyanogen to $[Ni(CO)_2(PPh_3)_2]$ have been reported. The postulated mechanism involves loss of CO followed by competitive cyanogen attack on the $[Ni(CO)(PPh_3)_2]$ intermediate, and subsequent oxidative addition. Of interest is the fact that the product, $[Ni(CN)_2(PPh_3)_2]$, crystallises as a clathrate containing 1 mol of C_2N_2 [171]. In addition, the related complexes $[Ni(CN)_2(P(CH_2OH)Ph_2)_3](C_6H_6)_{0.5}$ and trans$[Ni(CN)_2(P(CH_2OH)Ph_2)_2]$ have been synthesised and their crystal and molecular structures reported. The former complex is essentially square-pyramidal in structure and contains one extremely long Ni-P bond {2.400(3)A}, while the latter complex exhibits simple trans-square-planar geometry at nickel [172].

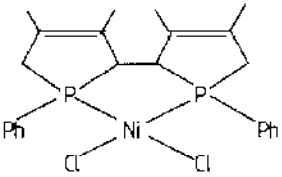
Mono-organonickel(II) complexes, trans$[Ni\{C_2Cl_2(C_6H_4Y)\}Cl(PMe_3)_2]$ (Y= NMe_2-4, Me-4, Me-3, Cl-4), have been prepared by thermolysis of the corresponding complexes trans$[Ni(CCl{=}CCl_2)(C_6H_4Y)(PMe_3)_2]$. The reaction pathway corresponds to reductive elimination followed by oxidative addition [173].

$[NiCl_2(CO)(PMe_3)_2]$ has been synthesised and its crystal and molecular structure determined. The complex has a trigonal bipyramidal structure with CO and the two chlorides located in the equatorial plane. Of interest is the uncommonly short Ni-C bond {1.730(2)A} which indicates extensive π back bonding from the Ni dx^2-y^2, dxy orbitals to π^*(CO) [174].

Work on the synthesis and structures of free and coordinated phosphaalkenes has been continued. The complex $(Me_3P)_2Ni[(Me_3Si)_2CPC(H)(SiMe_3)_2]$ has been prepared and its structure determined by single-crystal X-ray diffraction. The geometry at nickel is essentially square-planar and the phosphaalkene is η^2-bonded [175].

1.3.5.2 Bidentate ligands

The new ligand complex (33) has been prepared by thermolysis of 1-phenyl-3,4-dimethylphosphole in the presence of $NiCl_2$. X-ray crystallography indicates that the nickel atom occupies a near-perfect square-planar environment. The thermal dimerisation is surprisingly stereoselective as is manifested by the fact that (33) is isolated as a racemic mixture of the R,R and S,S forms of the ligand with none of the R,S isomer being detected [176].



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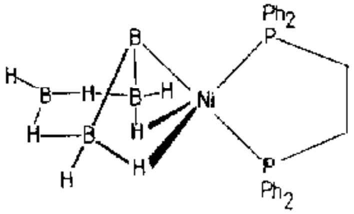
1,2-Bis(diethylphosphino)ethane reacts with Ni(II) yielding planar complexes of the type $[NiL_2]X_2$ {L= 1,2-bis(diethylphosphino)ethane; X = PF_6^-, ClO_4^-}. The complexes have been analysed using electronic absorption and magnetic circular dichroism spectroscopy. Detailed band assignments are given [177].

Reaction of the enantiomers of (R^*,R^*)-(±)- and (R^*,S^*)-(±)-1-(methylphenylarsino)-2-(methylphenylphosphino)benzene with $Ni(ClO_4)_2$ yields square-planar complexes of the type $[NiL_2](ClO_4)_2$. Addition of Cl^- to the square-planar species yields the corresponding penta-coordinate square-pyramidal complexes $[NiL_2Cl]ClO_4$. ^1H- and ^{31}P-n.m.r. have been used to investigate the behaviour of these complexes in solution, and all the possible stereoisomers of the different species have been detected and identified [178].

$[Ni(\eta^3-B_4H_8)\{(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2\}]$ has been synthesised and characterised by means of I.R. and ^{11}B n.m.r. spectroscopy. A pseudo-trigonal-bipyramidal structure containing bridging protons has been proposed (34) [179].



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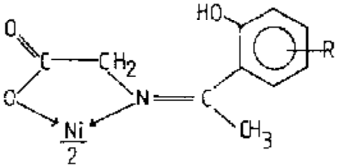
1.3.6 Mixed-donor ligands

1.3.6.1 N,O-donor ligands

Schiff base ligands, and their related ligands such as hydrazones, carbazones, semi-carbazones, oximes and azines, continue to dominate this category, with the primary focus being on Schiff base and hydrazone ligands.

Table 4 lists a variety of Schiff base ligands and their Ni(II) complexes that have been isolated in the solid state [180-199]. Bidentate Schiff bases generally coordinate via the imino nitrogen atom and a deprotonated hydroxyl oxygen moiety. As a result, there is an abundance of square-planar complexes of the type [NiL_2] [180,182,184-5]. Noticeable exceptions are a series of o-hydroxyacetophenone-glycine imines which coordinate via their imino nitrogen and carboxylate oxygen moieties (35) [186].



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Aromatic tridentate Schiff bases (H_2L) have been used to isolate paramagnetic complexes of the type [NiL] [187-8]. The complicated magnetic behaviour of the N-salicylideneanthranilatenickel(II) complex has been analysed using ^1H n.m.r. spectroscopy. Contact shifts of the ligand resonances have been interpreted and a mechanism for spin delocalisation into the ligand and ground state electronic configuration of the metal has been proposed [187].

TABLE 4. Some Schiff base ligands and their Ni(II) complexes

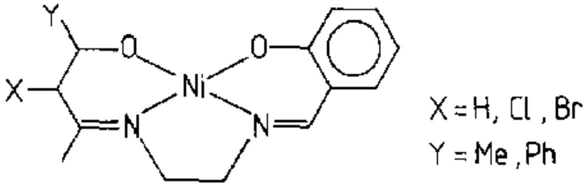
LIGAND	COMPLEX	COMMENTS	REF.
N-(2-hydroxyethyl) salicylaldimine (HL)	$[NiL_2]$	Infrared study	[180]
2-(2-hydroxyacetophenone)imino-5-(p-anisyl)-1,3,4-oxadiazole (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[181]
2N-(3,5-dinitrosalicylidene)-5-phenyl-1,3,4-thiadiazole (HL)	$[NiL_2]$		[182]
1,3,5-trisubstituted-phenyl-2S-benzylisobiuret (HL)	$[Ni(HL)(H_2O)_2Cl_2]$ $[Ni(HL)(O_2CCH_3)_2]$	Octahedral Octahedral	[183]
1-(X-hydroxy-R-tolyl)ethylideneamine (HL) {X = 2- or 6-; R = 3- or 5-bromo}	$[NiL_2]$	Diamagnetic square-planar	[184]
(R)imino-2-phenylethylamine (HL) {R = various 2-hydroxycarbonyl compounds}	$[NiL_2]$ $[Ni(HL)_2(OAc)_2]$	Square-planar Octahedral	[185]
(2-hydroxy-R-acetophenone)iminoglycine (H_2L) {R = H; 3-,4-,5-methoxy; 5-chloro}	$[Ni(HL)_2]$	Square-planar	[186]
N-salicylideneanthranilate (H_2L)	$[NiL]$	^{1}H-n.m.r. spectral analysis	[187]
Salicylidene-o-hydroxyaniline (H_2L)	$[NiL]$	Paramagnetic	[188]
Biguanidoethylacetate (H_6L)	$[Ni(H_5L)_2]\cdot 2H_2O$	D_4h symmetry	[189]
Biguanidoacetic acid (H_7L)	$[Ni(H_6L)_2]\cdot 2H_2O$	D_4h symmetry	[189]
N-[2-(2-aminoethylamino)ethyl]salicylideneamine (H_4L)	$[Ni(H_3L)](B\{C_6H_5\}_4)$	Irregular square-planar; Crystal structure	[190]

TABLE 4. Some Schiff base ligands and their Ni(II) complexes (continued)

LIGAND	COMPLEX	COMMENTS	REF.
N-[N-(3-hydroxy-5-hydroxymethyl-2-methyl-4-pyridenemethylene)glycyl]glycine (H_4L)	[Ni(H_2L)·3H_2O	Square-planar; Crystal structure	[191]
N,N'-disalicylidene-2-methyl-4-(2-hydroxy-5-methyl phenyl)-1,2-butanediamine (H_2L)	[NiL]	Planar configuration	[192]
Bis(2-hydroxynaphthylidene) (H_2L)	[NiL]	Square-planar	[193]
N,N'-butyleneiminо*bis*(2-hydroxy-3-bromo-5-methylbenzophenone (H_2L)	[NiL]	Square-planar	[194]
1-(2'-hydroxy-R)-2,5-diazo-6-methylnona-1,6-diene-8-one (H_2L) {R = variously substituted phenyl or napthyl}	[NiL]	Square-planar	[195]
N,N'-1,4-butylene-(2-hydroxynaphthaldehyde)(R) (H_2L) {R = salicylaldehyde or 2-hydroxyacetophenone}	[NiL]	Asymmetric azomethine complex: Template synthesis	[196]
N,N'-*bis*(R-*o*-hydroxyacetophenone)R'-diamine (H_2L) {R = various methyl and chloro substituents; R'-diamine = ethylenediamine or propylenediamine}	[NiL]	Square-planar	[197]
N,N'-*bis*(2,3-dihydro-2-hydroxy-4H-1-benzopyran-4-one)-R-diamine (H_4L) {R-diamine = 1,2-diaminoethane or 1,3-diaminopropane}	[Ni(H_2L)]	Square-planar; crystal structure	[198]
N,N'-*bis*(3-formylsalicylic acid)-1,2-diaminoethane (H_4L)	[Ni(H_2L)]	Square-planar	[199]

A variety of possible donor sets are available to tetradentate Schiff base ligands. However, it is the ONNO donor set which predominates, usually leading to square-planar complexes of the type [NiL] (H_2L= dibasic tetradentate Schiff base ligand) [192-199].

Although most of the work to date has concentrated on symmetrical tetradentate Schiff base ligands, it is interesting to note the more frequent reporting of asymmetrical tetradentate azomethine ligands and their Ni(II) complexes [195-6]. In addition, the kinetics of both the nucleophilic [200] and electrophilic [201] ring substitution reactions of complex (36) have been investigated.



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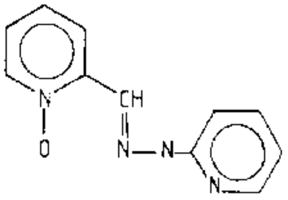
Template synthesis has been used to great effect in the preparation of a number of new fluorinated Schiff base complexes of Ni(II). Four-, five- and six-coordinate complexes have been isolated with the coordination mode of the ligands varying from bidentate to hexadentate [202-3]. In addition, the crystal and molecular structure of the complex derived from the template condensation of $CH_3C(O)CH_2C(CF_3)OH$ with 2-(2-aminoethyl)pyridine, in the presence of Ni(II), has been reported [203].

Solution studies of the complexation of the bidentate ligands N-(2-hydroxy-1-naphthalidene)-4-carbomethoxyanaline [204] and p-acetylaminophenylsalicylate [205] have been undertaken. In addition, the formation constants of Ni(II) with the tridentate Schiff bases 2-[(1H-benzimidazole-2-ylmethylene)amino]-4-R-phenol (R= chloro, nitro) have been reported [206].

Finally, dealkylation of the Ni(II) Schiff base chelates, [NiL_2] (HL= N-(R)salicylaldimine; R= alkyl), has been observed in alcohol and acetone solutions, in the presence of H_2O or NH_4^+. First order rate constants were determined spectrophotometrically and it was shown that the rate constants vary with alkyl chain length and H_2O concentration [207].

A substantial number of hydrazone and substituted hydrazone ligands have been complexed with Ni(II). Complexes containing bidentate [208-215], tridentate [216-221], tetradentate [222] and pentadentate [222] ligands have been reported (see table 5). Of particular interest are the ligands 2-pyridine carboxaldehyde 2'-pyridinylhydrazone 1-oxide (37) and 2-pyridine carboxaldehyde 2'-quinolinylhydrazone (38). Both ligands function as ONN donors with coordination occurring via the pyridine N-oxide oxygen, the imine nitrogen and a pyridine or quinoline nitrogen. However, the complexes of (37) with NiX_2 (X= halide, NCS) appear to be hexacoordinate with bridging N-oxide moieties whereas the analogous complexes of (38) appear to be halide-bridged hexacoordinate species [218].



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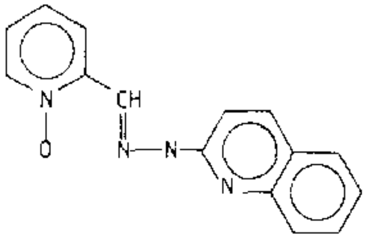


(38)

In addition, the reaction of $[NiL]^{2+}$ (L= 4,4,9,9-tetramethyl-5,8-diazadodecane-2,11-dione dihydrazone) (39) with acetylacetonate yields a pentadentate nickel(II)-hydrazone complex (40) or a tetradentate nickel(II)-hydrazone complex (41) depending on the reaction conditions employed [222].

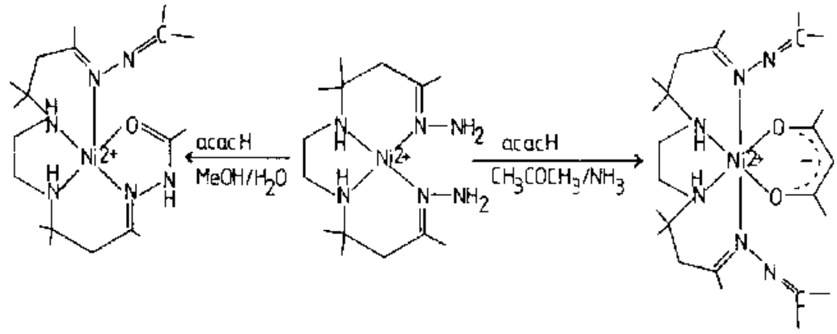
Turning to semicarbazone ligands, the nickel(II) complexes of naphthaldehyde semicarbazone [223], phenylpyruvic acid semicarbazone [224], salicylaldehyde semicarbazone [225], and the related ligand salicylidene ethyl carbazate [226] have been prepared. All of the above ligands react in their deprotonated form yielding octahedral complexes of the type $[NiL_2]$, in which the semicarbazone ligands functions as an ONO donor.

TABLE 5. Some hydrazone ligands and their Ni(II) complexes

LIGAND	COMPLEX	COMMENTS	REF.
Pyridine-4-carboxylic isonicotinoyl hydrazone (HL)	$[Ni(HL)X_2]$ $[NiL_2]\cdot H_2O$	Octahedral ($X=Cl^-, Br^-, NCS^-, SO_4^{2-}$) Octahedral	[208] [208]
2-Thenoylacetone hydrazone (HL)	$[Ni(HL)_2Cl_2]$ $[NiL_2(H_2O)_2]$	Trans-octahedral Trans-octahedral	[209] [209]
Benzoinphenyl hydrazone (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[210]
Benzoin-2,4-dinitrophenyl hydrazone (HL)	$[NiL_2(H_2O)_2]$	Octahedral	[210]
R hydrazone (HL) {R=arylidene,salicyloyl,benzoyl}	$[Ni(HL)_2(H_2O)Cl]Cl$	Distorted octahedral	[211]
R hydrazone (HL) {R=furan-2-carboxylic acid, nitrobenzoic acid}	$[NiL_2]$		[212]
2,4-Dihydroxyacetophenone hydrazone (HL)	$[NiL_2]$	Square-planar	[213]
R-N-phenyl hydrazone (HL)	$[NiL_2]$	Square-planar	[214]
Chromone 3-R-hydrazone (HL) {R=benzoyl or acetoyl}	$[Ni(HL)Cl_2]$ $[Ni(HL)_2Cl_2]$	Square-planar Octahedral	[215] [215]
2-Benzoylpyridine Benzoylhydrazone (HL)	$[NiL_2]$	Octahedral	[216]
2-Benzoylpyridine Salicyloylhydrazone (H_2L)	$[Ni(HL)_2]$	Octahedral	[216]
N-(2-benzoxazolyl)-N'-(2-oxo-3-indolinylidene) hydrazine (H_2L)	$[Ni(H_2L)(H_2O)Cl_2]$	Cis-octahedral	[217]

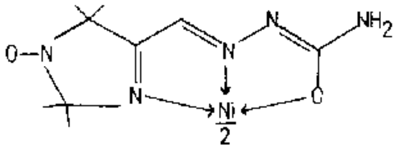
TABLE 5. Some hydrazone ligands and their Ni(II) complexes (continued)

LIGAND	COMPLEX	COMMENTS	REF.
2-Pyridinecarboxaldehyde 2'-pyridinylhydrazone 1-oxide (HL)	$Ni(HL)X_2 \cdot nH_2O$ ($n = 0$-2)	Various structures depending on X;(X = Cl^-,Br^-,NO_3^-,NCS^-)	[218]
2-Pyridinecarboxaldehyde 2'-quinolinylhydrazone 1-oxide (HL)	$Ni(HL)X_2 \cdot nH_2O$ ($n = 0.5$-1)	Various structures depending on X;(X = Cl^-,Br^-,NO_3^-,NCS^-)	[218]
Isatin-2-hydroxy-1-naphthylidene hydrazone (H_2L)	$[Ni(HL)_2]$		[219]
2-Hydroxy-1-naphthylidene-R hydrazone (H_2L) {R = phenyl, benzoyl, salicyloyl}	$[Ni(HL)_2]$		[219]
R-salicylidene hydrazone (H_2L) {R = phenylacetic and α-naphthoic acid}	$[Ni(H_2L)(HL)]X \cdot H_2O$ $[Ni(HL)_2] \cdot H_2O$	Octahedral; (X = Cl^-,NO_3^-) Octahedral	[220] [220]
Biacetylmonoxime-R-benzoylhydrazones (H_2L) {R = o-chloro and o-methyl}	$[NiL(H_2O)]$	Square-planar	[221]
4,4,9,9-Tetramethyl-5,8-diazadodecane-2,11- dione 2-isopropylidenehydrazone 11-acetylhydrazone (L)	$[NiL(ClO_4)](ClO_4)$	Octahedral; Crystal structure	[222]



(40) (39) (41)

4-Formyl-2,2,5,5-tetramethyl-3-imidazoline-1-oxyl semicarbazone (HL) is an interesting ligand containing both semicarbazone and nitroxide groups. Reaction with Ni(II) yields the distorted octahedral complex [NiL_2] in which the deprotonated ligand functions as an NNO donor as shown below (42) [227].

