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COORDINATION CHEMISTRY REVIEWS

Nickel 1986

Gary A. Foulds

Contents

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1. Introduction

This article reviews the coordination chemistry of nickel appearing in 1986, including volumes 104 and 105 of Chemical Abstracts. The format of previous reviews in this series [1–3] has been adopted, with material arranged by oxidation state, with further subdivision in terms of ligand donor type. Complexes with mixed oxidation states or mixed ligands have, wherever possible, been arranged according to the principle theme of the article in which they appeared.

Articles of general interest that have appeared include a review of iron, cobalt and nickel containing 303 references for 1984 [4], and a simple method for calculating Jahn-Teller distortions of spin-paired nickel(II) complexes [5]. In addition, the *cis* and *trans* influences in planar Ni(II) complexes of the type $[NiL_3X]^q$ (L = NH_3, Cl; X = F, Cl, Br, OH, CH_3, H, NO, NO_2, NCS, CN, H_2O, NH_3, H_2S, PH_3, CO) have been investigated by geometric optimisation within the CNDO version of the MO-LCAO-SCF approach [6]. Furthermore, nonstoichiometric nickel complexes of diethylenetriamine, in which nickel is divalent and a variable amount of halide is present in channels and bonded to the ligand, have been prepared from complexes of the type $[NiL_2]X_2$ (L = diethylenetriamine; X = Cl, Br, NO_3, ClO_4) [7].

Nickel complexes have also been used very effectively in the facilitation and elucidation of a number of organic reactions. These include the synthesis of cyclooctatetraene from ethyne [8] and the facile cyclisation of the valeronitrile group bound to a nickel macrocycle [9]. In addition, the poisoning of Co-Mo-alumina hydrodesulfurisation catalysts by nickel tetraphenyl porphyrins has been investigated [10].

2. Nickel(IV)

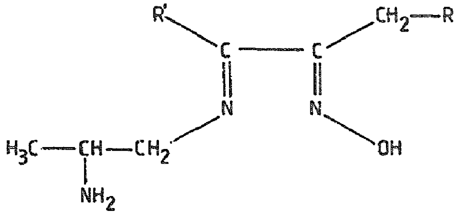
Interest in the +4 oxidation state continues, as manifested by a review containing 34 references, in which ligand types which stabilise Ni(IV) and Ni(III), as well as those that exist as Ni(II)-stabilised radicals, have been discussed [11].

2.1. Complexes with nitrogen donor ligands

Spectroscopic and electrochemical methods have been used to study a number of Ni(IV) and Ni(III) complexes derived from oximato ligands. Tridentate ligands of the type HL (**1**) have been complexed with Ni(II) perchlorate, yielding octahedral complexes, $Ni(HL)_2(ClO_4)_2$, which were oxidised by $(NH_4)_2S_2O_8$ to $Ni(HL)L(ClO_4)_2$. These complexes were further oxidised to $NiL_2(ClO_4)_2$ using nitric acid as the oxidant [12,13].

2.2. Complexes with phosphorus and arsenic donor ligands

Pseudo-octahedral nickel(IV) complexes of the type $[Ni(L)_2X_2][ClO_4]_2$ (L = *o*-$C_6H_4(PMe_2)_2$, *o*-$C_6H_4(PMe_2)(AsMe_2)$, or *o*-$C_6H_4(AsMe_2)_2$; X = Cl or Br) have been prepared and characterised. Cyclic voltammetry has been used to study



R, R' = Me, Et, Ph

(1)

the Ni(II)-Ni(III)-Ni(IV) redox potentials as a function of L, while EXAFS has been used to determine the first coordination sphere bond lengths, which indicate metal centred oxidation [14].

3. Nickel(III)

Macrocyclic nitrogen-donor and oxime ligands continue to dominate Ni(III) complex chemistry. However, by way of introduction to this section, a number of biologically relevant, novel Ni(III) complex interactions have been reported.

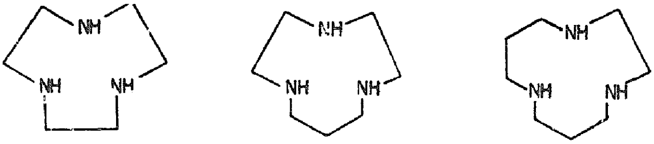
Evidence of hydrogen binding to Ni(III) in bacterial hydrogenase indicates that H_2 may be coordinated in its molecular form rather than by the more usual binding via oxidative addition to give a dihydride [15]. In addition, a number of Ni(III)-peptide complexes have been studied in solution [16] and as frozen aqueous gasses [17].

In a study of the production of compounds containing highly oxidised nickel, γ-NiOOH has been prepared in high purity by electrochemical oxidation of $NiO.xH_2O$. Other methods of oxidation proved to be less effective in producing pure γ-NiOOH [18].

3.1. Complexes with nitrogen donor ligands

Some general articles concerning Ni(III)-macrocyclic chemistry have appeared recently. These discuss redox and substitution reactions of diaquonickel(III) macrocyclic complexes [19,20], the effect of ring size and medium on the Ni(III)/Ni(II) redox couple potential for bis nickel(III) complexes of the triaza macrocyclic ligands (2) [21], and the effect of ring size on the chemical properties of tervalent nickel complexes with the tetraaza macrocyclic ligands (3) in aqueous solution [22].

The crystal structure of bis[bis(1,4,7-triazacyclononane)nickel(III)] dithionate heptahydrate has been determined. The coordination sphere at the Ni(III) centre consists of six nitrogen atoms of two facially coordinated 1,4,7-triazacyclononane



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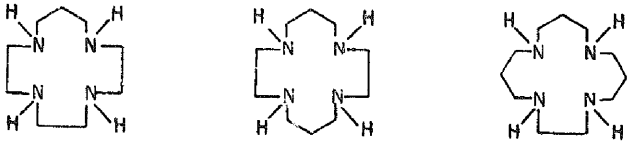


(3)

rings in a tetragonally distorted octahedral arrangement. Ni-N bond lengths vary from 1.964(5) to 2.111(5) Å [23].

Similarly, the crystal structure of $[Ni(III)L(H_2O)]ClO_4.2H_2O$ (H_2L = 15-benzyl-1,4,7,10,13-pentaazacyclohexadecane-14,16-dione) has been determined. The complex is hexa-coordinate, with equatorial Ni-N bonds varying from 1.963(5) to 1.890(4) Å, while the apical Ni-N bond is 2.067(4) Å in length. The sixth position is occupied by a water molecule [24].

The electrochemical behaviour of the Ni(II) complex of 11-(2′-hydroxyphenyl)-1,4,7,10-tetraazacyclotridecane in aqueous solution is most novel. Upon oxidation to Ni(III), the *cis* macrocyclic configuration of the ligand rapidly rearranges to a nominally square-planar form, which is reversible upon reduction [25].

Electrochemical investigations on the heterobinuclear complex, $NiCu(biscyclam)(ClO_4)_4$, have been undertaken in anhydrous acetonitrile and 70% perchloric acid. Differential-pulse polarograms indicate that oxidation of the two metal centres to their +3 oxidation states occurs, with oxidation of Cu(II) to Cu(III) being more difficult in the presence of Ni(III) [26].

Resonance Raman spectroscopy has been used to study intramolecular electron transfer in the one-electron oxidation product of (tetraphenylporphinato)nickel(II). The study shows that Resonance Raman spectroscopy is able to distinguish between oxidation of the porphyrin ring or of the metal [27].

Oxidation of oxime complexes of the type $[NiL_2]$ (HL = salicylaldoxime or related oxime ligand) with $H_2O_2/HClO_4$, Br and nitric acid yielded $Ni(HL)_2(ClO_4)_3$, $[Ni(H_2Q)(HQ)]Br$ (H_2Q = bromosalicylaldoxime) and $Ni(HL)(NO_3)_3$ respectively [28]. A similar dependence on the oxidant was also observed in the preparation of a number of Ni(III) complexes with Schiff bases derived from diacetyl monoxime [29].

3.2. *Complexes with sulfur donor ligands*

The reaction of NiX_2 (X = diethyl dithiophosphate) with tetraethylthiuram disulphide (L-L) yielded NiL_3, in which the reduced tetraethylthiuram disulphide functions as a S-S donor ligand [30].

3.3. *Complexes with nitrogen - sulfur donor ligands*

The electrooxidation of the nickel(II) complexes of variously-substituted 8-mercaptoquinolines in a variety of solvents yielded complex species of Ni(III) [31].

4. Nickel(II)

4.1. *Complexes with halide ligands*

The equilibria of nickel(II) bromide has been studied in *N,N*-dimethylformamide solution using conductivity and spectral methods. UV/visible spectroscopy indicates the presence of a tetrahedral $NiBr_4^{2-}$ species in solution [32].

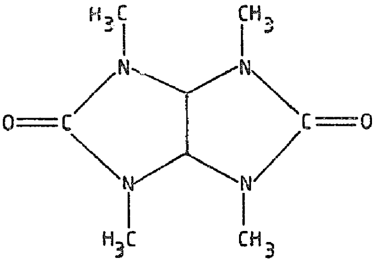
4.2. *Complexes with oxygen donor ligands*

A number of carboxylic acid ligands have been complexed with Ni(II). These include naphthenic acid [33], *o*-hydroxybenzylamine-*N,N,O*-triacetic acid [34] and 2-carbamoylphenoxyacetic acid [35]. The crystal structure of tetraaquabis(2-carbamoylphenoxyacetato)nickel(II) has been determined, and shows that the acid ligands function in a unidentate fashion, occupying *trans* axial positions {Ni-O = 2.072(2) Å}. Four water ligands complete the octahedral coordination sphere {Ni-O = 2.069(2) Å} [35].

Various nickel(II) amide complexes have been investigated. Complexes of urea, acetamide, benzamide, acetanilide and bromoacetanilide [36], furan-2-carboxamide and thiophene-2-carboxamide [37], as well as dimethylformamide [38], have been prepared and characterised in the solid state. In addition, ^1H and ^{13}C NMR studies of solvent exchange on hexakis(*N,N*-dimethylacetamide)nickel(II) and hexakis(*N,N*-diethylformamide)nickel(II) have been undertaken [39].

The coordination compounds of Ni(II) with 2,4,6,8-tetramethyl-2,4,6,8-tetraazabicyclo[3.3.0]octan-3,7-dione {L = (4)}, have been synthesized. Reaction with nickel(II) bromide yielded $[NiL_2Br_2(H_2O)_2]$ in which L functions as a unidentate O-donor ligand, whereas reaction with nickel(II) nitrate yielded $[NiL(H_2O)_4](NO_3)_2$ in which L functions as a didentate ligand [40].

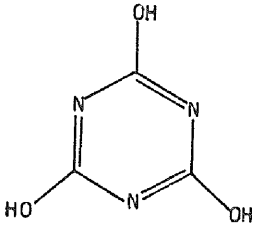
The thermal properties of nickel(II) complexes of pyridine *N*-oxide and its methyl



(4)

derivatives (2-, 3- and 4-methylpyridine *N*-oxide) have been studied. Water molecules were released prior to decomposition of the ligands [41].

The crystal structure of potassium nickel cyanurate pentahydrate, $K_2NiL_4.5H_2O$ {L=(5)}, has been reported. The ligand functions as a deprotonated unidentate O-donor [42].