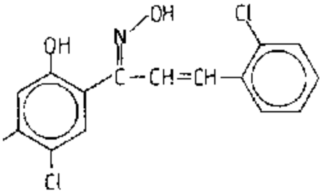


(42)

Salicylaldehyde S-methylthiosemicarbazone (H_2L) has the ability to coordinate via a number of donor atoms (ONNSN). Reaction with Ni(II) yields a variety of complexes depending on the nickel salt used. Both octahedral complexes, [$Ni(H_2L)_2$](NO_3)$_2$ and [$Ni(H_2L)(HL)$](ClO_4), as well as square-planar complexes, [Ni(L)(NCS)] and [Ni(L)(py)]Cl, have been isolated, and in all cases the ligand behaves as a NNO tridentate donor [228].

The use of oximes in the solvent extraction of metals has been studied for some time. Ortho-hydroxyoximes, generally marketed as LIX reagents, have been shown to be particularly useful in this regard. As a result it is not surprising to find that the complexing properties of LIX-64N (mixture of 2-hydroxybenzophenoneoxime and α-hydroxyoxime) [229], and LIX-63 (5,8-diethyl-7-hydroxy-6-dodecanoneoxime) [230] with Ni(II) have been investigated. In addition, the extractive properties of 1-hydroxy-2-acetonaphthenone oxime towards Ni(II) have been investigated spectrophotometrically [231].

2'-Hydroxy-2,5'-dichloro-4'-methylbenzalacetophenone oxime (43) [232] and the related ligands 2'-hydroxy-5'-X-chalcone oxime (X= H,Me,Cl) (44) [233] coordinate to Ni(II) in their deprotonated form via the oxime nitrogen and hydroxyl oxygen atoms. Complexes of the type [NiL_2] (HL=43) and [$NiL_2(Q)_2$] (HL=44; Q=H_2O, pyridine) have been obtained respectively.



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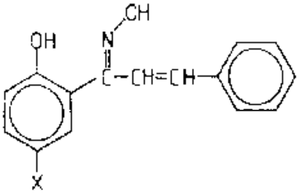


(44)

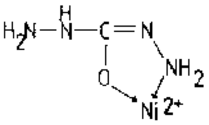
Ternary complexes of the type [NiLB] (HL= 1-nitrosonaphthol; HB = 2-aminobenzoic acid) [234] and (HL = 4-chloro-1-quinone-2-oxime; HB = dimethylacetylenedicarboxylic acid) [235] have been prepared. Magnetic and electronic data suggest octahedral geometry for both complexes. In addition, phenanthraquinone monoxime (HL) reacts with Ni(II) yielding an octahedral complex of the type [NiL_2] [236].

The stability constants of the binary complexes of 8-formyl-7-hydroxy-4-methyl-2H-[1]benzopyran-2-one and of its oxime with Ni(II) have been determined potentiometrically in methanol-water. I.R. data indicate that the ligand coordinates via its phenolic oxygen and azomethine nitrogen atoms [237].

The crystal and molecular structure of bis{2'-[α-(2-pyridyl)-benzylidene]salicylohydrazido}nickel(II) monohydrate has been reported. The nickel occupies a distorted octahedral environment and is coordinated to two azide ligands occupying cis positions. Coordination occurs via the oxygen, azo nitrogen and pyridine nitrogen moieties. Relevant data are Ni-N(azo)= 1.974-1.985(9)A, Ni-N(py) = 2.077-2.090(10)A and Ni-O= 2.086-2.090(8)A [238].

Hydrazide ligands, and their complexation with Ni(II), have once again attracted considerable interest. Enanthic acid hydrazide [239] and cyanoacetylhydrazine [240] have been reacted with nickel dithionate yielding tris-octahedral complexes of the type [NiL_3](S_2O_6). Phenoxyacetylhydrazine [241] and 2-furoylhydrazine [242] have been complexed with a variety of nickel(II) salts. Of interest is the fact that all of the above ligands coordinate via the amino and carbonyl groups.

Complex compounds of nickel(II) containing the deprotonated form of carbonic dihydrazide have been prepared. Coordination occurs, as is usually the case with hydrazides, via the carbonyl and amino groups (45). The bis complex, $[NiL_2]$, and tris complexes, $M[NiL_3]$ ($M= (CH_3)_4N^+, K^+$), have been isolated [243].



(45)

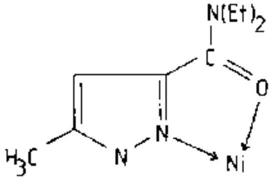
A variety of 2-substituted pyridine ligands have been complexed with Ni(II). These include 2-pyridine ethanol [244], 2-picolyl- and 2-lutidyl-methyl ketones [245], 2-picolyl-p-tolyl- and 2-picolyl-p-nitrophenyl-ketone [246], 2-pyridinecarboxaldehyde and 2-acetylpyridine [247]. The stereochemistry and nature of the complexes are dependent on the ligand substituents, the nickel salt, and the molar ratios of the reactants. Coordination generally occurs via the pyridine nitrogen atom and a hydroxyl moiety. Turning to solution studies, the kinetics and mechanism of complexation of Ni(II) by pyridine-2-carboxylic acid have been investigated [248].

The coordinative behaviour of 8-hydroxyquinoline has been investigated both in solution [249] and in the solid state [250]. The nickel(II) chelates, $[NiL_2]$, of 5- and 7-nonyl, 5- and 7-decyl and 5-chloro-7-decylquinoline (HL), as well as their adducts, $[NiL_2B]$ (B= py, H_2O, NH_3), have been prepared [250]. In addition, the synthesis of the nickel chelate, $[NiL_2]$, of 8-hydroxyquinolino-5-(p-tolyl)sulphonamide (HL) has been reported [251].

Complexes of 2-R-3-amino-quinazoline-4-ones [252] and 2-R-3-anilino-quinazoline-4-ones [253] (R= methyl, phenyl) with $NiCl_2$ have been prepared. Various coordination sites are available, but both series of ligands coordinate via the amino nitrogen and carbonyl oxygen atoms yielding octahedral complexes of the type $[NiL_2Cl_2]$.

Variously-substituted pyrazole ligands have been complexed with Ni(II). Of interest is the fact that N,N-diethyl-5(3)-methyl-pyrazole-3(5)-carboxamide (L) coordinates in a bidentate fashion (46) yielding complexes of the type $[NiL_2X_2]$ ($X= Cl^-, Br^-$,

I^-, SCN^-, NO_3^-, ClO_4^-, BF_4^-, $\frac{1}{2}SO_4^{2-}$) [254], whereas 1-guanyl-5-methyl-pyrazole-3-carboxylic acid (H_2L) coordinates in a tridentate manner (47) yielding square-planar complexes, [NiLB] (B= NH_3, py), and octahedral complexes of the type [NiLB(H_2O)] (B= bipy, o-phen) and [NiLB(H_2O)$_2$] (B= H_2O, α-picoline) [255]. In addition, various nitrogen bases have been reacted with [NiL_2] (HL=picrolonic acid), yielding the adducts [NiL_2Q_2] (Q=py, $PhNH_2$, p-toluidine, N-benzylimidazole), [$NiL_2(Et_3N)(H_2O)$] and [NiL_2B_5] (B= imidazole) [256].



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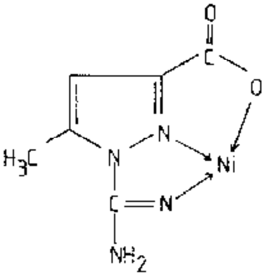
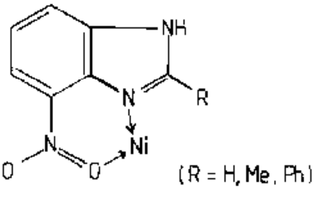


(47)

In a continuation of earlier work the interaction of uracil, acting as a bidentate ligand, with Ni(II) has been reported. The ligand coordinates in its anionic form via the 2-keto group and the nitrogen atom in position 3 of the heterocyclic ring. The resultant complex, [$NiL_2(H_2O)_2$] (HL= uracil), has been assigned a trans-octahedral configuration [257].

The reaction of 2-thiopyrrole-1,2-dicarboximide (HL) and N-carbamoylpyrrole-2-thiocarboxamide (HL') with Ni(II) in the presence of several N-bases has been investigated. Both ligands coordinate in a bidentate fashion with the former yielding square-based pyramidal complexes of the type [NiL_2B] (B= py, picoline, imidazole), while the latter yields the square-planar complex [NiL'_2] [258].

4-Nitrobenzimidazole and its 2-methyl and 2-phenyl analogues have been complexed with nickel acetate yielding the square-planar complexes [NiL'_2]$(AcO)_2$. The ligands coordinate in a bidentate fashion via the nitro and imidazole nitrogen moieties as shown (48) [259]. Another substituted benzimidazole ligand, 2-coumarinylbenzimidazole, complexes in a similar fashion (49) yielding the octahedral complexes [NiL_2X_2] (X= Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, NCS^-) [260].



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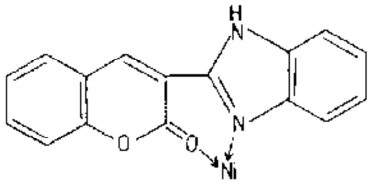
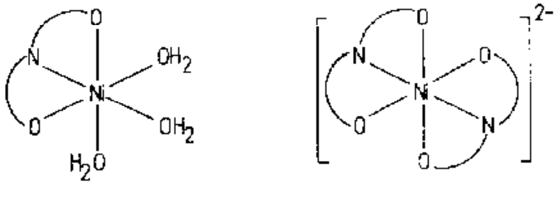


(49)

Various physicochemical techniques have been used to characterise the nickel(II) complexes of phthalanilic acid and its 4-methyl and 4-nitro substituted analogues. The anilic acids coordinate in their deprotonated form via the carboxyl oxygen and secondary amine groups yielding trans-octahedral complexes of the type $[NiL_2(H_2O)_2]$ (HL= anilic acid) [261]. While discussing ligands containing amine and oxygen donor groups, the complexing of acrylamide with various nickel salts has been reported [262].

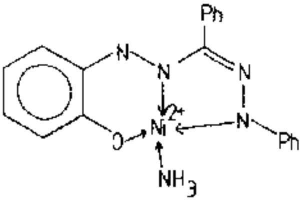
The mode of coordination of the iminodiacetate ligand has been investigated crystallographically. The structure of tris-(iminodiacetato)dinickelato potassium hexahydrate is fascinating in that it consists of K^+ cations, $[NiL_2]^{2-}$ complex anions, $[NiL(H_2O)_3]$ neutral complexes and molecules of water of crystallisation. The iminodiacetate ligand coordinates in a trans fashion as shown below (50) [263].



(50)

In a continuation of earlier work, the complexes $[NiL(en)(H_2O)]\cdot H_2O$, $[Ni(en)_3][L]\cdot 2H_2O$ and $[Ni(en)_3][NiL_2]$ (H_2L = pyridine-2,6-dicarboxylic acid) have been isolated from solutions of nickel(II), pyridine-2,6-dicarboxylic acid and 1,2-diaminoethane. The crystal and molecular structure of $[Ni(en)_3][NiL_2]$ shows two non-equivalent nickel atoms with L coordinating as a tridentate ligand giving rise to a trans-octahedral structure [264].

Continuing with tridentate ligands, the crystal and molecular structures of $[NiL(NH_3)]$ (H_2L = 1-(2-hydroxyphenyl)-3,5-diphenylformazan) (51) and $[NiL'(py)]$ (H_2L'= 1-(2-hydroxyphenyl)-5-phenyl-3-(p-tolyl)formazan) (52) have been reported. Both complexes exhibit essentially square-planar coordination, but the mode of coordination varies as shown below [265].



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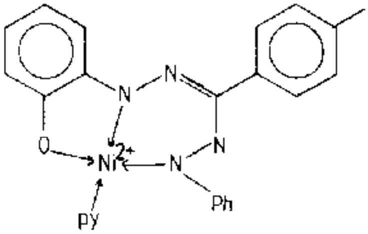
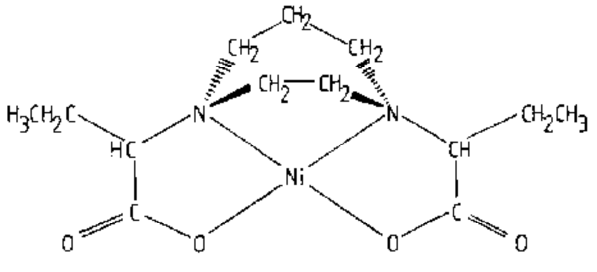


(52)

Turning to tetradentate ligands, the X-ray structure of bis[3N,7N-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)diacetato]-nickel(II) has been determined. The complex, in which the ligating atoms and nickel are closely coplanar, is formed by the condensation of bis(glycinato)nickel(II) with formaldehyde and ammonia. Some important data are Ni-N= 1.911(7) and 1.907(7)A and Ni-O= 1.846(5) and 1.842(5)A [266].

A similar tetradentate ligand, 1,4-diazacycloheptanediacetic acid (H_2L), and its alkyl derivatives, have been complexed in their deprotonated state with Ni(II). The crystal structure of the ethyl derivative has been determined and confirms an essentially square-planar configuration (53) [267].

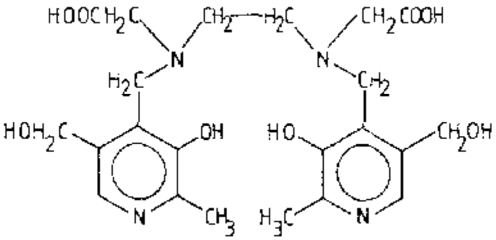


(53)

The related tetradentate ligands 6,6'-bis(dimethylamino)-4,4'-(ethane-1,2-diyldiimino)bispyrimidine-5-carbaldehyde and 6,6'-bis(dimethylamino)-4,4'(propane-1,3-diyldiimino)bis-pyrimidine-5-carbaldehyde have been prepared and reacted with Ni(II) in the presence of various diamines. A neutral nickel complex of the diaminodialdehyde rather than the expected macrocyclic complex was obtained for the former ligand, whereas the latter ligand failed to complex. This phenomenon is explained in terms of the ring strain associated with a six-membered chelate ring [268].

The complexing properties of N,N'-bis(β-carbamoylethyl)R-diamine (R= ethylene, trimethylene, propylene and 2-hydroxy-trimethylene) with Ni(II) have been studied in aqueous solution. Potentiometric and spectrophotometric techniques have been utilised to investigate the Ni–O to Ni–N bond rearrangements at the two amide sites of these complexes [269].

The synthesis of a new sexadentate ligand, N,N'-dipyridoxylethylenediamine-N,N'-diacetic acid (54) and its affinity for various metal ions has been described. Potentiometric studies of the ligand and its nickel(II) chelate are reported and compared with those of analogous ligands [270].

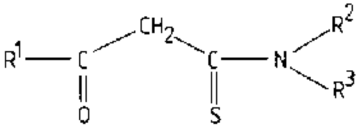


(54)

1.3.6.2 S,O-donor ligands

Studies of the complexation reaction of 2,4,6-trihydroxydithiobenzoic acid (H_2L) with Ni(II) in aqueous-acetone solution have been undertaken. Depending on the pH, complexes of the type $[Ni(H_2L)]^{2+}$, $[Ni(HL)_2]$ and $[NiL_2]^{2-}$ are observed [271].

N-substituted- and N,N-disubstituted-2-acylthioacetamide ligands (55) have been complexed with Ni(II). Coordination occurs via the sulphur and oxygen atoms and square-planar complexes of the type $[NiL_2]$ (HL= (55)) have been isolated. The formation of the pyridine adducts, $[NiL_2(py)_2]$, has also been reported [272].

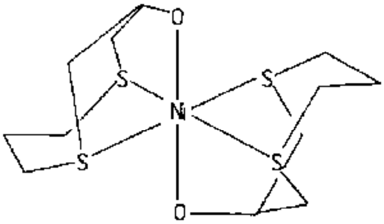


(55)

A variety of N-aryl-N'-benzoylthiocarbamides have been reacted with Ni(II)-phthalimide yielding the mixed ligand complexes $[NiL_2L'(H_2O)_2]$ (HL= phthalimide, L'= N-aryl-N'-benzoylthiocarbamide). Magnetic and spectroscopic data indicate that the complexes have a trans-octahedral structure with some tetragonal distortion [273].

1-Phenyl-5-benzoyl-4-thiobiuret (HL) has three potential sites (OSO) available for coordination. Reaction with Ni(II), depending on the salt and reaction conditions employed, yields $[Ni(HL)_2Cl_2]$ or $[NiL_2]$. The former complex is octahedral while the latter is assigned a square-planar configuration. In both cases the ligand functions as a bidentate SO donor ligand [274].

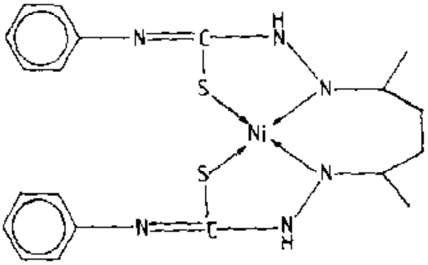
The crystal and molecular structure of bis(1,5-dithiacyclooctan-3-ol-O,S,S')nickel(II) diperchlorate dimethanol, $[Ni(C_6H_{12}OS_2)_2](ClO_4)_2 \cdot 2CH_4O$, has been reported. The coordination geometry for nickel is rhombohedrally distorted tetragonal with each ligand coordinating in a facial manner (56). Some relevant data are Ni-S= 2.398(1) and 2.396(1)A, Ni-O= 2.046(3)A [275].



(56)

1.3.6.3 N,S-donor ligands

The chemistry of this group, like its oxygen analogues, is dominated by Schiff base and related ligands. Table 6 lists those complexes that have been isolated in the solid state [276-285]. Coordination usually occurs via the azomethine nitrogen atom and a deprotonated thiol group. As a result, the bidentate ligands usually result in square-planar complexes of the type $[NiL_2]$ [276-279], whereas the tridentate ligands result in octahedral complexes of the same formula [279, 282-284]. Of particular interest is the complex, hexan-2,5-dione bis(4-phenyl-thiosemicarbazanato)-nickel(II), the crystal structure of which has been reported. Coordination in this case does not occur via the azomethine nitrogen atoms but rather via the amine and sulphur moieties as shown below (57) [285].



(57)

Turning away from the solid state, the polarographic behaviour of N-(α-pyridyl)benzaldehyde thiosemicarbazone, and its nickel(II) complex, has been studied. The nickel(II) complex and ligand both exhibit an irreversible reduction [286]. In addition, as part of an ongoing study of the reactivity of metal chelates of sulphur-containing ligands towards Lewis bases, the reactions of [NiLX] (HL= S-methyl-N-(2-pyridyl)methylenehydrazinecarbodithiol; X= Cl^-, Br^-, I^-, NCS^-) with pyridine [287] and of $[NiL_2]$ (HL= bis(S-methyl-N-arylidenehydrazinecarbodithiol)) with variously-substituted pyridines and 2,2'-bipyridyl [288], have been studied spectrophotometrically.

Ethoxythiocarbonyl hydrazide (HL) reacts with nickel(II) yielding both octahedral, $[Ni(HL)_3]Cl_2$, and square-planar, $[NiL_2]$ complexes. Coordination occurs via the terminal nitrogen and sulphur atoms regardless of whether the ligand is neutral or in a uninegative state [289].

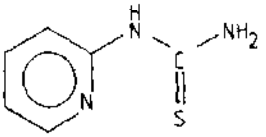
A variety of thiosemicarbazide ligands have been complexed with nickel. 1-Benzoyl-4-phenyl-3-thiosemicarbazide (HL) functions

TABLE 6. N,S-donor Schiff base, hydrazone and semicarbazone ligands and their Ni(II) complexes

LIGAND	COMPLEX	COMMENTS	REF.
Bidentate			
2-Thiophen-yl-(N-phenylen-2-thiol)aldimine (HL)	$[NiL_2].H_2O$	Square-planar; Novel synthesis	[276]
S-benzyl-N-phenylthiocarbamoylthiobenzamide (HL)	$[NiL_2]$	Square-planar	[277]
Vanillin thiosemicarbazone (HL)	$[NiL_2]$		[278]
S-benzyl-N-(2-furfural)methylendithiocarbazate (HL)	$[NiL_2]$	Square-planar	[279]
Benzalacetone thiosemicarbazone (HL)	$[Ni(HL)_2X_2]$	Octahedral; ($X = Cl^-, NCS^-$)	[280]
	$[Ni(HL)X_2]$	Square-planar; ($X = ClO_4^-, NO_3^-$)	[280]
Salicylaldehyde ethoxythiocarbonylhydrazone (H_2L)	$[Ni(H_2L)Cl_2].2H_2O$	Changes from NS donor to ONS	[281]
	$[Ni(HL)_2]$	donor when doubly deprotonated;	[281]
	$[NiLB_2]$	($B = H_2O, NH_3, EtOH$)	[281]
Tridentate			
S-benzyl-N-(2-benzil)methylendithiocarbazate (HL)	$[NiL_2]$	Octahedral	[279]
S-methyl-N-(2-R)methylendithiocarbazate (HL)	$[NiL_2]$	Octahedral	[282]
{R = quinolinyl,isoquinolinyl}	$[NiLX]$	Square-planar; ($X = Cl^-, Br^-, I^-, NO_3^-, NCS^-, NCSe^-$)	[282]
Biacetylmonoxime 4-phenylthiosemicarbazone (H_2L)	$[Ni(H_2L)]X_2$	Octahedral; ($X = NO_3^-, 1/2\ SO_4^{2-}$)	[283]
	$[Ni(HL)X]$	Square-planar; ($X = Cl^-, Br^-, ClO_4^-$)	[283]
	$[NiL(H_2O)]H_2O$	Square-planar	[283]
1,5-Diphenyl-2-S-benzyliso-4-thiobiuret (HL)	$[NiL_2]$	Tetragonal	[284]
Tetradentate			
Hexan-2,5-dione bis(4-phenylthiosemicarbazone) (H_2L)	$[NiL]$	Distorted square-planar; Crystal structure	[285]

as a bidentate NS donor in its deprotonated form yielding the tetrahedral complex [NiL_2]. Coordination occurs via the thioenol and NH groups [290]. In addition, the electronic absorption spectra of the complexes [$NiLCl_2$] and [NiL_2Cl_2] (L= thiosemicarbazide, 1-phenyl- or 4-phenylthiosemicarbazide) have been investigated in a number of solvents [291].

Pyridyl-2-thiourea (58) complexes with $NiCl_2$ in its neutral form yielding the octahedral complex [NiL_2Cl_2] {L= (58)}. The complex is monomeric with coordination occurring via the pyridine ring N and thione S atoms [292]. The structurally related ligand, N-(pyrid-2-yl)-thiobenzamide (59), reacts with nickel(II) yielding the square-planar complex [NiL_2] {HL= (59)}. Coordination occurs via the same two moieties [293].



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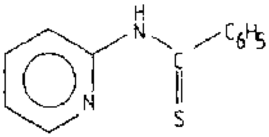


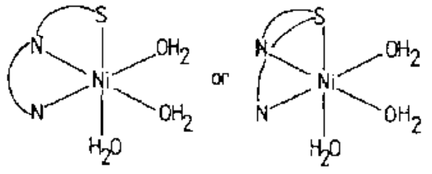
(59)

The composition and stability constants of the Ni(II) complexes of 8-mercaptoquinoline and its various alkyl-substituted derivatives have been determined potentiometrically in dimethylformamide. Distorted tetrahedral complexes are postulated with the highest stability constants being found for the 8-mercapto-7-methylquinolate derivatives [294].

1-Phenyl-3-formamidinothiocarbamide (HL) has been complexed with various nickel salts. Reaction with $NiCl_2$ yields the square-planar complex [$Ni(HL)_2$]Cl_2, whereas reaction with Ni(II)acetate yields the square-planar complex [NiL_2] [295]. The related ligand, benzimidazole-2-thiocarboxy-arylamide (HL) has also been complexed with nickel(II). Coordination occurs via the imidazole N and S atoms [296].

Dithio-oxamide and N,N'-dihexyldithio-oxamide (H_2L) have the ability to coordinate in a number of ways depending on the reaction medium used. Reaction with Ni(II) in a neutral medium yields complexes of the type [$Ni(HL)_2$] and [$Ni(L)$]$_n$ in which the ligands are bi- and tridentate respectively, with coordinatioon occurring via the sulphur and nitrogen atoms. Reaction in strongly acidic media yields complexes of the type $[NiL_2]Cl_2$ in which the ligands are coordinated via the sulphur atoms [297].

Turning to tridentate ligands, the Ni(II) complexes of a series of linear tridentate ligands containing one sulphur and two nitrogen donors have been studied in aqueous solution. It is shown that the percentage facial isomer in the NiL^{2+} complexes (60) becomes more important with increasing substitution on the N or S donor atoms. The $[NiL_2]^{2+}$ complexes are assigned a trans-facial tetragonally distorted structure (61) [298].



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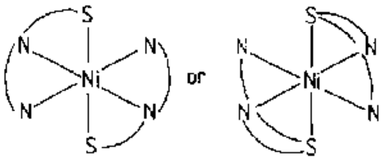
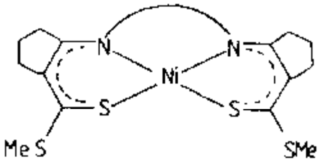


(61)

A similar study has been undertaken in which the complexation behaviour of a number of N,S donor ligands of the type o-$C_5H_4N(CH_2)_{n-1}S(CH_2)_mNH_2$ (n and m = 2 or 3) with Ni(II) was examined. Electronic data indicated that both NiL^{2+} and $NiL_2{}^{2+}$ have distorted octahedral structures [299].

Square-planar complexes, [NiLX] (X= Cl^-, Br^-, I^-, NCS^-), have been obtained via the deprotonation of the ligands 2-(β-aminoethylamino)cyclopent-1-enedithiocarboxylate, methyl-2-(β-aminoisopropylamino)cyclopent-1-enedithiocarboxylate and methyl-2-(β-diethylaminoethylamino)cyclopent-1-enedithiocarboxylate (HL). In addition, diamagnetic complexes of the composition [NiL(MeCN)]-(ClO_4) and $[Ni_2L_2(HL)_2](ClO_4)_2$ have also been isolated [300].

The potentially hexadentate ligands N,N'-1,2-propane-bis-(methyl 2-aminocyclopent-1-ene-dithiocarboxylate) (H_2L) and N,N'-1,3-propane-bis(methyl 2-aminocyclopent-1-ene-dithiocarboxylate) (H_2L) have been reacted with $NiCl_2$ yielding square-planar complexes of the type [NiL] (62). In both cases, the ligands behave in a tetradentate fashion, with coordination occurring via the amine and thione moieties. In addition, the potentially heptadentate ligand N,N'-[bis(methyl 2-aminocyclopent-1-enedithiocarboxylate)]diethylenetriamine (H_3L) has been reacted with a series of nickel salts, NiX_2 ($X= Cl^-$, Br^-, I^-, NCS^-). The resultant complexes are square-planar and have the molecular formula $[Ni(H_2L)X]$ (63) [301].



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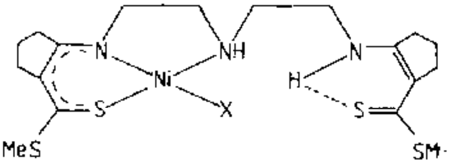


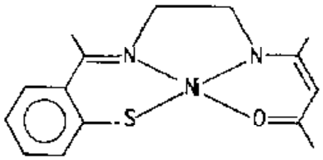
(63)

1.3.6.4 N,O,S-donor ligands

Schiff bases and their related ligands form the bulk of ligands containing NOS donor atoms. This is substantiated by an article published by Tandon and Lakworthy, in which the synthesis and characterisation of a series of nickel(II) complexes with Schiff base ligands incorporating sulphur, nitrogen and oxygen donor atoms is reported [302]. Other Schiff base ligands containing NOS donor atoms that have been complexed with Ni(II) are salicylaldehyde thiosemicarbazone [303] and acetylacetone ethoxythiocarbonyl hydrazone [304].

Of particular interest are the two asymmetric tetradentate Schiff base nickel(II) complexes (64) [305] and (65) [306]. Both ligands function as ONNS donors, with both complexes exhibiting square-planar geometry.

Finally, multidentate open-chain ligands containing 2,2'-bipyridine and/or pyridine moieties, connected by CH_2-X-CH_2 bridges, in which X is the heteroatom O,S or N have been prepared and complexed with Ni(II) [307].



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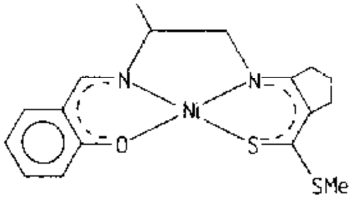

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1.3.7 Macrocyclic ligands

As has become customary in recent years, macrocyclic Ni(II) complexes continue to generate much interest. In order to facilitate clarity, complexes will be dealt with in order of increasing ring size. By way of introduction, a few novel results are reported.

High-resolution electron microscopy has been used to study the nonstoichiometric compound $[NiLI_x]$ (H_2L = phthalocyanine; $x < 1.0$). Local changes of the molecular orientations of [NiL] induced by iodine doping were observed and the effect of the substrate on the axial correlation between the original and the complex crystal discussed [308].

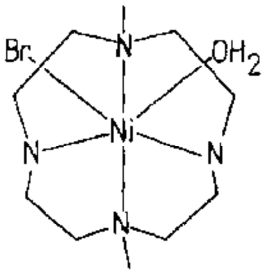
The uptake and activation of molecular oxygen by a series of novel macrocyclic polyamine-nickel(II) complexes has been reported. The Ni(II) complexes react with O_2 forming 1:1 Ni(II)-O_2 adducts in aqueous solution, with the uptake being first order in O_2 and [NiL] (H_2L= macrocyclic polyamine) [309,310].

1.3.7.1 Nitrogen-donor ligands

The use of metal template reactions in the synthesis of macrocyclic nickel(II) complexes has been discussed in great detail in a series of articles by Black et al. Macrocyclic complexes discussed include those derived from malonamido dicarbonyl precursors [311], 2,6-diacetylpyridine and a variety of primary diamines [312], 2,2'-imino-bisbenzaldehyde and a variety of primary diamines [313] and 4,6-dimethoxy-3-methylindole-2,7-dicarbaldehyde and a variety of primary diamines [314].

While discussing tetraaza macrocycles in general, a molecular mechanics and crystallographic study of hole sizes in nitrogen-donor tetraaza macrocycles has been undertaken. The crystal and molecular structure of $[NiL(NO_3)_2]$ (L= 1,4,8,11-tetraazacyclotetradecane) is also reported [315]. In addition, X-ray structural and ab initio molecular orbital studies have been used to establish a correlation between axial and in-plane coordination bond lengths in tetragonal complexes of the type *trans*[$NiLX_2$] (L= tetraazacycloalkanes with different ring sizes; X= Cl^-, NCS^-). In the Ni(II) systems, it was shown that complexes having stronger ligands (X= NCS^-) in the axial positions show weaker correlation than those with weaker ligands (X= Cl^-) [316].

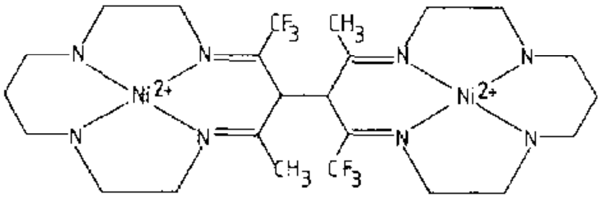
The new polyaza macrocyclic ligand, 1,7-dimethyl-1,4,7,10-tetraazalcyclododecane (H_2L), has been prepared and reacted with a variety of nickel(II) salts. Complexes that have been isolated are [NiL] [317], [$Ni(H_2L)$]$(ClO_4)_2$ and [$NiL(H_2O)Br$]Br. The first two complexes are square-planar whereas the latter complex has *cis*-octahedral geometry (66) as verified by single-crystal X-ray analysis (Ni-N= 2.051 (12) to 2.160 (12); Ni-O= 2.136(9); Ni-Br = 2.610(2)A) [318].