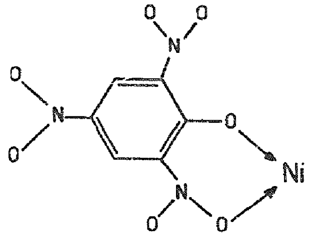


(5)

Carboxylic acid complexes of Ni(II) have attracted some interest. Nickel(II) picrate, when reacted with trithianonane (L), gave the complex, [NiL(picrate)(H_2O)](picrate). The crystal structure of this complex reveals that picrate, generally considered a non-coordinating anion, coordinates to the nickel ion via two oxygen donor atoms (**6**) [43].

Other carboxylic acid-nickel(II) complexes that have been isolated in the solid state include those of *p*-cyanobenzoic acid [44] and diphenic acid [45]. In addition, kinetic and equilibrium studies of the complex formation of Ni(II) with malic acid, tartaric acid [46], malonic acid and tartronic acid [47] have been undertaken in aqueous solution. Similarly, the stability constants of mono- and polynuclear tartrato-complexes of nickel(II) have been determined over a wide pH range [48].

1,2-Dihydroxybenzene and its variously-substituted analogues have been complexed with nickel(II). Nickel complex formation with 1,2-dihydroxy-3-nitrobenzene [49], 1,2-dihydroxy-4-nitrobenzene [50] and quercetin-5′-sulphonic acid [51] has been investigated in aqueous solution, while the mixed ligand complexes [NiLQ]



(6)

(L = ethylenediamine, propylenediamine; H_2Q = 1,2-dihydroxybenzene, 2,3-dihydroxynaphthalene) have been utilised in the template preparation of the Schiff bases *N,N'*-ethylbis(2-hydroxy-1-benzylmethyleneimine) and *N,N'*-propylbis(2-hydroxy-1-naphthylmethyleneimine) [52].

1-Hydroxyxanthone (HL) reacted with Ni(II) in aqueous solution, yielding the complex $NiL_2.2H_2O$ [53]. Structurally similar ligands that have been complexed with Ni(II) in aqueous solution include substituted 3-hydroxy-4*H*-pyran-4-ones [54] and picolinic acid *N*-oxide [55].

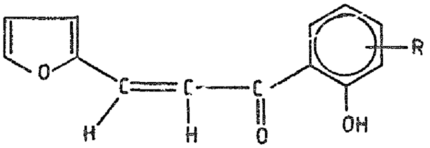
Cyclic voltammetry has been used to study the electrochemical behaviour of some mixed-ligand Ni(II) complexes of 2,4-pentanedione (acac) and 1-phenyl-1,3,5-hexanetrione (H_2BAA). Complexes studied include $Ni(acac)_2(H_2O)_2$, $Ni(acac)_2en$ and $Ni(HBAA)_2en$ [56].

Triketones have the ability to form both mononuclear and dinuclear complexes with Ni(II). The kinetics and mechanisms of the reaction of nickel(II) with 1-phenylhexane-1,3,5-triketone have been investigated in methanol/water (70/30). Rate constants have been determined for the formation of both the 1:1 and 2:2 complexes. Conversion of the 1:1 complex into the 2:2 complex was found to take place *via* a two step mechanism [57]. Similarly, the electrochemical behaviour of both the mononuclear and dinuclear nickel(II) complexes of 1-phenyl-1,3,5-hexanetrione and 1,5-diphenyl-1,3,5-hexanetrione has been investigated [56].

2-Carboxyphenoxyacetic acid (H_2L) reacted with nickel(II) acetate in water to yield the complex, $[NiL(H_2O)_3]$. X-ray diffraction data indicate octahedral stereochemistry for the complex, with the ligand L occupying three coordination positions about the square plane, with three meridional water molecules completing the hexacoordination sphere [58].

The thermal, spectroscopic and magnetic properties of the nickel(II) complexes of a number of variously-substituted chalcones have been reported. The ligands HL (7) function as uninegative, tridentate O_3-donor ligands in the octahedral complexes NiL_2 [59].

The vibrational spectrum of the nickel oxalate-hydrazine complex, $NiC_2O_4.N_2H_4$, has been studied. The oxalate ligand functions in a tetradentate manner in the polymeric complex [60].



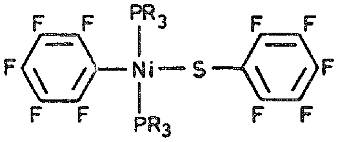
R = H, CH_3

(7)

4.3. Complexes with sulfur and selenium donor ligands

A novel synthesis for the preparation of discrete thiolato complexes of nickel has been reported. Essentially, careful choice of solvent and the use of excess thiolate prevent the precipitation of insoluble polymers. In addition, the structure of tetraethylammonium tetrakis(*p*-chlorobenzenethiolato)nickelate(II) has been determined. The S atoms are arranged in a distorted tetrahedral configuration around the nickel ion, with the average Ni-S distance being 2.281 Å [61].

The oxidative addition of aryl sulphides to low valent nickel complexes has been employed in the synthesis of two series of complexes that involve C-S bond cleavage. Exposure of diaryl sulphides to *tris*(tributyl)phosphinonickel(0) facilitates oxidative addition, with Ni inserting into the C-S bond (**8**) [62]. Similarly, exchange between the Ar and Ar′ groups in *trans*-$Ni(Ar)(SAr')(PEt_3)_2$, synthesized from $Ni(cod)_2$, to give a mixture of $Ni(SAr)(Ar')(PEt_3)_2$ and $Ni(Ar)(SAr')(PEt_3)_2$ occurs *via* reversible reductive elimination and oxidative addition of diaryl sulphides involving C-S bond cleavage and formation at the nickel centre [63].



R = Bu^n

(8)

Variously-substituted thiourea ligands have been complexed with nickel(II). These include arylsulphonated thioureas [64] and phenylthiourea [65]. The complexes NiL_2X_2 (L = phenyl-thiourea; X = CN, SCN) were found to be high spin tetrahedral.

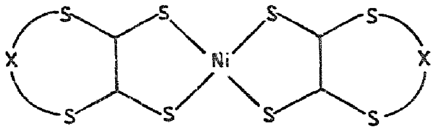
Dithiocarbamate ligands and their Ni(II) complexes are listed in Table 1. The complexes are mostly square planar with the ligands functioning in a didentate fashion. Of interest are the number of mixed ligand complexes that have been reported [69–71].

A range of new multi-sulfur 1,2-dithiolene complexes of nickel(II) has been

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

Ligand (HL)	Complex	Comments	Ref.
N-Acetyl-*N*-benzyldithiocarbamate	$[NiL_2]$	Square planar; X-ray crystal structure	[66]
Diethyldithiocarbamate	$[NiL_2]$	Complex hydrolysis in acidic H_2O-MeOH solutions.	[67]
N-(4-R-thiazol-2-yl)dithiocarbamate R = 4-methoxyphenyl, 4-chlorophenyl, 2,5-dimethylphenyl, 2-naphthyl.	$[NiL_2]$	Spectral and thermogravimetric analysis.	[68]
Piperidine dithiocarbamate	[NiLQ]	Mixed ligand complexes; HQ = ethylxanthate, salicylaldoxime, dimethylglyoxime.	[69]
N,*N*-Diethylthioselenocarbamate	$NR_4[NiLQ]$	R = *n*-butyl, H_2Q = 1,2-dicyanoethene-1,2-dithiol; X-ray crystal structure.	[70]
N,*N*-Diethylamino-dithiocarbamate	[NiLQ]	Mixed ligand complexes with Q being various Schiff bases derived from L.	[71]

prepared, in which the 1,2-dithiolene moiety has been extended by the incorporation of heterorings (**9**). X-ray diffraction, IR spectroscopy and cyclic voltammetry have been used to study these complexes. The crystal structure of n-$Bu_4N[Ni(C_4H_4S_5)_2]$ reveals a square planar configuration for Ni, with the Ni-S bond lengths varying from 2.139 to 2.143 Å [72].



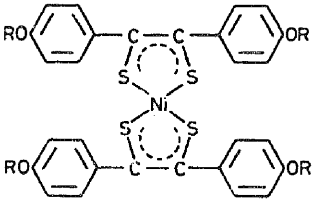
X
$-CH_2CH_2-$
$-CH_2CH_2CH_2-$
$-CH_2SCH_2-$
(**9**)

The synthesis, structural characterisation and electrical conductivity properties of the donor-acceptor complex, $TTF[Ni(dmit)_2]_2$ (TTF = tetrathiafulvalene; H_2dmit = 4,5-dimercapto-1,3-dithiol-2-thione), have been reported. The complex is essentially square planar with Ni-S bond lengths varying from 2.161(6) to 2.172(8) Å. A novel feature of the complex is its stacking arrangement which gives it its unique "3-dimensional" electrical conductivity properties [73].

Similarly, the crystal and molecular structure of the related complex, $TTF_2[NiL_2]$ (H_2L = maleonitrile-1,2-dithiol), have been determined. The Ni atom has an approximate square planar configuration, with Ni-S bond lengths of 2.175(1) and 2.179(1) Å. The anions and cations form a mixed stack along the diagonal of the *ab* plane, exhibiting the possibility of unusual electrical properties [74]. In addition, oxidative quenching has been observed in the transient spectra of $[NiL_2]^{2-}$. These results confirm the existence of excited states with lifetimes in the projected range (20-200 ps) [75].

A series of variously-substituted tetrakis((dialkylamino)phenyl)nickel dithiolene complexes have been prepared and characterised. The complexes, NiL_2 (HL = RC(S)C(SH)R'; R = R' = julolidinyl, *p*-$Et_2NC_6H_4$), exhibit the lowest electronic transition energy ever observed for a dithiolene complex [76].

Two new disc-like bis dithiolene nickel complexes, bis[1,2-di(*p*-n-nonyloxyphenyl)ethane-1,2-dithione]nickel (**10a**) and bis[1,2-di(*p*-n-undecyloxyphenyl)-ethane-1,2-dithione]nickel (**10b**), have been prepared by a novel synthetic route. The complexes exhibit discotic mesomorphism and are reportedly the first nickel complexes which are discotic liquid crystals [77].



a: R = C_9H_{19}
b: R = $C_{11}H_{23}$
(**10**)

The crystal structure of bis(*O*-ethylxanthato)nickel(II) has been redetermined. The nickel atom has a square planar coordination environment, with an average Ni-S bond length of 2.211(2) Å. In addition, there are two longer nickel sulphur interactions of 3.448(2) Å which lie close to the normal of the NiS_4 plane [78].

EHMO-SCCC calculations have been used to investigate the electronic structure and related properties of five Ni(II) complexes of chelating aromatic dithiocarboxylato ligands. The role of 3d sulfur AO's was revealed to be unimportant in determining the mode of bonding in these square planar complexes and overlap populations, two-centre energy terms, and computed atomic charges provided adequate information on the mechanism of the π-back-bonding effect [79].

O,O-Di(alkyl)aryl dithiophosphate complexes of the type $Ni[S(S)P(OC_6H_3R\text{-}2\text{-}R'\text{-}4)_2]_2$ (R = R' = H; R = H, R' = Me, *tert*-Bu; R = Me, R' = α-methylcyclohexyl) have been synthesised and characterised using UV-visible and IR spectra, and magnetic moment measurements. The complexes are diamagnetic and square planar in configuration [80]. Furthermore, amine adducts of nickel(II) diphenyldithiophosphinate, with substituted ethylenediamines, have been prepared and characterised. An interesting pentacoordinate dimeric structure was proposed for $2Ni(S_2PPh_2)_2TMEDA$ (TMEDA = *N,N,N′,N′*-tetramethylenediamine) [81].

The electronic spectra of $Ni(LH_2)_2X_2$ (LH_2 = planar dithiooxamide; X = Cl, Br, I) have been recorded in KX matrices. Metal ion and ligand substitution have been used to assign electronic transitions [82].

1-Thiocarbamoylthiocarbohydrazide (L), when reacted with NiX_2 (X = Cl, NO_3), yielded the complexes, $[NiL_3]X_2$. These complexes were characterised by using magnetic moment and susceptibility data, ESR and electronic spectra, and X-ray diffractometry [83].

4.4. *Complexes with nitrogen donor ligands*

The complexation of Ni(II) with simple amines continues to attract attention. This is exemplified by a review containing 62 references which describes the complexes of various aliphatic and aromatic mono- and diamines with Ni(II), Cu(II) and Co(II). Complex structures, as well as preparative methods were discussed [84].

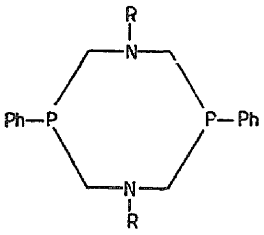
The phase diagram of $[Ni(NH_3)_6](NO)_6$ has been determined and compared with those obtained for Ni hexammines with other complex anions (ClO_4^-, BF_4^-). The effect of $[Ni(NH_3)_6](NO_3)_2$ on the phase transition was also reported [85].

Mixed ligand complexes containing aliphatic amines have been prepared using a heterogenous synthetic method. $[NiL_2(acac)_2]$ (L = NH_3, $EtNH_2$, Et_2NH, furfuralamine; Hacac = acetylacetone) have been synthesised from L and solid $[Ni(acac)_2(H_2O)_2]$ or solid $[Ni(acac)_2]_3$, at 50°C in a vacuum system containing solid KOH [86].

The complexation of *p*-methylaniline (L) with nickel(II) sulfate has been investigated. The resultant complex, $NiSO_4L_2$, reacted with acetyl halide, with acetylation of the amine group taking place. Acetylation does not affect coordination and the sulfato group is present as a bridging group [87]. In addition, 3,4-dimethylaniline has been utilised in the solvent extraction of Ni^{2+} ions from aqueous solutions containing benzoic acid. The extracted complexes have the composition $NiR_2.2B$ (HR = benzoic acid; B = 3,4-dimethylaniline) [88,89].

A number of more complex amines have been reacted with Ni(II). These include morpholine, which yielded complexes of the type $[NiCl_2(L)_3(H_2O)_2]$ and $[NiCl_2(L)_3]$ (L = morpholine) [90], as well as the related ligand piperazine, the complexing properties of which have been studied in aqueous solution [91]. Similarly, the complexing behaviour of variously-substituted 1,5-diaza-3,7-diphosphacyclooctanes (**11**) has been investigated spectroscopically in a number of solvents. Stability constants for the 1:2 (metal:ligand) complexes were determined in acetonitrile [92].

Pyridine and its variously-substituted analogues are still the most widely studied monodentate N-donor ligands (see Table 2). Of particular interest, are the two structural isomers of tetrakis(3-ethylpyridine)bis(isothiocyanato)nickel(II), which have been determined by single-crystal X-ray methods. Both isomers have a *trans* configuration, with the orientation of the *trans*-coordinated pyridine rings giving



R = $PhCH_2$, p-$CH_3C_6H_4$, p-BrC_6H_4, m-FC_6H_4, C_5H_5N

(11)

rise to the isomerism. The rings in isomer (I) are parallel, while for isomer (II) the rings are almost perpendicular [97].

The same authors have reported the X-ray crystal structure of the related complex bis(2,6-dimethylpiperidine)(dithiocyanato-N)nickel(II)-benzene. The Ni atom has a *trans* square planar coordination sphere, in this case due to the bulky nature of the 2,6-dimethylpiperidine ligand. Relevant data are Ni-NCS = 1.849(7) Å and Ni-N_{pip} = 1.984(7) Å [100].

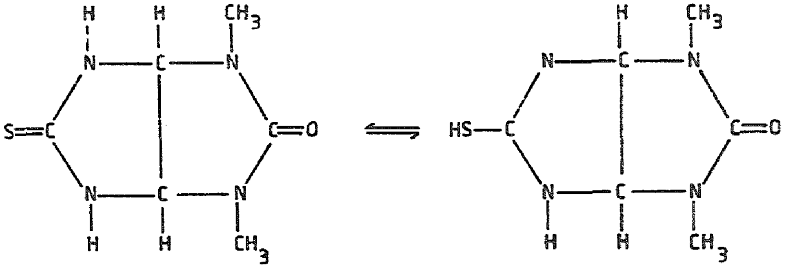
Complexes of the type NiL_2Q_2 (HL = thenoyltrifluoroacetone; Q = benzylamine,

Table 2
Pyridine and substituted pyridine complexes of Ni(II)

Ligand (L)	Complex	Comments	Ref.
Pyridine	$NiL_6(Mo_4O_{13})$	IR spectral study	[93]
Pyridine; 3,5-dimethylpyridine	$Ni(OS)_2 \cdot L$	OS = 2-thiopyridine *N*-oxide; Square-pyramidal structure	[94]
3-, 4-Methylpyridine; 3,4-dimethylpyridine	$Ni(OS)_2 \cdot 2L$	OS = 2-thiopyridine *N*-oxide; Elongated octahedral structure	[94]
Pyridine, 2-, 3-, 4-methylpyridine; 2,4-, 2,6-dimethylpyridine	$NiQ_2 \cdot L$	Q = 2-methyl-5-nitrophenylthiocarbazone; Pentacoordinated adduct	[95]
4-Methylpyridine	$[NiL_4(NCS)_2]$ $[NiL_4(NCS)_2] \cdot L$	IR spectroscopic study of clathrate formation	[96]
3-Ethylpyridine	$[NiL_4(NCS)_2]$	X-ray crystal structure of two *trans* isomers; Pyridine ring orientation gives rise to isomerism	[97]
4-Vinylpyridine	$[NiL_4(NCS)_2]$	X-ray crystal structures of the α-phase Werner complex and its β-phase clathrates with *o*-, *m*- and *p*-xylene	[98]
2-Aminopyridine	NiL_4^{2+}	Spectrophotometric study in EtOH and DMF	[99]

quinoline, benzoxazole, 2-methylbenzoxazole, benzothiazole, 2-methylbenzothiazole) have been prepared from nickel(II) acetate. The complexes are octahedral, with the benzothiazole complex exhibiting antibacterial activity [101].

The reaction of 2,4-dimethyl-2,4,6,8-tetra-azo-bicyclo(3,3,0)octan-3-one-7-thione (HL) (**12**) with nickel(II) has been studied in aqueous solution. The stability constant of the complex NiL^+ has been determined pH-potentiometrically [102].



(12)

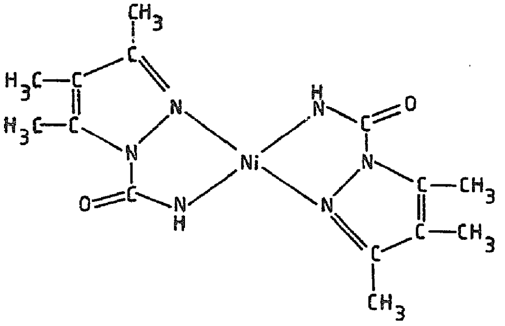
NiL_2Cl_2 (L = phthivazid) has been synthesised and characterised using IR and electronic spectra, and X-ray diffraction. L functions in a monodentate fashion and is coordinated to the nickel ion through the heterocyclic N atom [103].

Benzimidazole has been used to extract Ni from aqueous solution *via* solvent extraction, with benzyl alcohol as the solvent. Use of 2-methylbenzimidazole as extractant was not as effective, probably due to steric effects [104]. The ability of 1,4-dimethylimidazole to extract nickel(II) from aqueous solutions has also been investigated [105], while the stability constants for the formation of nickel(II) complexes with *N*-ethylimidazole have been determined in aqueous solution [106].

Pyrazole and its substituted analogues, when reacted with nickel(II) cyanate, yielded compounds of different stoichiometry, depending on the pyrazole ligand employed. Complexes of the type $Ni(NCO)_2L_4$ (L = pyrazole, 3,5-dimethylpyrazole, 3,4,5-trimethylpyrazole) and NiL_2 (HL = 3,4,5-trimethylcarbamoylpyrazole) have been prepared and characterised. The complexes $Ni(NCO)_2L_4$ (L = 3,5-dimethylpyrazole, 3,4,5-trimethylpyrazole) are polymeric, with two L ligands in the outer sphere and with N-bridging NCO groups [107]. The complex NiL_2 (HL = 3,4,5-trimethylcarbamoylpyrazole) contains L^- anions as chelate ligands, formed by C(NCO)N(imine) nucleophilic addition in the Ni(II) coordination sphere (**13**) [108].

Table 3 lists ethylenediamine and related diamine complexes of Ni(II). Effort has been maintained in the study of *tris*-ethylenediamine complexes [109–113], with emphasis being placed on the conformation of the ethylenediamine ligand. A particularly interesting study reports the isolation of two isomeric conformers of $[NiL_2(NCS)_2]$ (L = *N*,*N*-dimethyl-1,3-diaminopropane), postulated as having *trans* chair-chair (**14**) and *cis* chair-chair (**15**) conformations [120].

Ni(II) complexes of 2,2′-bipyridine and 1,10-phenanthroline continue to attract



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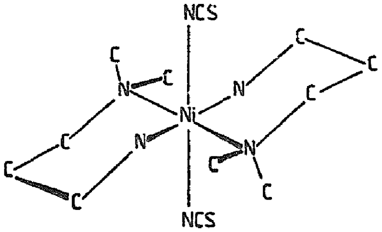
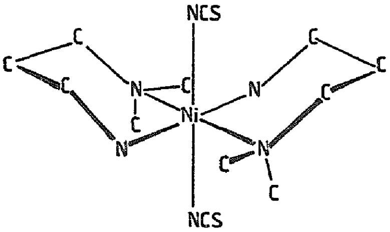




(14) (15)

interest [113,119]. In addition, the synthesis, aqueous absorption and reflectance spectra, cyclic voltammetry, and ligand field photochemistry of NiL_2Cl_2 (L=2,2′-bipyrimidine) have been reported. Ligand field electronic spectral assignments have been made using the analagous 2,2′-bipyridine complex [121]. Similarly, the stability constants of Ni(II) with 1,6-benzo[h]naphthyridine, an isomeric form of 1,10-phenanthroline, have been determined potentiometrically. The stability constants are lower than those for the corresponding phenanthroline complexes [122].

2,2′-Dipyridylmethane (L), when reacted with nickel(II), forms complexes of varying stereochemistry, depending on the nickel salt used. Reaction with nickel dichloride yielded the tetragonal complex, $[NiL_2Cl_2]$, which has a magnetic moment of 3.11 B.M., whereas reaction with nickel diperchlorate yielded the square planar complex, $[NiL_2](ClO_4)_2$ [123].

3,6-Di(2-pyridyl)-1,2,4,6-*sym*-tetrazine (L) has the potential to coordinate via four nitrogen donor atoms. Reaction with nickel(II) chloride hexahydrate in ethanol afforded the complex, $NiL_2Cl_2.H_2O$, in which the ligand functions in a didentate fashion [124].