(66)

The oxidation of [NiL](ClO_4) (HL= 11-methyl-13-(trifluoromethyl)-1,4,7,10-tetraazacyclotrideca-10,13-diene), using $Br_2^{\cdot -}$ radicals as oxidant, has been studied in aqueous medium. The reaction proceeds via four distinct steps yielding [Ni(HL)-$(H_2O)_2$]$^{3+}$ and a particularly interesting dimer (67) [319].

The effect of increasing chelate ring size on the coordination properties of tetraazacycloalkanes has been investigated. 1,4,7,10-Tetraazacyclopentadecane (68) [320], 1,4,8,11-tetraazacyclohexadecane (69) and 1,4,8,11-tetraazacycloheptadecane (70) [321] have been synthesised and reacted with Ni(II). In aqueous solution the nickel(II) complexes form dihydrates and exhibit planar ⇆ octahedral equilibrium. Comparison is made with other ligands listed in the literature.



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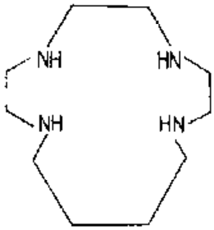

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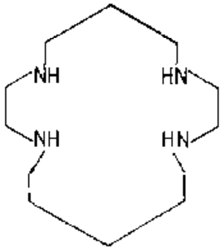

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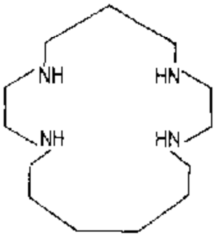


(70)

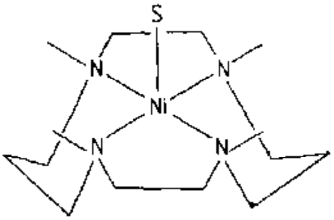
1,4,8,11-Tetraazacyclotetradecane (cyclam) and its variously-substituted analogues continue to dominate the field of N_4-donor macrocycles. Substitutents may be located on the nitrogen atoms or on carbon atoms at various points on the chelate rings, with the result that the possibility of many isomers exists.

O^{17}-n.m.r. and magnetic susceptibility measurements have been used to study the high-spin $\rightleftharpoons$ low-spin equilibria of the 1,4,8,11-tetraazaundecane-Ni(II) and cyclam-Ni(II) systems. The high-spin form contains two adducted H_2O molecules and the kinetic parameters for H_2O-exchange have been determined [322]. In addition, the kinetics of dissociation and isomerisation of cis$[NiL(H_2O)_2]^{2+}$ (L= cyclam) to planar $[NiL]^{2+}$ have been investigated in aqueous perchloric acid solution. It is suggested that the folded isomer is a likely intermediate in the slow acid dissociation of the planar complex [323].

The kinetics of reaction of several bidentate ligands with planar $[NiL]^{2+}$ to produce cis-octahedral $[NiLB]^{2+}$ (L= cyclam; B= glycinate, oxalate, ethylenediamine) have been examined. The proposed mechanism involves folding of the macrocycle, followed by rapid coordination of the bidentate ligand. Stability constants for the reaction of B with $[NiL]^{2+}$ are also reported [324]. The conductances for $[NiL]X_2$ (L= cyclam; X= BPh_4^-, ClO_4^-, I^-) have been measured in nitrobenzene. First and second ionic association constants are reported [325].

1,4,8,11-Tetrasubstituted cyclam continues to elicit much interest since its Ni(II) complexes may exist in a number of isomeric forms. The R,S,S,R and R,S,R,S isomers of 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane nickel(II) have been reported for some time, but it is only recently that evidence for the R,S,R,R isomer has been produced. Mixtures of the latter two isomers have been isolated in the solid state and indications are that the R,S,R,R isomer converts to the R,S,R,S isomer in solution [326].

The stability of the complex of Ni(II) with 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tmc) has been determined potentiometrically and spectrophotometrically. A particularly low value of log K_1 (8.66 to 8.63) is explained in terms of the unusual square-pyramidal coordination geometry forced on the metal ion by the ligand [327]. Furthermore, O^{17}-n.m.r. has been utilised to study the equilibrium and kinetics of solvent exchange with [NiLS] (L = R,S,R,S-tmc; S = D_2O, dmf) (71) and $[NiLS_2]$ (L = R,S,S,R-tmc; S = D_2O, dmso) (72). An associative-interchange mechanism is proposed for the pentacoordinate species, while a dissociative-interchange mechanism is proposed for the hexacoordinate species [328].



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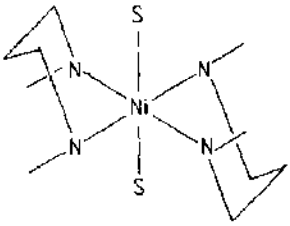
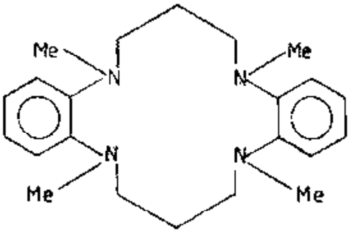


(72)

In addition, the molecular structure of R,S,R,S-[NiL(dmf)]-$(SO_3CF_3)_2$ has been determined by X-ray diffraction methods. The geometry about Ni(II) is midway between square-based pyramidal and trigonal bipyramidal with dmf occupying the axial or an equatorial site in these geometries respectively.Some relevant data are Ni-O= 1.974(6) and Ni-N= 2.091(7) to 2.121(9)A [329].

Apart from tetramethylcyclam, much interest has centred on the nickel(II) complexes of cyclam ligands that contain functionalised nitrogen substituents. These ligands add another facet to the chemistry of the macrocycle in that they open the possibility of coordination via the functional group on the pendant arm attached to the macrocycle nitrogen atoms. Examples of these ligands that have been complexed with Ni(II) include 1,4,8,11-*tetrakis*(2-hydroxyethyl)cyclam [330], 1-(2-aminoethyl)- and 1-(2-dimethylaminoethyl)-4,8,11-trimethylcyclam [331], 1,4,8,11-*tetrakis*(2-cyanoethyl)cyclam and 1,4,8,11-*tetrakis*(2-carbamoylethyl)cyclam [332]. Furthermore, the crystal and molecular structures of the α and β isomeric forms of the nickel(II) complexes of the last two ligands have been reported [332].

The synthesis of 1,4,8,11-tetramethyl-1,4,8,11-tetraazadibenzo[b,i]cyclotetradecane (L) (73) and its nickel complexes, $NiLX_2$ (X = ClO_4^-, Br^-, NO_3^-), have been reported [333]. The perchlorate complex is assigned a square-planar structure whereas the bromide and nitrate complexes are assigned hexacoordination. A single-crystal X-ray structure of the nitrate complex reveals unusual coordination in that the distorted octahedral arrangement around the nickel is formed by (L) in an unexpected folded form and by a nitrate ion functioning as a bidentate ligand occupying two *cis*-positions. The second nitrate ion is uncoordinated giving the resultant complex $[NiL(NO_3)]NO_3$ (74) [334].



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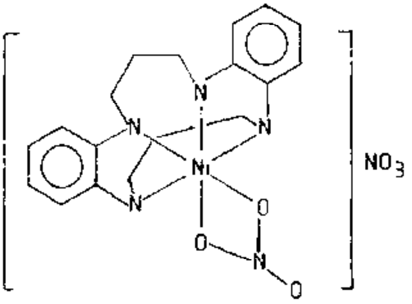
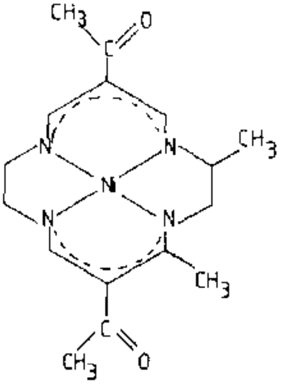


(74)

Turning to substituents that are located on the chelate rings, five stereoisomers of the complex (5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) have been prepared. Spectroscopic analysis reveals that four of these isomers are *meso*-complexes while the remaining one is a *rac*-complex. Of particular interest is the fact that twenty diastereoisomeric forms of the complex are theoretically possible [335].

The crystal and molecular structure of a related complex, 2,9-dimethyl-1,4,8,11-tetraazacyclotetradecane nickel(II) diperchlorate has been reported. The complex exhibits square-planar geometry for Ni(II) and is found to be the *meso*-isomer. Relevant data are Ni-N= 1.943(2) and 1.951(2)A [336].

The reaction of [3,3'-[ethylene*bis*(nitrilomethylidyne)]di-2,4-pentanedionato(2-)]nickel(II) with ethylenediamine has been studied in thf-ethanol solution. The rate is first order in nickel complex, second order in ethylenediamine and first order in added base. A multistep mechanism is proposed resulting in formation of the macrocyclic complex (75) [337]. In addition, the kinetics of the acid dissociation of 5,7-dioxo-1,4,8,11-tetraazacyclotetradecane (76) have been studied and a kinetic scheme has been proposed [338].



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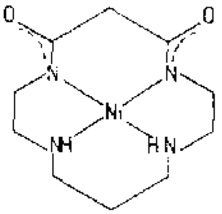
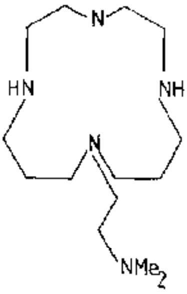


(76)

Two new pendant-arm quinquedentate aza-macrocyclic ligands (77,78) have been prepared and reacted with Ni(II). The nickel complexes are found to undergo reversible rearrangements between approximately trigonal-bipyramidal structures at neutral pH and protonated square-planar structures at low pH, in which the pendant arms are protonated and do not take part in coordination. Furthermore, the crystal and molecular structure of $[NiL](ClO_4)_2$ {L = (77)} has been reported and verifies an approximately trigonal-bipyramidal geometry for the complex [339]. In a continuation of the above work, the square-planar complex $[Ni(HL)](ClO_4)_2$ {L=(77)} which was previously reported to be a mixture of two isomers has been found to isomerise in hot aqueous solution giving two further isomers. Hexacoordinate complexes of formula $[NiL(NCS)](ClO_4)$ and $[Ni(HL)(NCS)_2](ClO_4)$ (L=(78)) have also been isolated [340].



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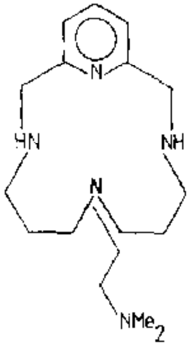
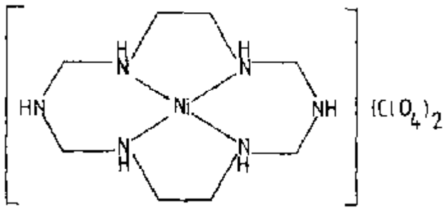


(78)

In a continuation of their earlier work, Busch *et al* have reported a general synthetic procedure for the production of a wide variety of variously-substituted versions of previously reported lacunar macrobicyclic nickel(II) complexes. The X-ray crystal structure of one such multiply substituted complex, (3,11-dibenzyl-14,20-dimethyl-2,12-diphenyl-3,11,15,19,22,26-hexaazatricyclo[11.7.7.$1^{5,9}$]octacosa-1,5,7,9 (28),12,14,19,21,16-nonaene-K^4N)nickel(II) hexafluorophosphate, has also been determined. The structure is a good illustration of the demanding steric requirements that are placed upon the lacuna size and shape by the peripheral substituents of the macrocycle [341].

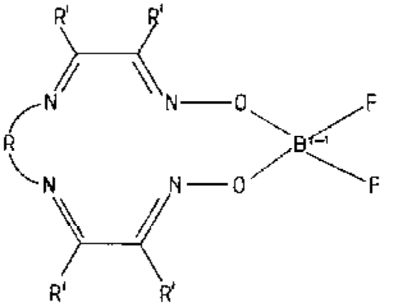
A macrocyclic complex of nickel(II) (79) with the potentially



(79)

hexadentate ligand, hexaazacyclotetradecane, has been prepared in a stepwise metal ion assisted template synthesis by the action of formaldehyde and NH_3 on *bis*(diaminoethane)nickel(II) perchlorate. Spectral data indicate that the ligand functions in a tetradentate fashion [342].

Fluoro-borobridged macrocyclic ligands and their Ni(II) complexes continue to attract interest. The macrocyclic complexes of nickel(II) with the fluoro-boro ligands (80) (R'= CH_3) have been prepared by the template condensation of the parent dioxime ligand complexes $[Ni(H_2L)]Cl_2$ (H_2L= parent dioxime ligand) with BF_3 [343]. A similar synthetic procedure has been utilised to synthesise the corresponding phenyl derivatives (80) (R'= Ph) [344]. The tetraaza-coordinated complexes are diamagnetic whereas the penta- and hexacoordinated complexes exhibit subnormal magnetic moments. Finally, a series of pentacoordinate square-pyramidal adducts of NiL^+ (L= 1,1-difluoro-4,5,11,12-tetramethyl-1-bora-3,6,10,13-tetraaza-2,14-dioxacyclotetradeca-3,5,10,12-tetraenate) with the axial ligands NCS^-, I^-, pyridine and N-benzylimidazole, have been prepared. In addition, two binuclear ligand-bridged complexes, $[Ni_2L_2X](ClO_4)$ (X= I^-, N_3^-), have been isolated [345].

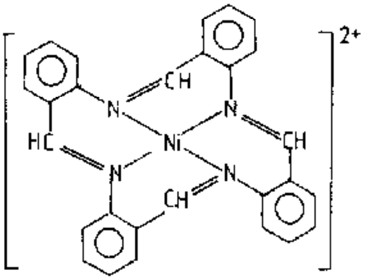


R = $(CH_2)_2$, $(CH_2)_3$, C_6H_4, $(CH_2)_2NH(CH_2)_2$, $(CH_2)_2NH(CH_2)_2NH(CH_2)_2$

R' = CH_3, C_6H_5

(80)

Reaction of o-aminobenzaldehyde with a variety of organic nickel salts yields unusual complexes of the type [NiL]X or Y_2 (L=tetrabenzo[b,f,j,n][1,5,9,13]tetraazacyclohexadecine; X= succinate, phthalate and Y= anthranilate ion). The complex is square-planar with the ligand functioning in a tetradentate fashion (81) [346].



(81)

Porphyrin complexes, probably because of their natural abundance and biological importance, continue to be the subject of much interest. A variety of variously-substituted porphyrin ligands have been complexed with Ni(II). The resultant complexes are usually square-planar having the general formula [NiL] (H_2L= substituted porphyrin) [347-349]. In addition, a high-pressure stopped-flow technique has been used to study the kinetics of incorporation of Ni(II) into N-methyl-5,10,15,20-tetraphenylporphine. The rate is first order in metal ion and a positive activation volume indicates a dissociative activation process [350].

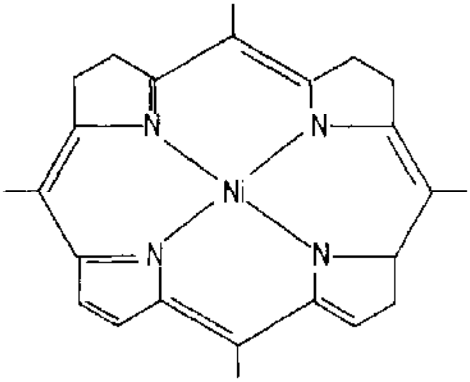
High-field ^{1}H-n.m.r. and nuclear Overhauser effect difference spectroscopy have been used to elucidate the structure of abselonite, a C_{31} nickel-porphyrin of the deoxophylloerythroetioporphyrin type. The structure strongly suggests that abselonite is derived from a chlorophyll [351].

The electron-transfer mechanisms of five nickel(II)porphyrins have been investigated in nonaqueous media. Different oxidation mechanisms were found to occur depending on the porphyrin whereas a universal reduction mechanism was found to occur for all the complexes. Of interest is the fact that three of the tetraalkylporphyrins investigated showed no evidence for Ni(III) formation [352]. While on the subject of electrochemistry, redox couples including a nickel macrocycle and a nickel porphyrin have been incorporated into _p_-chlorosulphonated polystyrene film, which can be cast onto virtually any surface [353].

Infrared and visible excitation resonance Raman spectra for a series of nickel(II) acetyl and formyl deuteroporphyrins have been reported. Virtually all of the in-plane porphyrin skeletal modes and a number of internal vibrations for the conjugating groups are assigned and compared with those of the analogous octaethylporphyrin complex [354]. In addition, the resonance coherent anti-Stokes Raman scattering spectrum of nickel(II)-octaethylporphyrin has been reported [355].

In a series of articles on the chemistry of corphinoids, Eschenmoser _et al_ have synthesised a Ni(II) complex containing the chromophore system of coenzyme F430. The pronounced axial electrophilicity of the Ni(II)ion when complexed by ligands of the type occurring in coenzyme F430 has been verified using magnetic, electrochemical and X-ray methods [356-358].