The crystal structure of square planar bis(1,5-diazacyclooctane)nickel(II) perchlorate, as well as its low temperature magnetic susceptibility, have been reported.

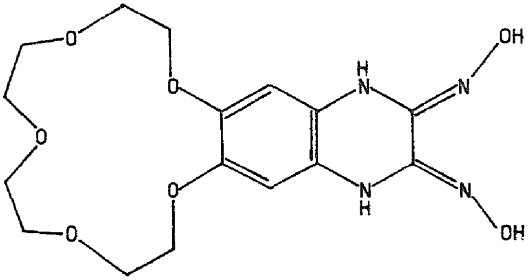
Table 3
Ethylenediamine and related-diamine complexes of Ni(II)

Ligand (L)	Complex	Comments	Ref.
Ethylenediamine	NiL_3R_2	R = sulphadimethoxinate; Crystal structure, NiL_3^{2+} has λ,λ,λ conformation	[109]
	$[NiL_3]X_2$	$X = Cl^-$, NO_3^-, SO_4^{2-}; Study of the effect of anion on conformational structure of NiL_3^{2+}	[110]
	$[NiL_3]SO_4$	Conformational study using γ radiation	[111]
	$Ni_2L_3A \cdot 4H_2O$	A = edta; Crystal structure	[112]
Ethylenediamine; 1,3-diaminopropane	$[NiL_3]F_2$	Bridging structure proposed for $[L_2Ni(\mu\text{-}F_2)NiL_2]F_2$	[113]
	$[L_2Ni(\mu\text{-}F_2)NiL_2]F_2$		
Ethylenediamine; *N*-methyl-, *N*,*N*-dimethyl-, *N*,*N*′-dimethyl-, *N*,*N*,*N*′-trimethylethylenediamine	$[NiL_2(H_2O)_2]X_2 \cdot nH_2O$	$X = Cl^-$, Br^-, I^-, NO_3^-, ClO_4^-; n = 0, 2, 3;	[114]
	$[NiL_2X_2]$	Thermal stability investigation	
N,*N*-Dimethylethylenediamine	$[NiL_2]X_2$	Polarographic study in various media	[115]
N,*N*′-Dimethylethylenediamine	$[NiL_2X_2]$	$X = Cl^-$, $CF_3CO_2^-$, $CCl_3CO_2^-$, $CBr_3CO_2^-$;	[116]
	$[NiL_2C_2O_4].H_2O$	$X = Br^-$, 0.5 SO_4^{2-}, 0.5 SeO_4^{2-};	
	$[NiL_2X_2] \cdot 2H_2O$	Synthesis via solid state pyrolysis.	
1-Phenyl-1,2-ethanediamine	$[NiL_2](ClO_4)_2$	Thermal behaviour investigated in solid phase;	[117]
	$[NiL_2(H_2O)_2]X_2$	$X = Cl^-$, Br^-, NO_3^-.	
1-Phenyl-1,2-ethanediamine, 2-methyl-1,2-propanediamine, *m*-, *dl*-butanediamine, *dl*-1,2-diphenyl-1,2-ethanediamine	*trans*-$[NiL_2X_2]$	$X = Cl^-$, Br^-, NO_3^-;	[118]
	cis-$[NiCl_2L_2]$	L = *dl*-1,2-diphenyl-1,2-ethanediamine;	
	cis-$[Ni(NO_3)_2L_2]$	L = *dl*-1,2-diphenyl-1,2-ethanediamine.	
1,2-, 1,3-Diaminopropane	NiLL′	HL′ = Schiff base; Octahedral mixed ligand complexes.	[119]
N,*N*-Dimethyl-1,3-propanediamine	*trans*-$[NiL_2(NCS)_2]$ $[NiL(NCS)_2]$	Two isomeric forms isolated; Octahedral polymeric structure.	[120]

Axial sites in the structure are open for ligation, but the Ni-N bonds are sterically protected by coplanar N-H bonds, allowing maximum ligand field stabilization for the square planar geometry around the nickel atom [125].

Nickel(II) salts were shown to react rapidly with the cyclic diamine 5,5,7-trimethyl-1,4-diazepane (L), yielding *bis* complexes of the type $[NiL_2]X_2$ ($X = ClO_4$, CNS, $ZnBr_4$). Attempts to prepare octahedrally coordinated derivatives of $[NiL_2]^{2+}$ were unsuccessful due to severe steric crowding of the axial coordination sites [126].

The synthesis of the dioxime ligand, 2,3-bis(hydroxyimino)-1,2,3,4,7,8,10,11,13,14,16,17-dodecahydro[1,4,7,10,13]pentaoxacyclopentadecino[2,3-*g*]quinoxaline {$H_2L = (\mathbf{16})$}, and its complexing properties with Ni(II), have been reported. The resultant complex, $(LH)_2Ni.2NaClO_4.2H_2O$, is reddish in colour and diamagnetic, indicating a square planar configuration for the nickel ion [127].



(**16**)

Nickel(II) complexes of some sterically hindered 1,2-hydroxylamine oxime ligands have been prepared and characterised. Complexes isolated include [Ni(HL)L]X ($HL = HON{:}C(CH_3)C(CH_3)_2NHOH$; X = Cl, ClO_4) and $[Ni(HL')_2Cl_2]$ ($HL' = HON{:}C(C_6H_5)C(CH_3)_3NHOH$) [128]. The thermal properties of these complexes have also been investigated using DTA and TGA [129].

Isonitrosopropiophenone (HL), when reacted with Ni(II) sulphate in the presence of NH_3, yielded the complex NiL'_2 ($HL' = C_6H_5C({:}NH)C({:}NO)CH_3$). Reaction of HL with Ni(II) yielded the octahedral complex NiL_2. Complexes were characterised on the basis of magnetic and spectral studies [130].

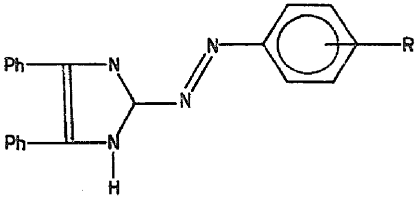
The formation of N,N-didentate 1:2 complexes of nickel(II) with various N,N,O-terdentate 2-(2-pyridylazo)phenolic ligands has been studied spectrophotometrically in ethyl acetate. The effects of Brønsted base, nickel(II) salt, solvent basicity, and steric requirements around the nitrogen donor atoms of the ligand were investigated. Complexation appears to be most affected by the counter ions, X, associated with the nickel salt NiX_2 [131].

Diacetylhydrazone ($L = H_2NN{:}CMeCMe{:}NNH_2$) is a didentate ligand with two imine N-atom donors. The complexes $[NiL_3](NO_3)_2$ and $[NiL_3](NO_3)_2.H_2O$ have been prepared and characterised in two independent studies [132,133]. Both complexes were assigned mononuclear octahedral configurations for the nickel(II) ion.

Continuing with hydrazone ligands, the complex, $[Ni(HL)_2(H_2O)_2](NO_3)_2$ (HL = pyrrole-2-carboxaldehyde N-acetylhydrazone), has been synthesised. X-ray crystallography and IR spectra indicate that coordination about Ni is centrosymmetric octahedral and involves two didentate equatorial HL molecules and two *trans* apical water molecules [134].

3-Picolylamine (L) produces a number of stereochemical configurations when complexed with different nickel(II) salts. NiX_2L_2 (X = NCS, Cl, Br), $Ni_3Cl_6L_4$, $NiCl_2L_4$ and $NiBr_2L$ have been prepared and characterised. TGA and DTA have been used to study the decomposition of some of these complexes [135].

Substituted imidazole ligands have attracted considerable interest. The nickel(II) complexes of variously-substituted arylazo-4,5-diphenylimidazole ligands {L = (17)} have been isolated and characterised. The molecular formulae of the 1:1 and 1:2 complexes were suggested to be $[NiLX_2(H_2O)_2]$ and $[NiL_2X_2]$ or $[NiL_2X_2].2H_2O$ respectively. It was suggested that the complexes have a distorted octahedral geometry [136].



R = 4-CH_3, 4-OCH_3, 2-OCH_3, 4-NO_2, 2-NO_2

(17)

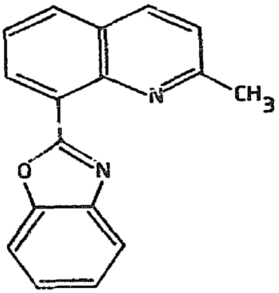
2-1-(Benzenesulfonamido)-3-(methylthio)propylbenzimidazole (HL) has the possibility of coordinating via a number of coordination sites. When complexed with Ni(II), it yielded the square planar diamagnetic complex, NiL_2, in which it functions as a N,N-didentate ligand [137].

The nickel(II) chloride and bromide complexes of 2-(2′-methyl-8′-quinolyl)benzoxazole {L = (**18**)}, 2-(2′-methyl-8′-quinolyl)benzimidazole {L′ = (**19**)} and 2-(4′-methyl-8′-quinolyl)benzimidazole {L″ = (**20**)} have been synthesised and characterised. The ligands function as didentate N-donors yielding complexes whose coordination geometry depends on the metal ion and steric hindrance. Complexes obtained include *pseudo*-tetrahedral or penta-coordinate $NiLX_2.nH_2O$ (or EtOH) and $NiL'X_2.nH_2O$ (or EtOH) (n = 0-1.5), and tetragonal $NiL''_2X_2.nH_2O$ (n = 3 or 4) [138].

2-(4′-Thiazolyl)benzimidazole (L) reacted with $NiCl_2$ yielding the hexa-coordinate complex NiL_2Cl_2. X-ray photoelectron, infrared and electronic absorption spectra indicate that the ligand functions in a didentate manner and is essentially planar [139].

Complex formation between 4-methoxy-2-(5-methoxy-3-methylpyrazl-l-yl)-6-methylpyrimidine (L) and Ni(II) has been investigated in aqueous solution. Visible-UV spectra indicate the presence of NiL_2 [140].

The X-ray crystal structure of the triazenido complex, *cis*-bis(pyridine)bis(1,3-diphenyltriazenido)nickel(II), has been determined. The complex has a distorted octahedral coordination around the metal ion and has a



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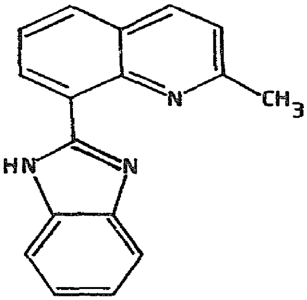

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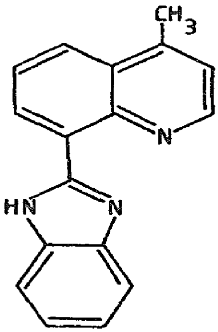
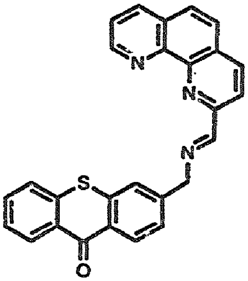


(20)

crystallographic 2-fold symmetry. The triazenido ligand functions as a didentate ligand, forming an unusual strained four membered chelate ring [141].

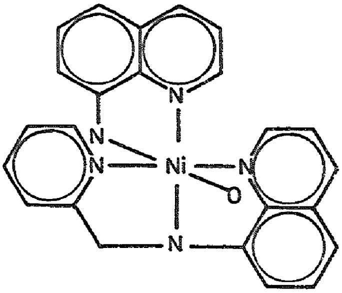
1,4,7,11-Tetraazaundecane (L) has been prepared from 1,4,7-triazaheptane by monocyanoethylation followed by reduction with Na. Reaction with $Ni(ClO_4)_2$ yielded the complex, $[NiL_2](ClO_4)_2.H_2O$ [142].

The ligand (**21**), acting as a template in the presence of Ni^{2+}, can catalyse the chlorination of 3-α-cholestanyl nicotinate. The active site for reaction involves the Ni(II) ion coordinated in a *cis* fashion to the nitrogen donor atoms of the ligand. Greater turnover numbers were achieved when only one Ni(II) ion was coordinated, as this facilitates close proximity of the Ni(II) ion and sulfur atom [143].



(21)

As part of an investigation of the properties of 8-aminoquinoline derivatives, the crystal and molecular structure of the complex *N*-(8-quinolyl)pyridine-2-carbaldimine, 8-aminoquinoline monohydrate, nickel(II)-di-perchlorate, have been determined. The nickel(II) ion is surrounded by five N atoms of the didentate and tridentate ligands and one O atom of the water molecule, forming an irregular octahedron (**22**) [144].

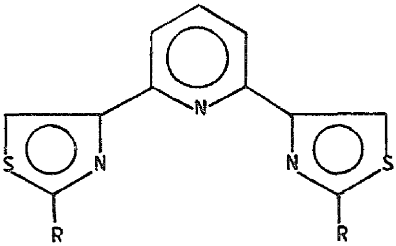


(22)

The crystal structure of diaquachloro(2,2′:6′,2″-terpyridyl)nickel(II) chloride monohydrate has been determined. The Ni atom is hexacoordinated with the

2,2′:6′,2″-terpyridine ligand being essentially planar. Two water molecules, occupying *cis* positions, and a chlorine atom complete the coordination sphere. Inter- and intramolecular hydrogen bondings are present in the compound [145].

Structurally related to 2,2′:6′,2″-terpyridine are the ligands L (**23a,b,c**). Bis ligand complexes, $[NiL_2]X_2$ (X = ClO_4, BF_4), were isolated when L = (**23a,b**), but attempts to prepare the analogous complex with L = (**23c**) failed, probably due to the bulky nature of the ligand. The ligands function in a tridentate fashion and are essentially planar, similar to analagous 2,2′:6′,2″-terpyridine complexes [146].



a: R = H; b: R = Me; c: R = Ph

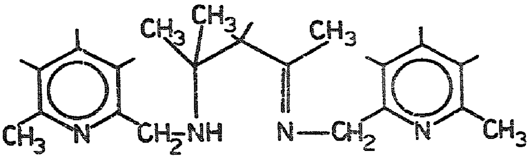
(**23**)

A number of tridentate nitrogen donor Schiff bases have been prepared and complexed with Ni(II). These include complexes of 2-hydroxyimino-3-(2′-iminopyridyl)butane [147] and Schiff bases derived from 4-formyl-1,3-diphenyl-2-pyrazolin-5-one and 4-formyl-l-phenyl-3-methyl-2-pyrazolin-5-one with aniline, *m*-, *p*-toluidine, *m*-, *p*-chloroaniline and ethanolamine [148].

The tetradentate ligand, 3,3′-(1,4-butanediyldiamino)bis(3-methyl-2-butanone)dioxime (H_2L), reacted with nickel(II) to form the complex $[Ni(HL)]I.H_2O$. The X-ray crystal structure reveals a slightly distorted square planar geometry for Ni(II) and an intramolecular O-O contact of 2.417(7) Å [149].

Bis(6-methyl-2-pyridylmethylamine)nickel(II) complexes, when reacted with acetone, yielded nickel(II) complexes of the tetradentate ligand 2,6-diaza-1,7-bis-(6′-methyl-2′-pyridyl)-3,5,5-trimethyl-hept-2-ene {L = (**24**)}. The X-Ray crystal structure of $[Ni(L)NO_3]NO_3$ reveals a *cis-β* configuration for the tetradentate ligand about the metal. The coordination sphere is completed by a nitrate ligand functioning in a didentate fashion. Ni-N bond lengths vary from 1.991(5) to 2.105(4) Å, while the Ni-O bond lengths are 2.185(4) and 2.201(4) Å respectively [150].

A variety of nickel(II) salts have been reacted with *N*,*N*′-bis-8-quinolylethylenediamine (L). Complexes that have been prepared include $NiLX_2$ (X = Cl, Br, I, NO_3, SCN), $Ni(H_2O)(L)X_2$ (X = ClO_4, BPh_4) and $Ni(L)(NO_2)X$ (X = ClO_4, BPh_4, PF_6, I, BF_4). All of the complexes are mononuclear with octahedral coordination [151].



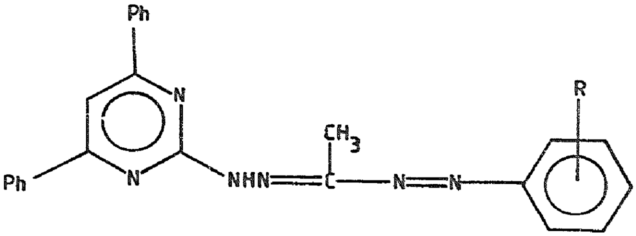
(24)

A template synthetic approach has been used in the preparation of some coordination complexes of Ni(II) with pentan-2,4-dione bis(*S*-alkyl- and *S*-benzylthiosemicarbazones) (H_2L) and 3-oxopentan-2,4-dione bis(*S*-alkyl- and *S*-benzylthiosemicarbazones) (H_2L'). The complexes [Ni(HL)]X.nH_2O (X=I, NO_3; n=0-3), [NiL] and [NiL'] are diamagnetic and have a square planar structure [152].

The equilibria of adduct formation between several nickel(II) tetraamine complexes and acetonitrile have been determined in acetonitrile solution using the Evans NMR magnetic susceptibility method. The stability order for adduct formation of the paramagnetic complex in terms of ligand was found to be 2,2,2-tetraamine = 3,3,3-tetraamine > 3,2,3-tetraamine > 2,3,2-tetraamine > cyclam [153].

N,N,N',N'-Tetrakis(3-aminopropyl)ethylenediamine (L) has been prepared and potentiometric and spectrophotometric studies of its equilibria with Ni(II) have been undertaken. In the 1:1 complex L functions as a pentadentate ligand. In addition, the presence of a minor, square planar, low spin species was detected [154].

A number of 1-aryl-3-methyl-5-(4,6-diphenyl-2-pyrimidinyl)formazans (**25**) have been prepared and complexed with Ni(II) [155].



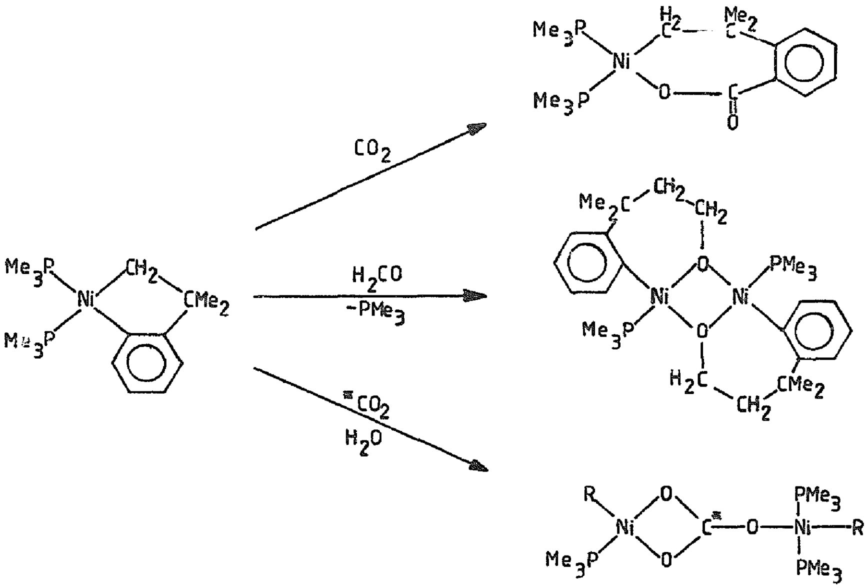
R = H; *o*-, *p*-MeO; *p*-CO_2H; *o*-OH; *p*-Cl; *p*-Br; *p*-CO_2Me

(**25**)

4.5. Complexes with phosphorus and arsenic donor ligands

Trialkyl- and triarylphosphine ligands have been used to great effect in the stabilisation of nickel complexes containing nickel-carbon σ-bonds. The synthesis of $(Me_3P)_2Ni(CH_2CMe_2\text{-}o\text{-}C_6H_4)$ and its reactivity towards CO_2, CO and CH_2O have been reported. The reactions investigated are shown below (26) [156].

The metallathietane-3,3-dioxide complexes, $[Ni\{CHPhS(O)_2CHPh\}L_2]$ ($L = PMe_3$, $L_2 = Ph_2PCH_2CH_2PPh_2$), have been prepared. The complexes have been synthesized in high yield by the action of $[PhCHS(O)_2CHPh]^{2-}$ upon either *cis*- or *trans*-$[NiCl_2L_2]$ [157].

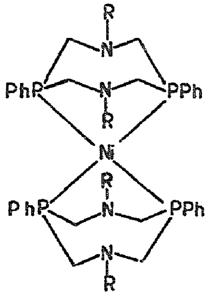


(26)

A number of 3,7-diphenyl-1,5-diaza-3,7-diphosphacyclo-octanes, with various substituents on the nitrogen atoms, have been complexed with Ni(II). Coordination occurs via the phosphorus donor atoms, with the ligand functioning in a didentate fashion (27) [158].

The X-ray crystal and molecular structure of bis[2,2′-biphenyldiyl(dimethylarsine)]diiodonickel(II) have been reported. The Ni(II) atom has a tetragonally distorted octahedral configuration with the I^- ligands occupying *trans* axial positions. The diarsine ligands and the Ni atom form unusual seven-membered chelate rings. Relevant structural data are Ni-I(average) = 2.751 Å and Ni-N(average) = 2.515 Å [159].

Some novel tetradentate tripod ligands have been synthesized and complexed with Ni(II). Tris(2-(diphenylphosphino)ethyl)phosphine, PP_3, when reacted



$R = C_6H_5, C_6H_4CH_3, C_6H_4Br, CH_2C_6H_5$

(27)

with Ni(II) salts, yielded the complexes, $[Ni(PP_3)(PR_3)]X_2$ (R = Me, Et, OCH_2CF_3; X = AsF_6BF_4). In addition, the complex, $[Ni(PP_3)(P(OMe)_3)](AsF_6)_2.MeOH$, has been further characterised by X-ray crystallography. The cation has a slightly distorted trigonal bipyramidal structure, with the three equatorial phosphorus atoms being crystallographically non-equivalent. The Ni-P bond lengths vary from 2.181(2) to 2.325(2) Å [160].

The arsenic analogues of the above complexes have also been prepared. The new tripod ligand tris(*o*-(dimethylarsino)phenyl)phosphine (Ptas), when complexed with various nickel(II) salts, yielded the complexes, $[Ni(Ptas)L]X_n$ (L = Cl, Br, I, CN, $POMe_3$, NO_3, PEt_3, PPh_3, CNS; X = AsF_6; n = 1,2). All of the complexes possess trigonal bipyramidal coordination geometry in which the tetradentate ligand occupies one apical and three equatorial positions (**28**) [160].