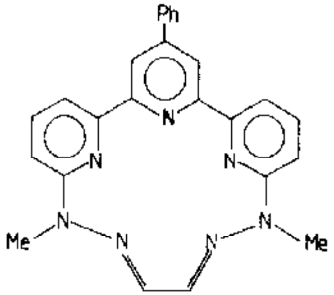
The synthesis and structure of the siroheme model compound, (5,10,15,20-tetramethylisobacteriochlorinato)nickel(II) (82), has been reported. (82) exhibits an S_4-ruffled conformation and a bond length pattern which is indicative of a reduction in aromaticity, both of which are more pronounced than in the corresponding porphyrin and chlorin nickel(II) complexes [359].



(82)

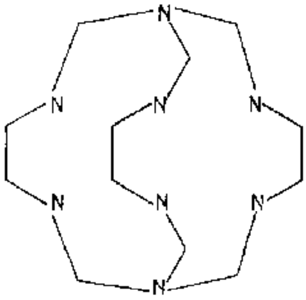
Hemiporphyrazine (H_2L) yields a variety of complexes with Ni(II) depending on the reaction conditions employed. Complexes that have been isolated are [NiL], [$NiL(H_2O)_2$] and [$NiL(HX)_2$], all of which are hexacoordinate [360]. Furthermore, the crystal and molecular structure of [$NiL(py)_2$] has been determined. The stereochemistry is rhombically compressed with the unique axis defined by the metal isoindole nitrogen atoms which are 1.97A from the nickel ion. The other macrocyclic and pyridine adduct Ni-N distances are 2.18 and 2.22A respectively [361].

The nickel(II) complex of the novel quinquedentate ligand (83) which incorporates a 2,2':6',2''-terpyridine moiety, has been prepared via a template condensation about the nickel ion. The crystal and molecular structure of [$NiL(EtOH)_2$]$(BF_4)_2$ {L=(83)} reveals a pentagonal-bipyramidal N_5O_2 coordination environment for the nickel ion. Some relevant data are, Ni-N = 2.015(4) to 2.324(3) A and Ni-O= 2.084(4) A [362].



(83)

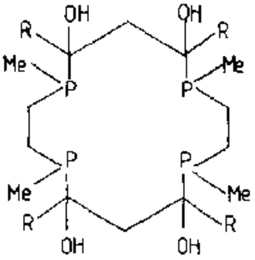
Finally, the preparation and molecular structure of the Ni(II) perchlorate complex of the hexadentate macrobicyclic ligand, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane (84), has been reported. The Ni(II) ion is coordinated to the six nitrogen atoms in a pseudo octahedral arangement with an average Ni-N bond distance of 2.10 A [363].



(84)

1.3.7.2 Phosphorus-donor ligands

A general synthetic route for the preparation of 14- to 16-membered tetraphosphacycloalkanes of the type (85) and (86) has been developed. The synthesis involves a template reaction and utilises bis(tertiary phosphines) with protected carbonyl groups in the alkyl side chains. Diastereoisomers are obtained and the degree of diastereoselectivity depends on the ring size and substituents present [364].



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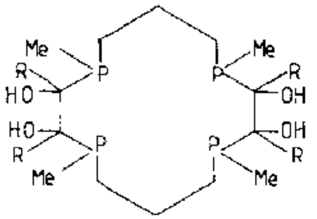
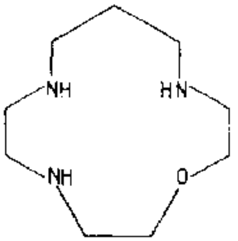


(86)

1.3.7.3 Mixed-donor ligands

The crystal and molecular structure of the nickel perchlorate complex of the macrocyclic ligand 1-oxa-4,7-diazacyclononane (H_2L), $[Ni(H_2L)_2](ClO_4)_2$, has been determined. The coordination around Ni(II) is octahedral with the centrosymmetric cation containing a pseudo-threefold axis [365].

1-Oxa-4,7,11-triazacyclotridecane (87) has been prepared and reacted with Ni(II). Indications are that (87) is too small to encircle a metal ion the size of Ni(II) and as a result, a folded structure for the complex is suggested [366].

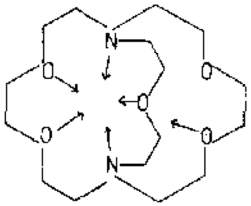


(87)

The preparation of 1,4,8,11-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane (H_4L) has been reported. Complexation with nickel(II) perchlorate (1:1 mole ratio) in ethanol generates a typical octahedral spectrum in the U.V. indicating that at least two of the pendant hydroxyl groups are participating in coordination [367].

X-ray crystallographic studies reveal that the potentially heptadentate ligand, 4,7,13,16,21-pentaoxa-1,10-diazabicyclo-

[8.8.5]tricosane, utilises only six donor atoms when coordinating to Ni(II) (88). The Ni^{2+} ion resides in the cryptand cavity in a highly distorted octahedral environment. Relevant data are: Ni-O= 2.054(4), 2.072(3), 2.093(3) and 2.106(4)A, Ni-N= 2.114(4) and 2.180(5)A [368].

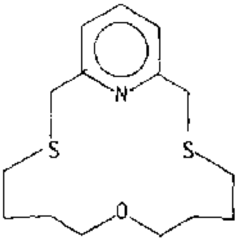


(88)

A method for specifying the size of bonding cavities available to metal ions in metal binding sites has been applied to a series of nickel(II) complexes of dibenzo-substituted quadridentate macrocycles. The procedure allows the goodness-of-fit of the metal ion for the binding site to be estimated by correcting the hole size of the donor set for the radii of the donor atoms. Two new X-ray structure determinations of 14-membered macrocyclic complexes have been included viz. the nickel chloride complex of 3,4:9,10-dibenzo-1,12-diaza-5,8-dioxacyclotetradecane, $[NiLCl_2]$, and the nickel thiocyanate complex of 3,4:9,10-dibenzo-1,5,8,12-tetraazacyclotetradecane, $[NiL(NCS)_2]$ [369].

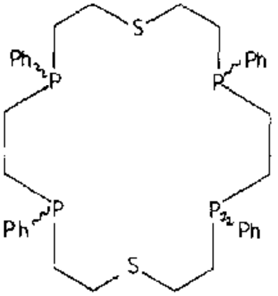
The new macrocyclic ligand, 7-oxa-2,12-dithia(13)(2,6)-pyridinophane (89) has been synthesised and its nickel halide complexes prepared. Although the complexes have the general formula $NiLX_2$ (L= (89), X= Cl^-, Br^-), the chloro complex is assigned hexacoordination whereas the bromo complex is assigned pentacoordination [370].

As part of continuing research in the field of macrocyclic phosphane ligands, the novel dithiatetraphospha-macrocycles 4,7,13,16-tetraphenyl-1,10-dithia-4,7,13,16-tetraphosphacyclooctadecane (90) [371-373] and 5,8,16,19-tetraphenyl-1,12-diathia-5,8,16,19-tetraphosphacyclodocosane (91) [374] have been prepared.



(89)

Five possible diastereoisomers exist for both ligands. All of the possible stereoisomers of (90) have been isolated [372], and of these the α (4RS,7RS,13RS,16SR), β (4RS,7RS,13SR,16SR) and δ (4RS,7RS,13RS,16RS) forms have been complexed with $NiBr_2$ yielding complexes of the type $[NiL]\ Br_2.nH_2O$. Three of the possible isomers of (91) have been isolated [374] and the β form has been complexed with Ni(II) yielding the unusual dinuclear complex $[Ni_2LBr_2](BPh_4)_2.MeOH$. The crystal structure reveals that each nickel atom occupies a distorted square-planar environment and is coordinated to two phosphorus and one sulphur atom of the macrocycle and to one bromide ion [374].



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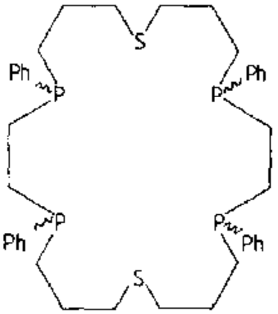


(91)

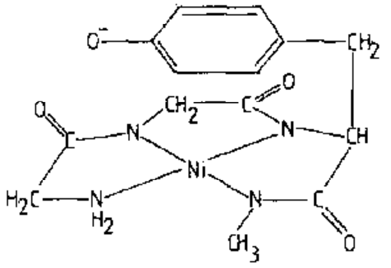
1.3.8 Biological ligands

Biological ligands that have been complexed with Ni(II) may be broadly divided into amino acids (including their derivatives such as peptides and proteins), carbohydrates and polyheterocyclic bases in which the imidazole framework is common. Not unexpectedly, the bulk of the work has been undertaken in aqueous solution as this most closely resembles the biological situation, although some complexes have been isolated in the solid state.

Noticeably it is the amino acids, peptides and proteins that predominate this year with glycine and its derivatives featuring prominently as can be seen from table 7 [375-387]. In addition, the reactions of ethylenimine complexes of Ni(II) with glycine and potassium glycinate have been investigated [388]. Furthermore, bis(glycinato)nickel(II) has been reacted with formaldehyde in the absence of base yielding the complex, bis[N-(1,3-dioxa-5-azacyclohexyl)acetato]nickel(II) dihydrate [389].

Other amino acids that have been reacted with Ni(II) are L-β-phenylalanine [390], 3,4-dihydroxyphenylalanine [391], DL-threonine [392], aspartic acid [393], α-glutamic acid [394], L-lysine [395] and DL-methionine [396]. The related ligands R-propylenediamine and R-ethylenediamine (R= diglycyl and dialanyl) have been complexed with Ni(II) in aqueous solution and their equilibria studied potentiometrically and spectrophotometrically [397].

Turning to peptides, the binding of nickel(II) to glycylglycyl-L-tyrosine-N-methylamide has been investigated. ^1H and ^{13}C n.m.r. indicate that a planar complex (92) is formed at high pH [398].



(92)

In addition, cyclo-L-histidyl-L-methionine (L) has been complexed with $Ni(ClO_4)_2$. The resultant complex has molecular formula $NiL_5(ClO_4)_2.H_2O$ [399].

A number of nickel metalloenzymes have been investigated. Electron Spin Echo spectroscopy [400] and EXAFS [401] have been utilised to characterise the average ligand environment of nickel in F_{420}-reducing hydrogenase obtained from Methanobacterium

TABLE 7 Some amino acids that have been complexed with Ni(II)

LIGAND	COMMENTS	REF.
Glycine (HL)	Functions as a monodentate N-donor ligand in $[Ni(HL)_3Cl_2(H_2O)]$	[375]
	X-ray diffraction study of $[NiL(H_2O)_4]^+$ and $[NiL_3]^-$ in aqueous solution.	[376]
	Potentiometric study of mixed ligand complex with xanthosine	[377]
	Solution study of the mixed ligand complexes with histidine or nitrilotriacetic acid	[378]
	Potentiometric study of the mixed ligand complexes with diaminocarboxylic acid	[379]
	Thermodynamic and potentiometric study of mixed ligand complex with thiazolidine-4-carboxylic acid	[380]
Phenylglycine (H_2L)	Solution study in H_2O/MeOH; NiL and NiL_2 species observed	[381]
N-Phenylglycine (H_2L)	Solution study in H_2O/MeOH; NiL and NiL_2 species observed	[382]
N-(2-hydroxy-4-nitro)-benzylglycine (H_2L)	Potentiometric study in aqueous solution; NiL and $NiL_2{}^{2-}$ species observed	[383]
N-(<u>m</u>-R-phenyl)glycine {R = H, CH_3, CH_3O, Cl, NO_2}	Stepwise formation constants of complex compounds determined in H_2O. Reaction of the above in the presence of 2,2'-bipyridine	[384] [385]
2-Mercaptopropionylglycine	Spectrophotometric study in aqueous solution	[386]
N,N'-<u>bis</u>(2-hydroxyethyl)-glycine	Potentiometric study of the mixed ligand complexes with 1,10-phenanthroline in aqueous solution	[387]

TABLE 7 Some amino acids that have been complexed with Ni(II) (continued)

LIGAND	COMMENTS	REF.
L-ß-phenylalanine (HL)	Physicochemical and structural study; $NiL_2 \cdot 2H_2O$ isolated	[390]
3,4-Dihydroxyphenylalanine	Formation constants of ternary complexes with bipy and phen	[391]
DL-threonine (HL)	Preparation of $NiL_2 \cdot 2H_2O$. Coordination occurs via N and O (carboxylate)	[392]
Aspartic acid (H_2L)	Potentiometric study of mixed ligand complexes with uracil or thymine	[393]
α-Glutamic acid	Potentiometric study in 50% aqueous dioxane	[394]
L-lysine (L)	Octahedral complexes of the type $NiLL' \cdot H_2O$ (H_2L' = L-glutamic acid) have been isolated	[395]
DL-methionine	Potentiometric investigation of mixed ligand complexes with DL-ethionine in aqueous solution	[396]

thermoautotrophicum. It is suggested that the nickel in F_{420}-reducing hydrogenase has equatorial S atoms with either one or two loosely held axial ligands. Similarly, X-ray absorption spectroscopy (XAS) has been used to study the nickel environment in the hydrogenase obtained from Desulfovibrio gigas. Tetracoordination with Ni-S interactions is suggested [402].

As part of a continuing series, X-ray diffraction has been used to investigate the structure of nickel(II)Carboxypeptidase A. The Ni^{2+} enzyme is shown to have only one nonprotein ligand, i.e. H_2O. An octahedral geometry, in which the sixth position is vacant, is assigned to the nickel ion [403].

Preliminary results of an EXAFS and XAS study of jack bean urease have now been confirmed. A detailed EXAFS analysis indicates that the nickel ion is hexacoordinate and that the coordination sphere is similar to that found in $[Ni(HL)_2L](ClO_4)$ (HL= 1-n-propyl-2-α-hydroxybenzimidazole). The crystal structure of the latter model compound has been determined [404].

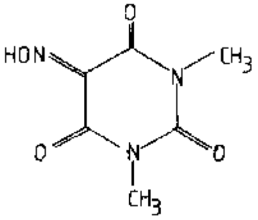
To conclude the discussion on nickel-enzyme complexes, it is interesting to note that the synthesis of active CO dehydrogenase in growing cells of Methanobrevibacter arboriphilus is nickel dependent. Results indicate that the CO hydrogenase of methanogens is a nickel protein [405].

A variety of aminocarboxylic [406] and polyaminocarboxylic acids have been complexed with Ni(II). Coordination usually occurs via the amino and carboxylate moieties. Of interest is the fact that some of the ligands were successful in removing nickel from body organs and subcellular fractions [407].

Nicotinic acid (HL) reacts with Ni(II) yielding the octahedral complex $[NiL_2(H_2O)_4]$ in which the water molecules occupy the equatorial sites [408]. The related ligands isoniazid (L) and nicotinamide (L') react with $NiCl_2$ yielding $NiL_2Cl_2.2H_2O$ and NiL'_2Cl_2 respectively [409].

l-Tyrosine hydrazide (HL) forms complexes of the type $[Ni(HL)_2Cl_2]$, $[Ni(HL)_2(OH)_2]$ and $[NiL(OH)]$ when reacted with Ni(II). The ligand functions as neutral bidentate ligand in the first two complexes, and as a uninegative tridentate ligand in the latter complex [410].

The complexation of 1,3-dimethylvioluric acid (HL) (93) with Ni(II) has been studied potentiometrically. In addition, the complex $NiL_2{\cdot}2H_2O$ has been isolated and characterised [411]. The interaction of Ni^{2+} with the related ligand, murexide (94), has been investigated spectrophotometrically [412].



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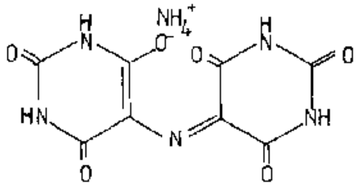


(94)

Nickel(II) complexes with histamine (L) of the type $[NiL_3]X_2$, $[NiL_2(H_2O)_2]X_2$ and $[NiL(H_2O)_4]X_2$ ($X= Cl^-$, NO_3^-, ClO_4^-, $\frac{1}{2}SO_4^{2-}$) have been prepared and isolated. The complexes are all assigned an octahedral configuration with histamine coordinating via its amino and unprotonated imidazole nitrogen atoms [413].

While on the subject of imidazole ligands, the coordination properties of 2-α-methoxybenzylbenzimidazole (L) have been described. Octahedral complexes of the type $[NiL_2X_2]$ ($X=Cl^-$, Br^-, I^-, NO_3^-, NCS^-) and $[NiL_3](ClO_4)_2$ are obtained on reaction with the appropriate nickel(II) salt [414].