$X = AsF_6$

(28)

4.6. *Complexes with nitrogen - oxygen donor ligands*

Schiff base and related ligands containing aldimine and ketoimine groups are virtually synonymous with this class of ligand, with Schiff bases dominating. Table 4

Table 4
N,O-donor Schiff base ligands and their Ni(II) complexes

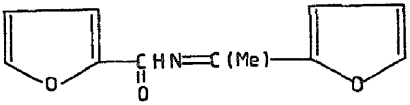
Ligand	Complex	Comments	Ref.
Sulfadimethoxinesalicylaldimine (HL)	[NiL_2]	Tetrahedral structure	[162]
1*H*-indole-3-ethylenesalicylaldimine (HL)	[NiL_2]	Square planar structure	[163]
2-(2-Aminophenyl)benzimidazole-salicylaldimine (HL)	NiL_2X_2 $NiL(NCS)_2$	X = Cl, Br, NO_3, ClO_4; *trans* Octahedral structures	[164]
N-Alkylsalicylaldimine (HL) *N*,*N'*-Dialkylaminotroponimine (HL) *N*-Alkylbenzoylacetoneimine (HL)	NiL_2	Kinetic study of ligand attack on square planar/tetrahedral configurations in solution	[165]
Salicylidenethiophene-2-carboxylic acid hydrazide (H_2L)	$NiL \cdot 3H_2O$	Dibasic ligand with O,N,O coordination	[166]
N-Salicylideneamino acid (HL); amino acid = β-alanine, various aminobutyric acids, L-glutamine and DL-asparagine.	NiL_2	Octahedral structures	[167]
Salicylidene-2-furoic acid hydrazide (H_2L)	$NiL_2 \cdot 2H_2O$	Dibasic ligand with O,N,O coordination	[168]
N-5-Methylpyrazole-3-carbohydrazidesalicylaldimine (H_2L)	$NiL \cdot 3H_2O$	Octahedral structure	[169]
N-4-Aryl-2-aminothiazole-R-salicylaldimine (HL) R = various substituents	NiL_2	Octahedral structures	[170]
4,4'-Dihexyl-*N*,*N'*-disalicylidene-ethylenediamine (H_2L)	NiL	Aggregation structure observed in solution by ^1H NMR	[171]
N,*N'*-3,4-Toluenebis(salicylaldimine) (H_2L)	NiL	Square planar monomeric structure	[172]
1,2-Di(*o*-salicylaldiminophenylthio) ethane (H_2L)	NiL	Dibasic ligand with O,N,N,O coordination	[173]
N-(1-Methyl-3-oxo-3-phenylpropylidene)-*N'*-salicylidene-ethylenediamine (H_2L)	NiL	Study of reaction of NiL with *N*-bromosuccinimide	[174]
N-(Acetylacetoneimine)-*N'*-(5-carboxysalicylidene)-ethylenediamine (H_2L)	NiL	Diamagnetic square planar structure	[175]
Ethylideneanthranilic acid (HL)	$NiL_2(HL)_2$	Octahedral; HL is O-bonded.	[176]
N-(*N*-Substituted-trimethylenediamine)-3-bromo-2-hydroxy-5-methylketoneimine (HL); ketone = acetophenone, propiophenone, benzophenone.	NiL_2	Pseudooctahedral or square planar geometry, depending on substituents	[177]
2-(*o*-Hydroxyphenylimino-methyl)-R R = pyrrole; thiophene (HL)	NiL_2	Both ligands function in a mono-negative didentate fashion	[178]

Table 4 (*continued*)

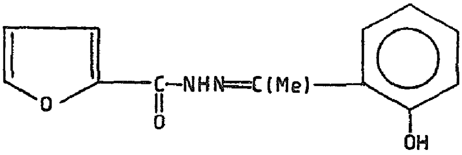
Ligand	Complex	Comments	Ref.
o-(*N*-Phenyl,2-hydroxybenzylideneimino)benzoic acid (H_2L)	$Ni(HL)_2$	Octahedral structures	[179]
N,*N'*-Bis(4-methyl-7-hydroxy-8-acetylcoumarin) ethylenediamine (H_2L)	NiL	Square planar geometry	[180]
N,*N'*-Phenylenediiminebis(3-formylsalicylic acid) (L)	[NiL(DMF)X]X	Octahedral; X=Cl, Br, I, NO_3, ClO_4, SCN	[181]
N,*N'*-Bis(8-aceto-7-hydroxy-4-methylcoumarin)- ethylenediamine (H_2L)	NiL	Square planar structure	[182]
2,3,6,7-Tetrahydro-(2-hydroxyphenyl)-7-phenyl- 1-*H*-1,4-diazepine (H_2L)	NiL	Square planar structure	[183]
N,*N'*-Bis(3-ethylaceto-acetylacetaldehyde)-phenylenediamine (H_2L)	NiL	^1H- and ^{13}C-NMR study; Comparison with analogous Pt and Co complexes	[184]
Oxalylbis(pent-3-en-2-one-4-amine) (H_2L)		Chromatographic and other properties	[185]
Pyridoxylideneimine (H_2L)	NiL	Square planar geometry for O_2N_2 coordination and octahedral geometry for O_4N_2 coordination	[186]
Pyridoxylideneglycine (H_2L)	NiL		
5'-Phosphopyridoxylideneglycine (H_2L)	Nil		
N'-(R)-N-(2-hydroxyethyl)ethylenediamine (H_2L) R=2,4-pentanedione, 1-benzoylacetone, 2-hydroxyacetophenone, 3-(ethoxymethylene)-2,4-pentanedione, salicylaldehyde.	NiL	Dimeric square planar structure with single O-H-O bridge	[187]
N'-(2,4-Pentanedione)-*N*-(R^2)-R^1-diamine (H_2L) R^2=2-hydroxy-1-naphthaldehyde, salicylaldehyde, *o*-hydroxyacetophenone; R^1= propyl, butyl, pentyl.	NiL	Asymmetrical tetradentate azomethine ligands with O,N,N,O coordination	[188]

lists a number of Schiff base ligands and their Ni(II) complexes. Two features are particularly outstanding. The first is the number of Schiff base ligands that utilise salicylaldehyde and its variously-substituted analogues as a starting material [161–175]. The second is an increase in the number of asymmetrical tetradentate Schiff base ligands that have been prepared and complexed with nickel(II) [174,175,187,188].

Turning to hydrazone ligands, 2-acetylfuran-2-furoylhydrazone {HL = (**29**)} [189] and *o*-hydroxyacetophenone-2-furoylhydrazone {H_2L' = (**30**)} [190] have been complexed with Ni(II). HL reacted with Ni(II) yielding $Ni(HL)_2Cl_2$ or $NiL_2(H_2O)_2$, depending on the pH of the medium. Both complexes are octahedral. H_2L' coordinates to Ni(II) in a variety of ways and complexes of the type $Ni(H_2L)_2Cl_2$, $Ni(HL)_2$ and $NiL(H_2O)_2$ have been isolated and characterised. $Ni(H_2L)_2Cl_2$ has been assigned a monomeric octahedral structure, while $Ni(HL)_2$ and $NiL(H_2O)_2$ have been assigned dimeric and polymeric octahedral structures respectively.



(**29**)



(**30**)

The crystal structure of the nickel(II) complex with pyridine and the isopropanoylhydrazone of benzoylacetone (H_2L) has been determined. The complex, [NiL(py)], has a square planar configuration about Ni(II), with the pyridine N atom *trans* to the N(2) atom of the hydrazone [191].

Acetone-5-methylpyrazole-3-carbohydrazone (L) has been complexed with a variety of Ni(II) salts. Complexes of the type NiL_2X_2 (X = Cl, Br, NO_3, BF_4, ClO_4, SCN, $0.5SO_4$) were isolated. Magnetic and spectral studies indicate that the complexes are octahedral, with L functioning in a neutral tridentate fashion, and that X is coordinated in most cases [192].

The chelating behaviour of 3-(*o*-, *m*-, *p*-sulfo- and 4-methyl-2-sulfophenylhydrazo)-2,4-pentanediones (L) with Ni(II) has been studied in solution. 1:1 and 1:2 (Ni:L) complexes were observed, with coordination occurring *via* one of the O atoms of the acetylacetone moiety and the azomethine N atom of the hydrazo group [193].

Complex formation of Ni(II) with benzoylhydrazine (L) has been investigated in aqueous dimethyl sulphoxide solution. Complex formation takes place in stages, with the formation of protonated $[Ni(HL)]^{3+}$ and deprotonated $[NiL]^{2+}$. DMSO was found to influence the stability of the complexes [194]. The related ligands, *m*- and *p*-bromobezoylhydrazine (H_2L), have been complexed with a variety of nickel salts in the presence of ethylenediamine (en). Complexes of the type $NiL(en)X_2.nH_2O$ ($X = NO_3$, SCN, $0.5SO_4$) were prepared. L^{2-} functions as a didentate ligand in the octahedral complexes, in which H_2O is coordinated [195].

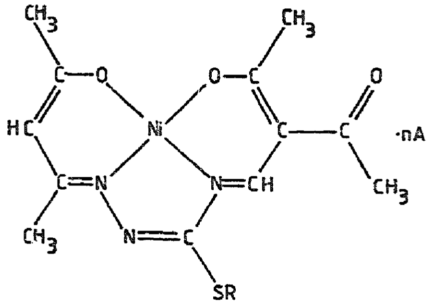
Ethoxycarbonylhydrazine (L), when reacted with $Ni(ClO_4)_2$, yielded the complex, $[NiL_3](ClO_4)_2$. This complex has been assigned an octahedral configuration, with L functioning as a N,O donor didentate ligand [196].

A series of complexes involving the semicarbazone ligand, benzylmethylketone semicarbazone (L), and its thiosemicarbazone analogue (L′), has been prepared using various nickel(II) salts. The complexes, NiL_2X_2($X = Cl, Br, I, NCS$), were assigned octahedral coordination geometry, whereas NiL_2SO_4 was assigned trigonal bipyramidal coordination geometry. The complexes NiL'_2X_2 exhibit stereochemical variations, depending on the anion involved [197].

In a continuing study of semicarbazides, thiosemicarbazides and their derivatives as ligands, the coordination of 4-phenylsemicarbazone of salicylaldehyde (H_2L) with Ni(II) acetate has been investigated. The resultant complex, $[Ni(HL)_2].H_2O$, was assigned an octahedral structure in which the ligand functions in a monovalent tridentate manner [198].

The ligand isatin *β*-semicarbazone (HL), when reacted with Ni(II), yielded the complexes $[Ni(HL)X_2H_2O]$ ($X = Cl$, NO_3) and $[NiL(py)_2Cl]$, depending on the reaction conditions employed. The ligand functions as an O,N,O tridentate donor and octahedral coordination was assigned to the complexes [199].

Template synthesis has been utilised in the preparation of the coordination compounds [7-alkylthio- and 7-benzylthio-10-acetyl-5,6,8-triazadodeca-2,4,6,8,10-pentaen-2,11-diolato(2″) *N*^{5}, *N*^{8}, *O*,*O*]nickel(II). The complexes are diamagnetic and have a square planar structure (**31**) [200].