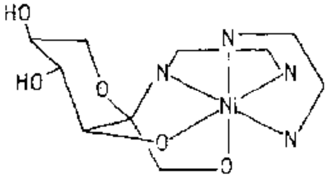
Ternary complexes of the type $NiAL^+$ (A= 2,2'-bipy or 1,10-phen; L= phenoxyacetic acid and a variety of its variously substituted analogues) have been investigated in solution. A linear correlation between pKa or stability constants and Hammett σ-values has been observed, indicating a common mode of coordination of the pesticide (L) [415].

A potentiometric investigation on the interaction of heavy metals with humic acid has been undertaken. The formation constants of the Ni(II)-humic acid complexes have been determined [416]. Continuing with solution studies, the temperature-jump method has been used to determine the rate constant for the formation of the Ni(II) complex in aqueous solution with bidentate acetohydroxamic acid [417].

The Ni(II)-citric acid system has been studied in some detail. Electrophoretic [418], potentiometric [419] and nuclear magnetic relaxation studies [420] have been undertaken. The latter study confirms the presence of $[NiH_2L]$, $[NiHL]^-$, $[Ni(H_2L)_2]^{2-}$, $[Ni(HL)_2]^{4-}$, $[Ni_2(HL)L]^{3-}$ and $[Ni_2L_2]^{4-}$ in solution (H_4L= citric acid).

The anxiolytic drug, bromazepan, reacts with Ni(II) yielding $NiL_2(ClO_4)_2 \cdot 4H_2O$ and $NiL_2SO_4 \cdot 4H_2O$ (L= bromazepan i.e. 7-bromo-1,3-dihydro-5-(2-pyridyl)-2H-1,4-benzodiazepine-2-one). The complexes are assigned a pseudo-octahedral structure, with very strong distortion to the square-planar environment [421].

Finally, a number of carbohydrates and their derivatives have been reacted with Ni(II). In an ongoing study, the synthesis and characterisation of a series of novel Ni(II) complexes containing N-glycosides, derived from a monosaccharide and a diamine, have been reported [422]. Another article in the same study reports the synthesis and crystal structure of the complex $[Ni(en)L]\,Cl_2 \cdot \frac{1}{2}MeOH$ (en= ethylenediamine; L= 2-[(2-aminoethyl)amino]-2-deoxy-L-sorbose), which was derived from the reaction of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ with L-sorbose. The nickel atom is octahedrally coordinated with a bidentate ethylenediamine and a tetradentate glycosylamine ligand of L (95) [423].

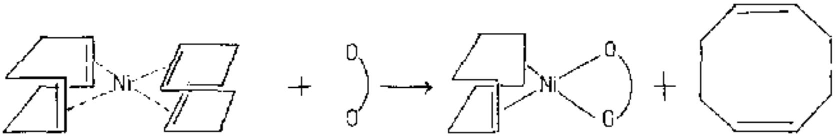


(95)

Other carbohydrate ligands that have been complexed with Ni(II) are pectin [424], glucosamine [425] and α-ketoglutaric acid [426].

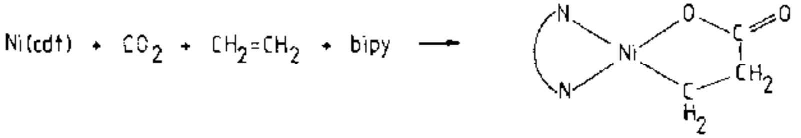
1.4 NICKEL (I)

A number of catalytically relevant Ni(I) complexes have been prepared by oxidation of the appropriate Ni(O) complexes. A number of β-diketones, α-acylcycloalkanones and α-diketones (HL) have been reacted with $[Ni(cod)_2]$ yielding the corresponding complexes, [NiL(cod)] (96).



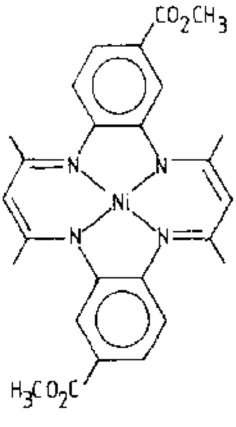
(96)

These complexes have been shown to be active catalysts for the homogeneous linear oligomerisation of 1-butene [427]. A similar complex, [Ni(cdt)] (cdt= 1,5,9-cyclododecatriene), has been utilised in the coupling of CO_2 with ethylene (97) [428].



(97)

Electrochemical reduction has been utilised in the preparation of a number of Ni(I) complexes. The reduction of the nickel(II)-tetradentate Schiff-base complexes [NiL] {L= N,N'-ethylene<u>bis</u>(acetylacetoniminato), N,N'-ethylene<u>bis</u>(salicylideneiminato) and N,N'-ethylene(acetylacetoneiminatosalicylideneiminato)} has been investigated. ESR data indicate that Ni(I) species are formed by exhaustive reduction [429]. In addition, the macrocyclic Ni(I)-complex (98) has been prepared by coulometric reduction of its corresponding Ni(II)-complex [430].



(98)

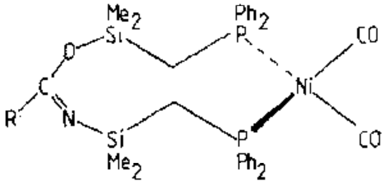
Reaction of trans[Li(μ-NHAr)(OEt$_2$)]$_2$ with [NiI$_2$(PPh$_3$)$_2$] yields a mixture of Ni(I)/Ni(II) amides, Ni(NHAr)$_{1,2}$(PPh$_3$)$_2$, which when reacted with CO affords cis[Ni(CO)$_2$(NHAr)$_2$] [431].

1.5 NICKEL(0)

Metal-vapour methods have been used to prepare the bis(bipyridyl)-nickel(0) complex [Ni(bipy)$_2$]. The electrochemistry of the complex is unusual, with five stable formal oxidation states ranging from +3 to -2 being observed. Reduction potentials indicate that a significant portion of the electron density of the lower valence complexes resides on the bipyridyl ligand [432].

The nickel(0) carbonyl derivative, [Ni(HL)CO]BPh$_4$ {L= tris(2-(diphenylphosphino)ethyl)amine}, has been prepared by reaction of CO with [Ni(L)H]BPh$_4$. A single-crystal X-ray analysis reveals that the nickel atom is tetrahedrally coordinated by three P atoms of L and by the carbonyl group [433].

Similarly, the nickel(II) hydrocarbyl complexes [Ni(R){N(SiMe$_2$CH$_2$PPh$_2$)$_2$}] (R = methyl, allyl, vinyl and phenyl), have been shown to react with CO yielding the nickel(0) dicarbonyl derivatives [Ni(CO)$_2${R$\overline{\text{C=N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)O}}$SiMe$_2CH_2PPh_2$}] (99). Of interest is the vinyl derivative, which loses CO under vacuum producing a new Ni(0) complex, [NiCO{(η^2-C$_2$H$_3$)$\overline{\text{C=N(SiMe}_2\text{CH}_2\text{PPh}_2\text{)O}}$-SiMe$_2CH_2PPh_2$}] (100), which contains a η^2-bonded acryloyl moiety. The latter complex has been structurally characterised by X-ray crystallography and the Ni atom is tetrahedrally coordinated [434].



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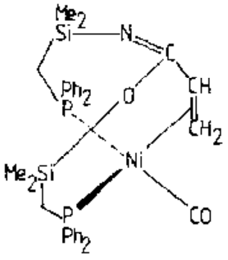
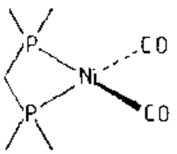


(100)

The highly basic bidentate ligand (CH$_3$)$_2$PCH$_2$P(CH$_3$)$_2$ (L) has been reacted with [Ni(CO)$_4$] and [C$_5$H$_5$NiCO]$_2$ yielding [NiL(CO)$_2$]

and $[Ni_2L_3(CO)_2]$ respectively. (L) coordinates in a bidentate fashion in the mononuclear complex (101), but functions as a bridging ligand in the binuclear complex (102) [435].



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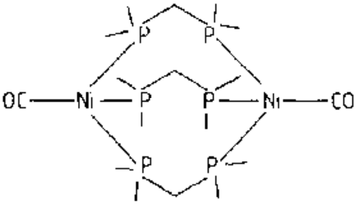

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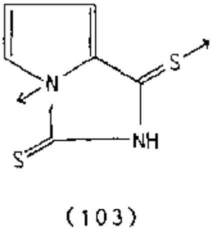
The crystal structures of the complexes $[Ni(triphos)(\eta^2-CS_2)]$ and $[Ni(triphos)(\eta^2-SCNPh)]0.5CH_2Cl_2$ have been reported and compared with their corresponding cobalt analogues. Indications are that the Co-S bond is stronger than the Ni-S linkage probably due to π bonding in the former case. Some relevant crystal data are for $[Ni(triphos)(\eta^2-CS_2)]$; Ni-P= 2.235(2) to 2.240(2), Ni-S= 2.197(3) and Ni-C= 1.86(1)A, while for $[Ni(triphos)(\eta^2-SCNPh)]$-$0.5CH_2Cl_2$; Ni-P = 2.156(6) to 2.258(6), Ni-S= 2.259(6) and Ni-C= 1.88(2)A [436].

Reaction of pyrrole-1,2-dithiodicarboximide (L) (103) with $[Ni(P(OPh)_3)_4]$ affords the tetrahedral complex $[NiL(P(OPh)_3)_2]$. L functions in a bidentate fashion coordinating via the thione sulphur and pyrrole nitrogen atoms [437].



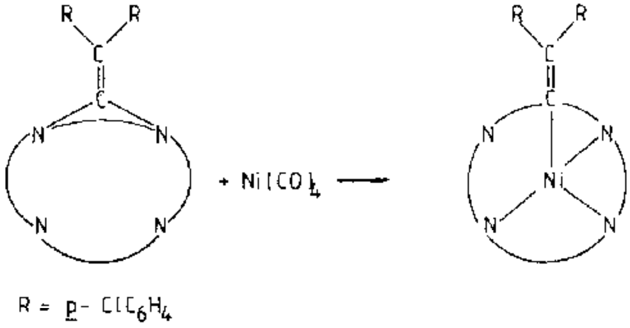
(103)

18-Crown-6 (L) has been used to great effect in influencing chemical reactions involving $K_4Ni(CN)_4$. Diphenylacetylene reacts with $K_4Ni(CN)_4$ in the presence of L and CH_3CN yielding the novel complex $(K^+-L)_2[Ni(CN)_2(PhC{=}CPh)]$. In addition, benzaldehyde reacts under similar conditions yielding the unexpected product

$(K^+-L)_2[Ni(CN)_2(\eta^2-PhCH=CHCN)]$ in which a deprotonated acetonitrile group has been incorporated [438].

The reaction of tetrakis(tri-p-tolylphosphite)nickel(0) with strong acids has been investigated using ^1H, ^{31}P and ^2H n.m.r. spectroscopy. Both five- and four-coordinate Ni hydrides are observed, with the suggestion that the latter complexes are the active species in a number of Ni(0)-phosphite catalysed reactions [439].

$[Ni(CO)_4]$ reacts with the N,N'-bridged tetraphenylporphyrin (104) yielding the metallocarbene complex (105) in which one N-C bond is broken. The molecular composition of (105) has been established from its field-desorption mass spectrum which exhibits a multiplet at m/e 916 due to the parent ion [440].



R = p- ClC$_6$H$_4$

(104) (105)

As is the case with Ni(I) complexes, Ni(0) complexes have been utilised in various catalytic applications. $[Ni(P(OPh)_3)_4]$ has been used to catalyse the addition of deuterium cyanide to cyclohexa-1,3-diene. The reaction has been shown to occur with cis-stereochemistry indicating that a cis-migration of the coordinated cyanide takes place in an intermediate π-allylnickel complex [441]. Other reactions that have been catalysed by Ni(0) complexes are the cyclopropanation of dimethylfumarate and maleate with gem-dihalides [442], and the production of sorbic acid from maleic anhydride [443].

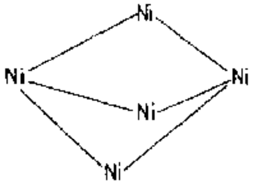
1.6 POLYNUCLEAR COMPLEXES

The large increase in the number of polynuclear nickel-containing complexes reported this year is a good indication of the interest that this area of research is receiving. For the sake of clarity, the complexes have been divided into those that contain nickel-nickel or nickel-metal interactions (clusters), and those that do not. It should also be recognised that some polynuclear complexes, which did not constitute the main theme of the article, have been reported in preceding sections.

1.6.1 Clusters

A series of homonuclear [444-449] and heteronuclear [450-457] nickel-containing clusters have been reported, most of which have been isolated in the solid state. Single-crystal X-ray methods are still favoured in the characterisation of these complexes, and table 8 lists some of the relevant crystallographic data.

Homonuclear clusters vary from those containing the Ni_3 framework to one containing a Ni_9 framework, with Ni-Ni interactions ranging from 3.074 to 2.55 A. Of particular interest is the complex $[Ni_5(CO)_6\{(Me_3Si)_2CHP{=}PCH(SiMe_3)_2\}_2Cl]$, prepared by reaction of $[Ni_6(CO)_{12}]^{2-}$ with $P[CH(SiMe_3)_2]Cl_2$. The crystal structure reveals a molecular geometry involving four of the five nickel atoms in a butterfly arrangement (106) and is unusual in that P-P double bonds are present [446].



(106)

In addition, the tetra-, penta-, and hexanuclear nickel carbonyl clusters, $[Ni_4(CO)_6(\mu\text{-}CO)_6]^{2-}$, $[Ni_4(CO)_6(\mu\text{-}CO)_3H]^-$, $[Ni_5(CO)_9(\mu\text{-}CO)_3]^{2-}$ and $[Ni_6(CO)_6(\mu\text{-}CO)_6]^{2-}$, have been theoretically investigated using a MO-LCAO INDO method [449].

Turning to heteronuclear clusters, clusters containing nickel and osmium [450-452], nickel and iron [453,4], and nickel and cobalt [455-457] have been isolated (see table 8). The complex $[(\eta^5\text{-}C_5H_5)NiOs_3(CO)_9(\mu\text{-}H)_3]$, for which a simple, high-yield synthesis has been reported [450], has been shown to be effective as a catalyst in the hydrogenation of <u>cis</u>- and <u>trans</u>-1,3-pentadiene [451]. Also of interest is the fact that replacement of

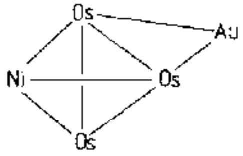
TABLE 8 Crystallographic data of some homonuclear and heteronuclear nickel-containing clusters

COMPLEX	STRUCTURAL DATA (A)	COMMENTS	REF.
<u>Homonuclear</u>			
$[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]BPh_4$	Ni-Ni(av.) = 2.93(5)	Not a significant Ni-Ni interaction	[444]
$[Ni_3\{\underline{o}\text{-}(SCH_2)_2C_6H_4\}_4]^{2-}$	Ni-Ni(av.) = 3.074(1)	Not a significant Ni-Ni interaction	[445]
$[Ni_5(CO)_6\{(Me_3Si)_2CHP{=}PCH(SiMe_3)_2\}_2Cl]$	Ni-Ni(av.) = 2.596(2)	Transition metal cluster with P-P double bonds	[446]
$[Ni_8Cl_4(PPh)_6(PPh_3)_4]$	Ni-Ni(av.) = 2.606(10)	Exhibits paramagnetic behaviour	[447]
$[Ni_8(CO)_4(PPh)_6(PPh_3)_4]$	Ni-Ni(av.) = 2.671(2)	Diamagnetic	[447]
$[Ni_9C(CO)_{17}]^{2-}$	Ni-Ni(av.) = 2.55	Isolated as Bu_4N^+ salt	[448]

TABLE 8 Crystallographic data of some homonuclear and heteronuclear nickel-containing clusters (continued)

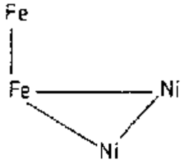
COMPLEX	STRUCTURAL DATA (A)	COMMENTS	REF.
Heteronuclear			
$[(\eta\text{-}C_5H_5)NiOs_3(CO)_9(\mu\text{-}H)_3]$	Ni-Os(av.) = 2.567 Os-Os(av.) = 2.871	New high yield synthesis	[450]
$[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_2(\mu\text{-}AuPPh_3)(CO)_9]$	Ni-Os(av.) = 2.577(5) Os-Os(av.) = 2.873(2) Au-Os(av.) = 2.761(2)	First gold-nickel-osmium cluster; $NiOs_3$ tetrahedron with an Os-Os edge bridged by an Au atom	[452]
$[Fe_3Ni(CO)_8(\mu\text{-}CO)_4(\mu_3\text{-}H)]^-$	Ni-Fe(av.) = 2.500(7) Fe-Fe(av.) = 2.668(4)	Tetrahedron of metal atoms with H^- located over the centre of an Fe_2Ni face	[453]
$[Ni_2Fe_2(\eta\text{-}C_5H_5)_2(CO)_6\{C_2(H)C(=CH_2)CH_3\}]$	Ni-Ni = 2.337(3) Ni-Fe(av.) = 2.384(2) Fe-Fe = 2.755(3)	Spiked-triangular metal atom frame. The alkyne ligand interacts with all four metal atoms	[454]
$[Co_6Ni_2C_2(CO)_{16}]^{2-}$	Ni-Co(av.) = 2.595(1) Co-Co(av.) = 2.610(1)	C-C distance between carbido atoms is 1.49 A	[455]
$[Co_3Ni_9C(CO)_{20}]^{3-}$	M-M varies from 2.408(3) to 2.722(3)	Square antiprism of metal atoms tetracapped on two alternate pairs of adjacent triangular faces	[456,7]

one hydrido-ligand in the above complex by $AuPPh_3^+$ yields the first gold-nickel-osmium cluster, $[(\eta-(C_5H_5)NiOs_3(CO)_9(\mu-H)_2-(\mu-AuPPh_3)]$. The metal framework in this cluster can be described as a $NiOs_3$ tetrahedron with an Os-Os edge bridged by an Au atom (107) [452].