$R = CH_3$, n = 0; $R = C_2H_5$, n = 1/2, $A = CH_3CN$;
$R = C_3H_7$, n = 1/2, $A = CH_3CN$; $R = CH_2C_6H_5$, n = 0

(**31**)

The coordination compounds of nickel(II) with 1-(4-methoxyphenylazo)-2-naphthol (L), 1-(4-methoxyphenylazo)-3-carboxy-2-naphthol (L′) and

1-(4-methoxyphenylazo)-3-ethoxycarbonyl-2-naphthol (L″) have been prepared. Electronic spectroscopy, in solution and in the solid state, has been utilised to elucidate the structures of the complexes, NiL_2, NiL′, NiL″ and $Ni(L'')_2$, which contain five- and six-membered chelate rings [201].

Oxime ligands, containing hydroxyl or carbonyl groups, constitute a good source of N,O donor ligands. These vary from simple ligands such as salicylaldoxime (H_2L) which, when complexed with Ni(II), yielded $Ni(HL)_2$ [202] to the dihydrogenviolurate anion (H_2V^-) which yielded the tetracoordinate complex $Na_4[Ni(HV)_3].5H_2O$ [203].

4-Formyloxime-3-methyl-l-phenyl-2-pyrazolin-5-one (HL) reacted with Ni(II) yielding the octahedral complex, $NiL_2(H_2O)_2$ [204], while the ligands $H_2L = RC(:NOH)C(NHOH)(CH_3)_2$ ($R = H$, CH_3, C_6H_5) yielded complexes of the type $Ni(HL)_2$ [205]. In addition, 1-(hydroyimino)-2-methyl-2-(hydroxyamino)cyclohexane (HL) afforded NiL_2 [205].

8-Hydroxyquinoline and its variously-substituted analogues have attracted considerable interest. Table 5 lists the Ni(II) complexes of 8-hydroxyquinoline and some of its variously-substituted analogues. Studies include complexation in solution [207–209], as well as some single-crystal X-ray determinations [210–212].

A number of 3-arylazo-1,2,4-triazole ligands have been complexed with nickel(II). Complexes of the type $NiLCl(H_2O)_3$ (HL = 3-(R-substituted)-azo-1,2,4-triazole; $R = 2\text{-HO-5-CH}_3C_6H_3$, 2-hydroxy-l-naphthyl, 3-OHC-4-HOC_6H_3) and NiL_2 (HL =

Table 5
Ni(II) complexes of 8-hydroxyquinoline and some of its variously-substituted analogues

Ligand	Complex	Comments	Ref.
8-Hydroxyquinoline (HL)	$NiL_2 \cdot 2Q$	Q = thf, dimethylformamide. Thermal study.	[206]
		Potentiometric study in aqueous solution.	[207]
	$HL[Ni_2\{H(L)_2\}_3]_2(ClO_4)_3$	Hydrogen bonded dinuclear complex; Crystal structure determination.	[211]
	$[Ni_2\{H(L)_2\}_3](SCN).H_2O$	Hydrogen bonded dinuclear complex; Crystal structure determination.	[212]
2-Methyl-8-hydroxyquinoline-5-sulphonic acid (H_2L)	NiL_2	Kinetic study.	[208]
2-, 5-, 7-Methyl-8-hydroxyquinoline (HL), 7-alkyl- and 7-alkenyl-8-hydroxyquinoline (HL)		Potentiometric study.	[209]
5-Chloro-8-hydroxyquinoline (HL)	$[NiL_2(py)_2] \cdot py \cdot 2H_2O$	*trans* Octahedral structure; Crystal structure determination.	[210]

2-hydroxy-l-naphthylazo-1,2,4-triazole) have been prepared and characterised. NiL_2 are tetrahedral, whereas the other complexes are octahedral [213].

Diphenyl(pyrid-2-yl)methanol (HL), when reacted with Ni(II), in the presence of Et_3N, yielded the complex, NiL_2. The uninegative ligand functions as a N,O donor in the tetracoordinate complex [214].

2-Cyanopyridine complexes with Ni(II) in a variety of ways, depending on the solvent employed, as coordination promotes nucleophilic addition of the solvent molecule. Thus, complexation in H_2O led to the formation of an octahedral complex which contains coordinated molecules of pyridine-2-carboximide, whereas complexation in CH_3OH yielded an octahedral complex containing *O*-methylpyridine-2-carboximidate [215].

Molecules containing amine and carboxylic acid functional groups provide a good source of N,O ligands. These include indole-2-carboxylic acid [216], pantothenic acid [217], maleanilic, 4-nitromaleanilic and 4-methoxymaleanilic acid [218] and orotic acid [219]. In addition, the ligand 1-phenyl-3-(3,5-di-*tert*-butyl-4-hydroxyphenylamino)-2-propen-1-one (HL) was prepared and reacted with Ni(II), yielding the complex, NiL_2. One electron reduction of NiL_2 gave the phenoxy radical complex $Ni(L)_2$, which was characterised using ESR [220].

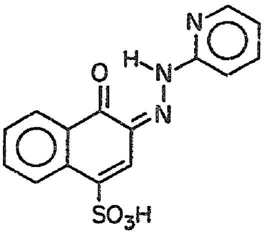
The complexes, $R[NiX_3]$, $R_2[NiX_4]$ and $R_2[NiX_2(NCS)_2]$ ($X = ONC(CN)C(O)NH_2$; $R = Ph_4As, Bu_4N$) have been prepared and characterised by IR and electronic spectra. In $[NiX_3]$, X^- functions as a didentate ligand coordinating through the nitroso N and carbonyl O atoms, whereas in $[NiX_4]^{2-}$ two X^- ligands are monodentate, coordinating via the nitroso N atom, while the remaining two X^- ligands coordinate via the nitroso N and carbonyl O atoms. In $[NiX_2(NCS)_2]^{2-}$ both X^- ligands function in a didentate fashion [221].

The formation constants of the complexes formed between Ni^{2+} and 2-amino-*N*-hydroxyacetamide and 2-amino-*N*-hydroxypentanamide have been determined potentiometrically. Mononuclear complexes, $[NiL]^+$ and $[NiL_2]$, were formed, with the ligands binding via the N atom of the amino group and the deprotonated NHO^- group. These complexes were assigned square planar geometry with strong intermolecular hydrogen bonding [222].

2-Methoxy-4-amino-5-chloro-N[2-(diethylamino)ethyl]benzamide, when reacted with a variety of nickel(II) salts, yielded the complexes, NiL_3X_2 ($X = 0.5SO_4$, Cl, NO_3). The octahedral complexes were characterised using a variety of spectroscopic and magnetic analytical techniques [223].

The kinetics of ternary complex formation between nickel 2,2′:6′,2″-terpyridine, $[Ni(terpy)]^{2+}$, and the isomeric α-PAN (**32**) and β-PAN (**33**) dyes have been reported. It was shown that rate enhancements in ternary complex formation are affected by the attached aromatic ligand, but its effect on the mechanism of complexation of the entering ligands was not fully understood [224].

Continuing with complexation studies in solution, the formation constants of a number of diamino-*N*,*N*,*N*′,*N*′-tetraacetates with Ni(II) have been determined. The ligands investigated include (bis(2-aminoethyl)ether)-*N*,*N*,*N*′,*N*′-tetraacetate, (bis(3-aminopropyl)ether)-*N*,*N*,*N*′,*N*′-tetraacetate and *N*,*N*-bis(2-aminoethyl)-ethylamine-*N*,*N*,*N*′,*N*′-tetraacetate [225].



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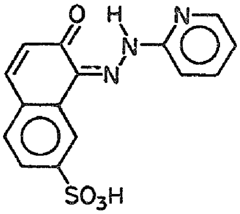

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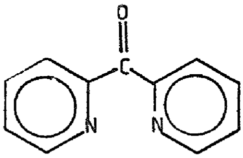
The stability constants of 3-(*N*-α-phenyl-2-hydroxybenzylideneimino)propanoic acid with Ni(II) have been determined in aqueous medium [226]. Similarly, the complexing properties of α-hydroxy-γ-aminobutyric acid and its *N*-acetyl derivative with Ni(II) have been investigated in aqueous solution [227].

Bis(2-pyridyl)ketone {L = (34)} has the possibility of coordinating in a didentate fashion as a N,O donor or a N,N donor, as well as a N,O,N tridentate donor. Reaction of L with nickel(II) sulphate yielded the complex, $Ni[C_{11}H_8N_2(OH)_2]_2SO_4$, the crystal structure of which reveals that the keto group of L has undergone hydrolysis during coordination. The complex has an essentially *trans* octahedral configuration with Ni-O = 2.098(4) Å, Ni-N = 2.062(4) and 2.087(4) Å [228]. Reaction of the related ligand, 2,2-bis (6-methyl-2-pyridyl)-1,3-dioxolane {L′ = (35)}, yielded the complex, $[Ni(C_{15}H_{16}N_2O_2)(H_2O)_3]Cl_2$, which has an octahedral configuration with the ligand functioning as a N,O,N donor, as determined by X-ray single-crystal methods [229].



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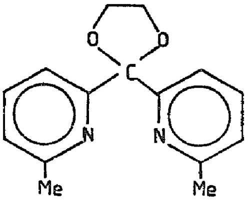
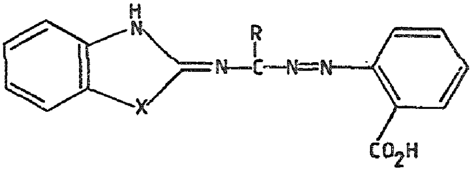


(35)

The crystal structure of lithium[(ethylenediaminetetraacetato(3-)]nickel(II) dihydrate has been reported. The structure consists of Li^+, $[Ni(HEDTA)H_2O]^-$ and H_2O molecules. Coordination around Ni is octahedral with HEDTA coordinating via two N and three O atoms [230].

A number of 3-substituted-1-(*o*-carboxyphenyl)-5-(2-benzazolyl)formazanate ligands {H_2L = (36)} have been complexed with nickel(II). The ligands are tetradentate in all cases yielding complexes of the type NiL, in which N_3O coordination has occurred [231].

The kinetics and mechanism of reactions of cyanide ion with [NiL] and $[Ni_2L]$

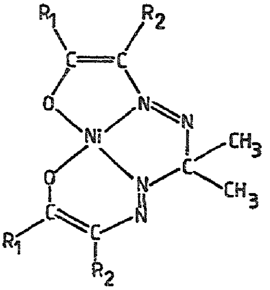


$X = S, NCH_2C_6H_5$; $R = CH(CH_3)_2, C_6H_5, CH_3, C_2H_5$

(36)

(L = hexamethylenediaminetetraacetic acid) have been studied spectrophotometrically in aqueous solution. The order with respect to [CN^-] was found to be one over a wide range of cyanide concentrations for both systems. The reverse reaction between [$Ni(CN)_4$]$^{2-}$ and [L]$^{n-}$ was found to be first order in each reactant and inverse first order in cyanide [232].

The electronic absorption and resonance Raman spectra of the planar Ni(II) N_2O_2-core complex (**37**) have been determined in solution as well as the solid state. In the solid state the electronic structure is dominated by the properties of a face-to-face dimer [233].