(107)

Finally, the synthesis and crystal structure of the new hetero-tetrametallic complex $[Ni_2Fe_2(\eta-C_5H_5)_2(CO)_6(C_2(H)C-(=CH_2)CH_3)]$ has been reported. The complex is unusual in that it shows a spiked-triangular metal framework (108) with the alkyne ligand interacting with all four metals via triple and double bonds [454].



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1.6.2 Miscellaneous

Work in the field of polynuclear nickel complexes has progressed at a tremendous rate. The bulk of the research centres on homo-binuclear nickel complexes, although a number of hetero-binuclear and polymeric complexes have been reported.

A large number of Schiff base and related ligands have been used in the synthesis of homo- and hetero-binuclear nickel(II) complexes. As can be seen in table 9, homo-binuclear complexes containing tridentate [458-463], tetradentate [464-468] and hexadentate ligands [469], have been reported, while hetero-

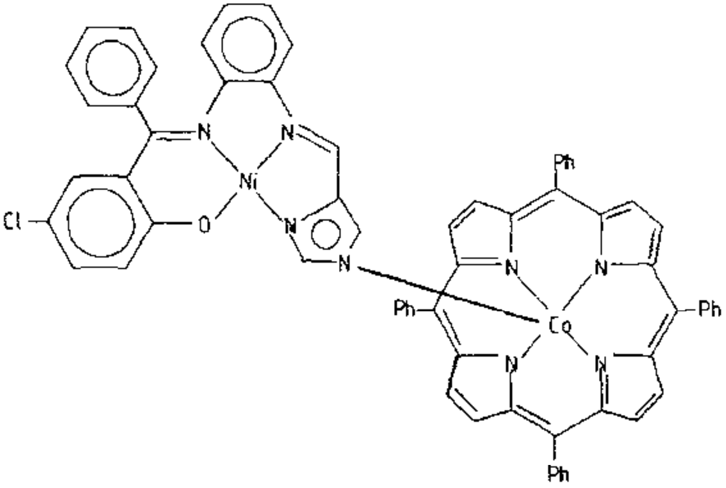
TABLE 9. Homo- and heterobinuclear Ni(II)-Schiff base complexes

LIGAND	COMPLEX	COMMENTS	REF.
Homonuclear			
2,5-Dihydroxy-R-*p*-iminoazobenzene (H_2L) {R = acetophenone, propiophenone, benzophenone}	$[Ni(HL)Cl]_2$	Tetrahedral geometry	[458]
R-benzoinimine {R = 2-amino-2-methyl-1-propanol, 1-amino-2-propanol} (H_2L)	$[Ni_2L_2(H_2O)_4]$	Octahedral geometry	[459]
o-N-(salicylidene)aminobenzoylhydrazine (H_2L)	$Ni[Ni(HL)_2]X_2.nH_2O$	Octahedral geometry; $X = Cl^-, Br^-, I^-, ClO_4^-$	[460]
N-(furan-2-carboxamido)salicylaldimine (H_2L)	$[Ni_2(HL)_2(H_2O)_2Cl_2]$	Octahedral geometry	[461]
p-(*p*'-aminophenyl)thiophenyliminomethyl-2-thienyl ketone (L)	$[Ni_2L_2Cl_2(H_2O)_2]$	Distorted octahedral geometry	[462]
2,6-Lutidyl-2-phenylketone thiosemicarbazone (HL)	$[NiL]_2X_2$	Square-planar; $X = Cl^-, Br^-, I^-$	[463]
N,N'-ethylenediimine*bis*(*o*-aminobenzaldehyde) (H_2L)	$[Ni_2L(thf)X]X \cdot nH_2O$	Tetrahedral or square-planar; $X = Br^-, NO_3^-$	[464]
m-Xylene*bis*[2-(1,3-propandiyl*bis*(2-pyridinecarbaldimine))] (L)	$[Ni_2LX_4]$	Distorted tetragonal structure; $X = Cl^-, N3^-, NCS^-$	[465]
m-Xylene*bis*[2-(1,3-propandiyl*bis*(2-pyrrolcarbaldiminate))] (L)	$[Ni_2L]$	Square-planar	[465]

TABLE 9. Homo- and heterobinuclear Ni(II)-Schiff base complexes (continued)

LIGAND	COMPLEX	COMMENTS	REF.
Bis(salicylidene)-4,4'-diaminophenylmethane (H_4L)	$[NiL(H_2O)_2]_2$	Octahedral structure	[466]
Bis(benzoinimine)-*p*-phenylenediamine (H_2L)	$[Ni_2L_2(H_2O)_4]$	Distorted octahedral geometry	[467]
Bis(2-hydroxy-1,2-diphenylethanone)-1,4-benzenediimine (H_2L)	$[Ni_2L_2(H_2O)_4]$		[467]
3-Formylsalicylic acid thiosemicarbazone (H_4L)	$[Ni_2L(H_2O)_2]$	Both square-planar and octahedral Ni ions present	[468]
N,N'-ethylene*bis*(*o*-acetoacetylphenolimine) (H_4L)	$[Ni_2L]$	Electrochemical study	[469]
Heteronuclear			
o-Phenylene*bis*(salicylaldimine) (H_2L)	$[NiLMX_2]$	M=Zn(II),Cd(II); $X=Cl^-,NO_3^-,ClO_4^-$	[470]
Ethylenediamine-3-formylsalicylic acid (H_4L)	[NiLM]	M=Si(IV),Sn(IV),Te(IV),Ti(IV)	[471]
Bis(R-salicylaldehyde)thiocarbohydrazone {R = H,CH_3,Cl,OCH_3} (H_2L)	$[NiLSnCl_4]$	Octahedral nickel(II)	[472]
N,N'-1,3-propylene-*bis*(salicylideneimine) (H_2L)	$[NiLMX_3]$	M=Ln; $X=NO_3^-,NCS^-,Cl^-,ClO_4^-$	[473]
N,N'-ethylene*bis*(*o*-acetoacetylphenol) (H_4L)	[NiLM(OH)]	M=Ln; Ni is square-planar	[474]

binuclear complexes containing tetradentate ONNO donor ligands [470-474] have also been isolated. A particularly interesting hetero-binuclear complex (109), prepared by reaction of the nicke Schiff base complex with cobalt tetraphenylporphyrin has been synthesised [475].



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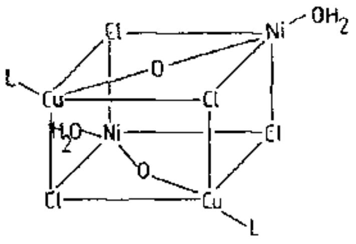
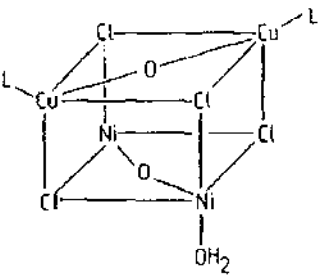
Reaction of $[LCuCl]_4O_2$ (L= N,N'-diethylnicotinamide) with $Ni(NS)_2$ (NS= S-methylisopropylidenehydrazinecarbodithioate; S-methyl(*p*-methylbenzylidene)hydrazinecarbodithioate) yields the tetranuclear complex $[LCuNi(H_2O)Cl_2]_2O_2$ which has been isolated in two isomeric forms (110-111). Reaction of (110) and (111) with CO_2 yields the corresponding dicarbonato derivatives [476].



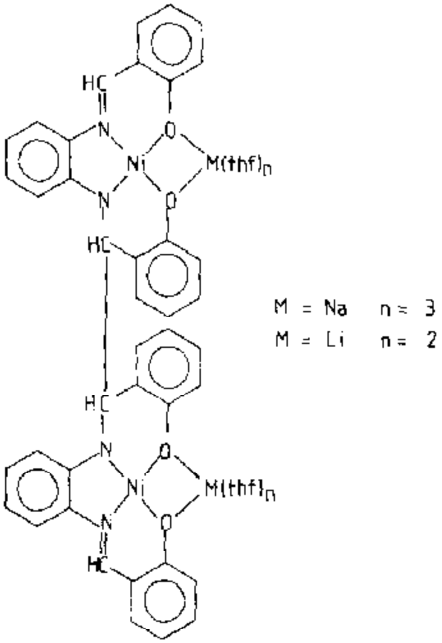


(110) (111)

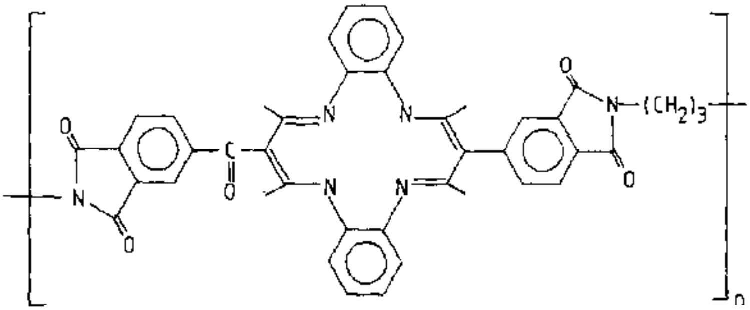
While on the subject of tetranuclear Schiff base complexes, carbon-carbon bond breaking and formation by a metal-assisted redox process has been observed in the nickel(II)-Schiff base complex [NiL] (H_2L=N,N'-*o*-phenylene*bis*(salicylideneimine)).

Reaction with Na or Li in the presence of thf yields the tetranuclear complex (112) [477].

(112)



A number of polymeric Schiff base complexes have been prepared. 2-Salicylideneimino-5-mercapto-1,3,4-thiadiazole (H_2L) [478] and its related Schiff bases derived from salicylaldehyde and variously-substituted 4-amino-5-mercapto triazoles [479] have been complexed with Ni(II). The resultant complexes $[NiL(H_2O)_2]_n$ are polymeric with an octahedral configuration assigned to the nickel ion. Other Schiff bases that give rise to polymeric complexes are those derived from 2-(2-aminophenyl)benzimidazole and benzaldehyde [480], and from 4,4'-(4,4'-biphenylene*bis*azo)-di(salicylaldehyde) and p-toluidine [481]. Finally, the novel macrocyclic Schiff base polymer ligand (113), has been synthesised and its solvent extraction of Ni(II) investigated [482].



(113)

The effect of substituent on mode of coordination has been clearly demonstrated in a series of nickel(II) complexes of p-chloro-, p-methyl- and p-methoxybenzoylhydrazone oximes (H_2L). Reaction with the p-chloro-ligand yields the octahedral complex $[Ni(H_2L)(H_2O)_3]Cl_2$, whereas reaction with the p-methyl- and p-methoxy-ligands gives rise to the diamagnetic binuclear complexes $[Ni(L)(H_2O)]_2$ [483].

Reaction of the structurally related ligands phenylazo-2-fural-doxime (HL) and phenylazo-2-thenaldoxime (HL') with Ni(II) is also of interest. The former ligand yields the binuclear complex $[NiL_2]_2$, whereas the latter yields the hexanuclear complex $[NiL'_2]_6$. Octahedral geometry is assigned to the metal ions in both complexes [484].

Polymeric nickel complexes of the type $[Ni(H_2L)]_n$ have been prepared by the reaction of Ni(II) with ethane-1,2-bis(thioglyoxime) (H_4L) [485] and benzene-1,2-bis(aminoglyoxime) (H_4L) [486] respectively. The coordination geometry of the nickel ion is square-planar in both polymeric complexes.

A variety of substituted nickel(II) salicylaldoximates $[Ni(HL)_2]$ (H_2L = R-salicylaldoxime; R = H, 3-Me, 4-Me, 5-Me, 5-Cl) have been reacted with Si(IV)chloride yielding tetrahedral complexes of the type $[Ni(HL)_2SiCl_4]$ [487]. Other hetero-binuclear complexes that have been isolated are $[NiCu_2(OR)_4(HL)_2]$ where R= CH_3, C_2H_5, n-C_3H_7, n-C_4H_9 and H_2L= benzildioxime [488].

Turning to oxygen-donor ligands and in particular ligands containing oxygen bridging moieties, a variety of dinuclear nickel complexes with carboxylate bridging groups have been reported (see table 10) [489-496]. Of particular interest is the complex $[Ni_2L_4(py)_4(H_2O)]\cdot H_2O$ (HL= 2-chlorophenoxyethanoic acid), the crystal structure of which reveals both bridging and monocoordinate carboxyl groups [493].

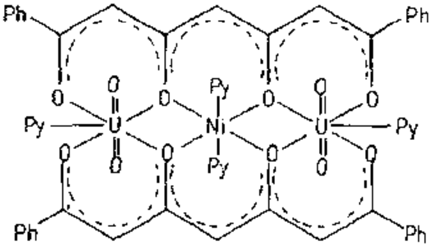
The crystal structure and magnetic properties of bis(acetylacetonato)nickel(II) recrystallised from isopropanol have been reported. The complex crystallises as the dimer $[Ni(acac)_2(i\text{-}PrOH)]_2$ in which both bridging and non-bridging acetylacetonato groups are present. The Ni-O bond lengths vary from 1.985(1) to 2.137(2)A [497].

The related mixed metal complexes $[Ni\{(OPPh_2)_2Pt(S_2CNR)\}_2]$ (R= i-Pr, Et) have been prepared by reaction of $[Pt(S_2CNR_2)(Ph_2PO)_2H]$ with $[Ni(acac)_2]$. Spectroscopic studies indicate square-planar geometry [498].

TABLE 10. Dinuclear nickel(II) complexes with bridging carboxylate groups

LIGAND	COMPLEX	COMMENTS	REF.
$R\text{-}PhCO_2H$ {R = H,$\underline{o}$-Me,$\underline{p}$-MeO,$\underline{o}$-Cl,$\underline{m}$-Cl,$\underline{p}$-Cl} (HL)	$[NiL_2B]_2$	B = 2- and 3-picoline N-oxide; Octahedral	[489]
$R\text{-}CO_2H$ {R = $CH_2Cl,CHCl_2,CCl_3$} (HL)	$[Ni_2L_4B]_2$	B = quinoline N-oxide;Octahedral	[490]
$R\text{-}C_6H_4CO_2H$ {R = H, $\underline{p}$-Me, $\underline{o}$-Cl, $\underline{p}$-NO_2} (HL)	$[NiLB]_2$	B = quinoline N-oxide;Octahedral	[491]
Thiodisuccinic acid (H_4L)	$[Ni_2L(H_2O)_6]$	Distorted octahedral	[492]
2-Chlorophenoxyethanoic acid (HL)	$[Ni_2L_4(py)_4(H_2O)]\cdot H_2O$	Both bridging and mono-coordinate carboxyl groups; X-ray structure	[493]
Malic acid (H_3L)	$[Ni_2L_2]$	Solution study	[494]
Ethylenediaminetetraacetic acid (H_4L)	$[Ni_2L(H_2O)_4]\cdot 2H_2O$	Large angle X-ray scattering investigation	[495,6]

1,7-Diphenyl-1,3,5,7-heptanetetrone (L), a β-polyketone, is potentially capable of forming polynuclear metal complexes. The X-ray crystal structure of the heterotrinuclear complex $[(UO_2)_2NiL_2(py)_4]\cdot 2py$ (114) has been reported. Relevant data are $Ni\text{-}O_{av.}$ = 2.029 and $Ni\text{-}N_{av.}$=2.175A [499].



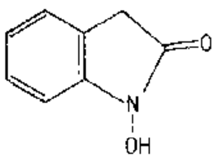
(114)

Simple alkoxides have been used to great effect as bridging moieties. Alcoholysis of $Ni[Al(O\text{-}i\text{-}Pr)_4]_2$ with various alcohols yields products of the type $Ni[Al(OR)_4]_2$ (ROH= methanol, ethanol, 2,2,2-trichloroethanol, n-butanol and 1,3-dichloro-2-propanol) [500]. In addition, polymeric complexes of the type $[Ni(OR)_2]_n$ (R= Me, Et, Pr, i-Pr, Bu, i-Bu, tert.-C_5H_{11}, tert.-C_6H_{13}) have been prepared [501].

The single-crystal X-ray and molecular structure of catena-{μ_4-(dihydrogen mellitato)-bis[bis(oxamide oxime-N,N')nickel(II)]} tetrahydrate has been determined. Ni(II) coordinates in an octahedral fashion with two bidentate oxamide oxime ligands and two oxygen atoms of different mellitic anions in *cis* positions. Four Ni atoms are bridged by each carboxylic acid anion giving rise to a one-dimensional ribbon-like structure [502].

4,4'-Phenylylenebisazodisalicylic acid (H_2L) complexes with Ni(II) yielding a polychelate of molecular formula $[NiL(H_2O)_2]_n$. An octahedral structure is suggested for nickel which is *trans*-hexacoordinated [503].

The coordination properties of the cyclic hydroxamic ligands, 1-hydroxy-2-indolinone (HL) (115) and 3-amino-3,4-dihydro-1-hydroxy-carbostryril (HL') (116) have been investigated. Oligomeric species of the type $[NiL_2(H_2O)_2]_n$ and $[NiL'_2]$ are obtained respectively on reaction with Ni(II). (115) functions as an OO donor whereas (116) functions as an O_2N donor [504].



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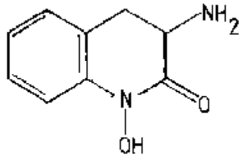


(116)

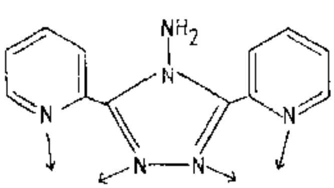
Other hydroxamic ligands, all of which yield polymeric nickel chelates, that have been complexed with Ni(II) are p-phenylene-diacrylyl-*bis*-N-phenyl-, isophthalyl-*bis*-N-phenyl-, and fumaryl-*bis*-N-phenylhydroxamic acid. The mode of coordination varies from octahedral to tetrahedral depending on the hydroxamic acid [505].

3-Acetylamino-2-benzofurancarboxamide (L) reacts with $NiCl_2$ yielding the polymeric complex $[NiL_2Cl_2]_n$. Magnetic susceptibility data (μ_{eff}=3.4) indicates that the coordination environment about nickel is essentially octahedral [506].

The crystal and molecular structure of polymeric diaqua-*bis*((R,R)-tartrato-$O^1,O^2:O^3,O^4$)dinickel(II)trihydrate at -162°C has been reported. Each dimeric unit contains one (R,R)-tartrato dianion chelated to two nickel ions (Ni-Ni= 5.202(1)A), with coordination occurring via two hydroxy oxygen and two carboxyl oxygen atoms. A second tartrato dianion coordinates in a similar fashion, but also binds two nickel ions of neighbouring dimeric units via the other carboxyl oxygen atoms [507].

Sodium selenite has been reacted with Ni(II) in the presence of base. The complexes analyse for $[Ni_2(SeO_3)(OH_2)(H_2O)_4]$ and have been assigned a polymeric structure with bridging selenito-O,O' groups. Spectroscopic data indicate that the coordination geometry around nickel is distorted octahedral [508].

Triazole ligands containing two or more nitrogen atoms have the ability to chelate, bridge or both. A variety of substituted 1,3,5-triazines [509], 3-amino-1,2,4-triazole [510] and 2-aminopyrimidine [511] have been shown to form 1:2 (Ni:L) complexes in which the ligands chelate, as well as polymeric 1:1 complexes in which the ligands bridge. Of particular interest is the novel dinucleating chelating triazole ligand, 4-amino-3,5-*bis*(pyridin-2-yl)-1,2,4-triazole (L) (117) which reacts with Ni(II) yielding the complex $[Ni_2L_2Cl_2(H_2O)_2]Cl_2 \cdot 4H_2O$. The crystal structure is unusual in that both water and chloride ion are present as axial ligands (118) [512].



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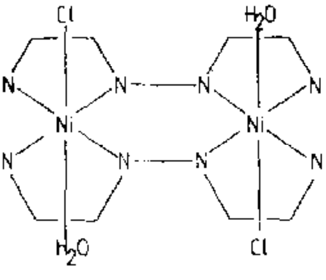


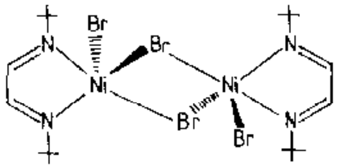
(118)

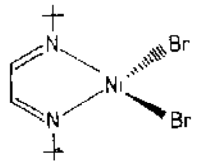
3(5)-Aminopyrazole (HL) reacts with $NiCl_2$ yielding a complex with general formula $[Ni(HL)_2Cl_2]$. Spectral and magnetic data indicate octahedral stereochemistry with the ligand bridging adjacent Ni atoms [513]. The related ligands 3,3',5,5'-tetramethyl-4,4'-bis-1H-pyrazole, 3,3',5,5'-tetramethyl-4,4'-methylene-bis-1H-pyrazole and 4,4'-methylene-bis-1H-pyrazole yield similar polynuclear complexes of the type $[NiLX_2]_n$ ($X= Cl^-$, NO_3^-) on reaction with NiX_2 [514].

Hydrazine and its related ligands have been utilised as bridging groups in a number of complexes. The preparation, characterisation and thermal properties of $[Ni(N_2H_4)_2(NCS)_2]$ have been reported. Hydrazine functions as a bridge between two metal ions which have a distorted octahedral environment [515]. Spectroscopic studies of the oxalate-hydrazine compound $[Ni(C_2O_4)(N_2H_4)]$ indicate a similar structure with only N_2H_4 occupying bridging positions [516]. In addition, complexes of the type $[NiL_2]$ (HL= acetylacetone monohydrazone) and $[Ni(acac)_2L'_2]$ (L'= phenylhydrazine) have been prepared by the reactions of hydrazine and phenylhydrazine respectively with nickel(II)-acetylacetonate [517].

The single-crystal X-ray structure of $[NiBr_2L]_2$ (L= N,N'-di-tert-butyldiazabutadiene) has been determined. The complex consists of a distorted trigonal-bipyramidal centrosymmetric dimer (119). Heating $[NiBr_2L]_2$ results in the formation of the tetrahedral complex $[NiLBr_2]$ (120), the crystal structure of which has also been determined [518].

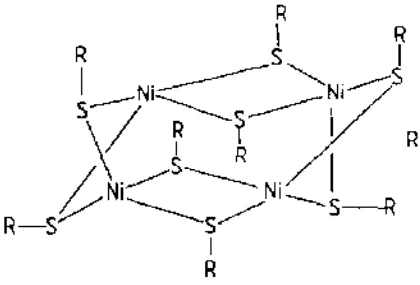
A number of structures containing thiocyanate groups as bridging ligands have been prepared. The crystal and molecular structures of $[Ni(NH_3)_3Ag(SCN)_3]_n$ [519] and $[NiHgL_3(SCN)_4(H_2O)]_2$ [520] have been determined. In both cases NCS coordinates to the nickel ion via nitrogen and the "softer" Ag and Hg ions via sulphur. Similar coordination is observed in the complexes derived from $NiHg(SCN)_4$ with the chelating NN-donor ligands 2,2'-bipyridine, 1,10-phenanthroline, 2,9-dimethyl-1,10-phenanthroline and diacetyl dihydrazone [521]. Finally, the unusual trimeric coordination compound $[Ni_3(HL)_6(NCS)_6]\cdot 2H_2O$ has been isolated and its crystal and molecular structure determined. Structural features of note are N-bonded bridging NCS groups and 1,2-bridging triazole ligands [522].


(119)


(120)

Turning to sulphur-donor ligands, the nickel(II) complex of trimethylolethane trithioglycolate has been prepared and its structure analysed using spectroscopic and magnetic methods. Coordination is found to occur via the sulphur atoms which function in a bidentate manner forming bridges between the metal ions. The metal ion is assigned octahedral symmetry while subnormal magnetic behaviour is observed [523].

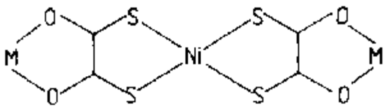
The synthesis and crystal and molecular structure of cyclo-*tetrakis*[*bis*(μ-N-methylpiperidine-4-thiolato)nickel(II)] has been reported. A cyclic tetranuclear array of nickel atoms, bridged by eight sulphur atoms is observed (121). The Ni-Ni distances average 2.665(5) A, whereas the closest S-S distances average 2.868(6)A [524].


R = N-methylpiperidine

(121)

Bimetallic tetramorpholine-4-carbodithioate complexes of the type $[NiML_4]_n$ (M= Zn(II), Cd(II), Hg(II); L= morpholine-4-carbodithioate) have been prepared. The nickel complexes are diamagnetic, and square-planar stereochemistry has been proposed for these polymeric complexes [525]. A polymeric S-bridged complex of a similar nature is obtained when bisphenylthiourea is reacted with Ni(II) in its deprotonated form [526].

Dithiooxalic acid (H_2L) has been utilised in the synthesis of some interesting bimetallic complexes. The crystal and molecular structures of $[NiMnL_2(H_2O)_3]\cdot4.5H_2O$ [527] and $[M_2(H_2O)_{2n}Ni_3L_6]\cdot XH_2O$ (M= rare-earth(III) metals Y, La, Ce, Nd, Sm, Eu, Gd, Dy, Er and Yb) [528] have been determined by single-crystal X-ray methods. In all cases the repeating unit consists of square-planar nickel(II) ions coordinated to the sulphur atoms of the bridging thiooxolate groups (122).

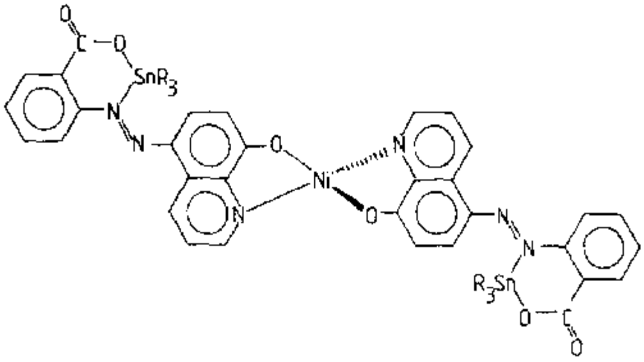


(122)

Polymeric $[NiL_2Cl_2]$ is obtained when 3-amino-2-acetylbenzofuran (L) is reacted with $NiCl_2$. The geometry around Ni(II) is essentially octahedral with L functioning as the bridging moiety [529]. Similarly, the polymeric complexes $[NiL'_2B_2]$ (HL'= picrolinic acid; B = PhN_2, p-methylaniline, 1-benzimidazole) have an octahedral structure with the picrolonate molecule functioning in a bridging fashion [530].

The mixed-metal complexes $[(R_3SnL)_2Ni]$ (H_2L = o-carbazoxine, R= Ph, Bu, Pr) are particularly interesting in that the chelating properties of the -COOH and phenolic -OH group towards Ni^{2+} and organotin groups have been exploited in their preparation. Spectral and magnetic moment data suggest tetrahedral stereochemistry around Ni(II) (123) [531].

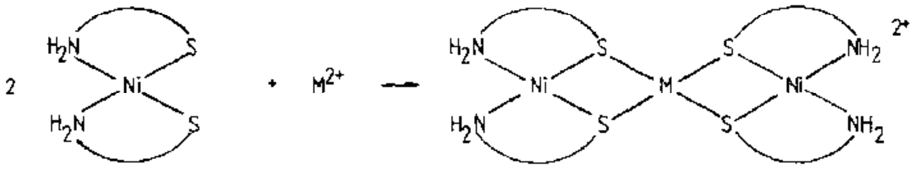
1,5-Diamino-3-pentanethiol (HL) has been synthesised and reacted with various nickel salts, NiX_2 (X= Br^-, ClO_4^-, NO_3^-, BPh_4^- and NCS^-). All the complexes $[Ni_2L]X_2$ are binuclear thiolate-bridged, with the nickel ion assuming square-planar coordination [532].



(123)

Oxidation of <u>bis</u>(thiosalicylohydrazato)nickel(II), $[Ni(HL)_2]$, in alkaline medium yields the disulphide complex $[Ni_2L_4]$ with liberation of H_2. During the oxidation process, the mode of coordination of the ligand changes from a NO donor set to a SO donor set [533].

The anion $[Ni(N_2S_2)_2]^{2-}$, formed by the reaction of alkali with $[Ni(HN_2S_2)_2]$, has the ability to function as a bidentate ligand. Reaction with Ni(II) yields the trinuclear complex anion $[Ni(NiN_4S_4)_2]^{2-}$ which has been isolated as its tetraphenylphosphonium salt. The crystal and molecular structure reveals a near planar environment for each of the nickel atoms [534]. Similarly, <u>bis</u>(2-mercaptoethylamine)nickel(II) (124) has the ability to function as a diamagnetic chelating agent. Reaction with CdX_2 ($X= Cl^-$, Br^-, I^-) yields the diamagnetic complexes $[(Ni(NH_2CH_2CH_2S)_2)_2Cd]CdX_4$. The analogous mercury complexes are paramagnetic with the exception of the iodide complex $[(Ni(NH_2CH_2CH_2S)_2)_2Hg][HgI_4]$ which is diamagnetic. Consequently the mercury complexes containing chloride and bromide have been assigned a polymeric structure [535].



M = Cd, Hg

(124)

Reaction of $NiCl_2$ with γ-mercaptopropylamine (HL) gives the trinuclear complex $[Ni_3L_4]Cl_2$, the crystal and molecular structure of which has been determined. Each sulphur atom of the ligand functions as a bridging moiety between the two Ni atoms, with nitrogen atoms completing the coordination sphere. The geometrical environment of the nickel atoms is square-planar [536].

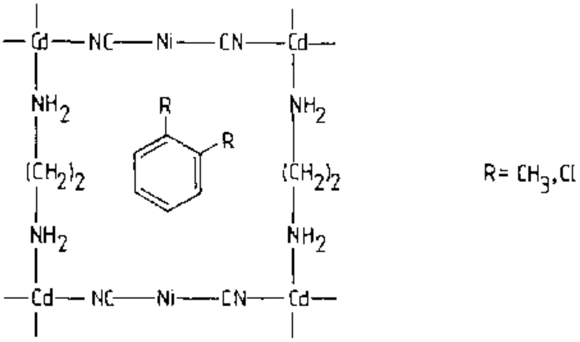
In a continuing study of transition metal complexes with polymer ligands, the structure of the Ni(II) complex with copolymer of methacrylamide and the sodium salt of methacrylic acid has been investigated [537]. In addition, the structure and catalytic properties of complexes of polyethylenimine and polytrimethylenimine with group VII metal salts has been reported [538].

Infrared absorption studies of a number of mixed metal nickel-containing complexes have been undertaken. These include $[NiL_2(SbCl_6)_2]$ (L= o-phen [539], 2,2'-bipy [540]), in which Ni(II) is tetracoordinate, and a series of complexes $NiL_6(MX_n)$ (M= Zn, In; X= Cl^-, Br^-; n=4: M= Sn; X= Cl^-, n=6) [541].

$[Ni(CN)_2]$ reacts with a variety of amine N-donor ligands yielding intercalation compounds. I.R. spectral and X-ray diffraction data indicate that the amine forms interlamellar compounds of compact structure with $Ni(CN)_2$. The bonding involves N-atom coordination of the amine to the N-tetracoordinated Ni^{2+} ions [542,3].

A modified Hoffman-type host lattice, $CdLNi(CN)_4$ (125), with 1,6-diaminohexane (L) as the bridging ligand has been prepared, with the aim of controlling the range of guest molecules which can be accommodated. Of particular interest is the observation that inclusion compounds are formed with the ortho and meta isomers only of xylene and dichlorobenzene [544]. Furthermore, the related complexes $ML_2Ni(CN)_4$ (M= Cd, Ni; L= quinoline) have been prepared and their infrared and Raman spectra reported. The structure of the complexes consists of two-dimensional polymeric sheets formed by $Ni(CN)_4{}^{2-}$ ions, bridged by $ML_2{}^{2+}$ cations [545,6].

Reaction of trans$[CrF(H_2O)L_2]ClO_4$ (L= 1,2-diaminopropane) and $[Ni(CN)_4]^{2-}$ yields the binuclear complex cis$[L_2FCr\text{-}NC\text{-}Ni(CN)_3]\cdot 3H_2O$, which contains a μ-cyano ligand [547]. In a continuation of the study, the synthesis and characterisation of the related complexes cis-$[L_2XCr\text{-}NC\text{-}Ni(CN)_3]$ (L= en; X= Cl^-, Br^-) has been described [548], while the solid-state kinetic parameters for the deaquation-anation of the tetracyanonickelate(II) of aquopentaammine cobalt(III) have been reported [549].



(125)

Finally, several new double complexes of the type $[NiL_n][Cr(NCS)_4(NH_2CSNH_2)_2]_2$ (L= various mono-,bi-,tri- and tetradentate bases and n= 1, 2, 3, 4 or 6) have been synthesised. Conductance measurements indicate that the complexes are ionic in nature [550].

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