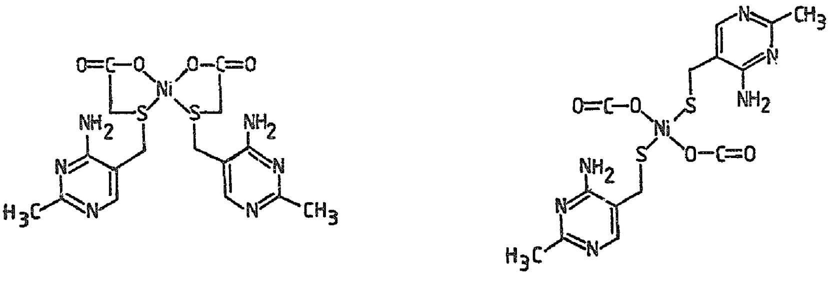


$R_1 = R_2 = C_6H_5$; $R_1 = C_6H_5, R_2 = H$; $R_1 = R_2 = CH_3$

(37)

4.7. Complexes with sulfur - oxygen donor ligands

(4-Amino-2-methyl-5-pyrimidinyl methylthio)acetate (H_2L) has been synthesised and complexed with nickel(II). The resultant complex, [$NiL_2(H_2O)_2$], is unusual in that coordination occurs via the S and O donor atoms (**38**) and does not involve the N(1′) position of the pyrimidine ring. This may be the first example of this type of coordination [234].



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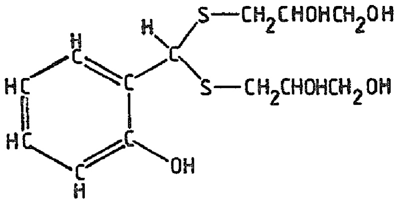
The complexation of a number of 2-mercaptoacid ligands with Ni(II) has been investigated in solution. Ligands studied include thiolactic acid [235], 2-mercapto-2-phenylacetic acid [236], and 3-(2-furyl)-2-mercaptopropenoic and 3-(2-furyl)-2-mercaptopropanoic acids [237].

Continuing with solution studies, the stability constants of the complexes of nickel(II) with 3-mercapto-1-(4-methylphenyl)-3-phenylprop-2-en-1-one (HL) were determined potentiometrically in aqueous dioxane. In addition, the complex, [NiL$_2$], was isolated and characterised [238].

Salicylaldehydedithioglycerol {H$_2$L=(39)}, when reacted with Ni(II), yielded the tetra-coordinate complex, [NiL]. Magnetic and spectral data indicate that the complex is tetrahedral, with coordination occurring via the sulfur and oxygen atoms of the alcohol groups [239].



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4.8. *Complexes with nitrogen - sulfur donor ligands*

The chemistry of this group is dominated by thiosemicarbazone and thiosemicarbazide ligands and their Ni(II) complexes. A number of didentate [240,241], tridentate [242–244] and tetradentate [245] ligands have been complexed with a variety of nickel(II) salts, as shown in Table 6.

The interaction of thiosemicarbazide (L) with Ni(II) has been studied in solution [246] and in the solid state [247]. The latter study reports the properties and

Table 6
N,S-donor thiosemicarbazone ligands and their Ni(II) complexes

Ligand	Complex	Comments	Ref.
Didentate			
Acetophenone thiosemicarbazone (HL)	$Ni(HL)_2LCl$ $Ni(HL)_2Br_2 \cdot 2H_2O$	Complexes characterised by molar conductance, magnetic susceptibility and spectral methods.	[240]
o-Aminobenzaldehyde thiosemicarbazone (HL)	$Ni(HL)LX$ ($X=Cl$, Br)	Complexes characterised by molar conductance, magnetic susceptibility and spectral methods.	[240]
Phosphorylated aldehyde (HL) and dialdehyde thiosemicarbazones (H_2L')	NiL_2 $Ni(L')$	Square planar stereochemistry; magnetic and spectroscopic study.	[241]
Tridentate			
4-Phenyl-1-diacetylmonoxime-3-thiosemicarbazone (H_2L)	$[Ni(HL)Cl(H_2O)]$ $[NiL(H_2O)]$	Diamagnetic; Spectral and magnetic study.	[242]
Acetylacetone thiosemicarbazone (HL)	NiL_2 $Ni(HL)_2X_2$ $Ni(HL)(NO_3)_2$	Complexes characterised by molar conductance, magnetic susceptibility and spectral methods; $X=Cl, ClO_4$	[243]
Tridentate			
Butanone thiosemicarbazone (HL)	$Ni(HL)_2X_2$ $Ni(HL)(NO_3)_2$	Complexes characterised by molar conductance, magnetic susceptibility and spectral methods; $X=Cl, ClO_4$.	[243]
1,2-Hydroxylaminothiosemicarbazone (H_2L)	$[Ni(H_2L)_2]X_2$	$X=Cl, NO_3, (C_2H_5O)_2PS_2$; Paramagnetic	[244]
	$[Ni(HL)_2]$	$X=Cl, NO_3, (C_2H_5O)_2PS_2$; Paramagnetic	
	NiL	Diamagnetic; Polymeric.	
Tetradentate			
(R^1R^2-substituted 1,2-ethanediylidene)-bis(*S*- methylhydrazinecarbodithiol) (H_2L) ($R^1, R^2=H$, Me, Ph)	[NiL]	Reaction of [NiL] with piperidine and morpholine; Reaction products affected by R^1 and R^2 as well as reaction conditions.	[245]

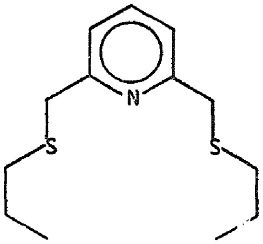
stereochemistry of two isomeric forms, α and β, of $[NiL_3]I_2$. In addition, the crystal structure of the β-form has been determined by X-ray methods. Ni is octahedrally coordinated by three molecules of (L) through their S and hydrazine N atoms [247].

A number of nickel(II) complexes with 4-phenylthiosemicarbazide (L) have been prepared. These include $[NiL_2]X_2$ ($X=Cl, NO_3$) and $[NiL_4]X_2$. In $[NiL_4]^{2+}$, L is monodentate and coordinated via the S atom, whereas in $[NiL_2]^{2+}$, L is didentate and coordinated through the S atom and hydrazine N atom [248].

Pyridine-4-carboxaldehyde thioisonicotinoylhydrazone (HL) has been reacted with a variety of nickel(II) salts. Reaction with NiX_2 (X=Cl, Br, I) yielded complexes of the type $Ni(HL)X_2$, which have been assigned polymeric octahedral geometry. Reaction with $Ni(NCS)_2$ yielded $Ni(HL)_2(NCS)_2$, which has been assigned octahedral geometry [249].

The ligand, 1,3-diphenyl-5-(*o*-mercaptophenyl)-1,2,4-triazole (HL), has been prepared and reacted with Ni(II). The resultant complex, NiL_2, is square planar with coordination occurring via the S and N(4) atoms [250].

2,6-Bis((ethylthio)methyl)pyridine {L=(**40**)} has been prepared and characterised. Reaction with $NiCl_2$ yielded $NiLCl_2.H_2O$. Comparison of this complex with its Zn analogue suggests that (**40**) functions as a tridentate ligand with coordination taking place via the nitrogen and sulfur atoms [251].



(**40**)

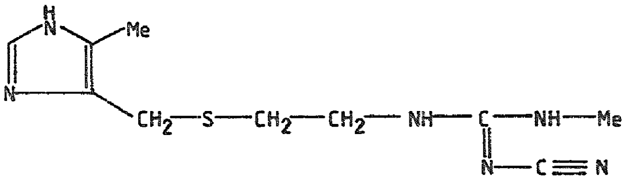
Turning to liquid extraction studies, the complexation of 1,1,1-trifluoro-5,5-dimethyl-4-amino-3-hexene-2-thione (L) with Ni(II) has been investigated in H_2O/hexane. The complex, NiL_2, was extracted into the organic phase [252]. Similarly, the kinetics and mechanism of extraction of Ni(II) with 3-mercapto-1,5-diphenylformazan into chloroform, in the presence of 1,10-phenanthroline or pyridine, have been investigated [253].

Continuing with solution studies, the solubility products of the 2-methylhydrazinedithiocarboxylate, 3,3-dimethylhydrazinedithiocarboxylate and 3-methyl-3-phenyl-hydrazinethiocarboxylate complexes with Ni(II) have been determined at 25°C and I=0.01 M. The solubility data were obtained by atomic absorption measurements [254].

Cimetidine {L=(**41**)}, when reacted with NiX_2 ($X=BF_4$, NO_3), yielded the complexes, $[NiL_2]X_2$. The complexes were assigned *pseudo*-octahedral stereochemistry with $NiN_2N_2^{\ddagger}S_2$ chromophore [255].

4.9. Complexes with nitrogen - oxygen - sulfur donor ligands

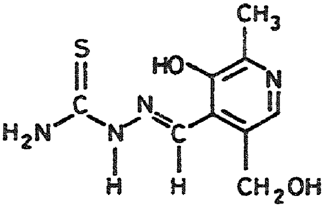
Schiff base and structurally related ligands contribute extensively to this category, with ligands derived from salicylaldehyde in abundance. These include 5-mercapto-



(41)

3-*n*-propyl-4-salicylideneamino-*S*-triazole (as well as 4-amino-5-mercapto-3-*n*-propyl-*S*-triazole) [256], 2*N*-3,5-dibromosalicylidene-5-phenyl-1,3,4-thiadiazole [257], Schiff bases formed by the condensation of salicylaldehyde with *S*,*S*-dibenzyldithiocarbazate and *S*-methyl-*S'*-benzyldithiocarbazate [258], as well as 2-hydroxybenzal-4-(2,6-dimethylphenyl)thiosemicarbazone [259].

In a study examining thiosemicarbazones as coordinating agents, pyridoxal thiosemicarbazone $\{H_2L=(\mathbf{42})\}$ has been prepared, characterised and reacted with Ni(II). Complexes of the type $[Ni(HL)(NO_3)].2H_2O$ and $[NiL].2H_2O$ were prepared and characterised using conventional analytical methods and infrared spectroscopy. Spectroscopic shifts on coordination indicate that the ligand functions as a uninegative or binegative O,N,S donor [260].

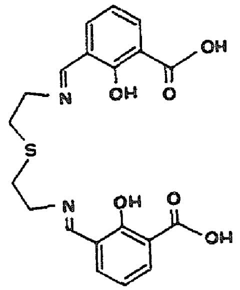


(42)

1-Cyanoacyl-4-phenyl-3-thiosemicarbazide (HL), when reacted with nickel(II) chloride, yielded the complex, $[NiLCl(H_2O)]$. The deprotonated ligand, L^-, coordinates via the O,S and N(1) atoms. The complex is rather unusual in that it was assigned a mixture of square planar and octahedral coordination geometry [261].

The heptadentate compartmental ligand $\{H_4L=(\mathbf{43})\}$ has been synthesised by the condensation of 3-formylsalicylic acid and 1,5-diamino-3-thiapentane in methanol. The ligand reacted with Ni(II) yielding mononuclear $Ni(H_2L).2H_2O$, as well as dinuclear $Ni_2L.4H_2O$, complexes. In $Ni(H_2L).2H_2O$, the ligand functions as an O,N,S,N,O donor, whereas in $Ni_2L.4H_2O$, the ligand functions as an O,O,N,S,N,O,O donor [262]. Structurally related ligands, $H_4L'=(\mathbf{44})$, prepared from 4-chloro-2,6-diformylphenol and polyamines of the type $NH_2\text{-}(CH_2)_2\text{-}X\text{-}(CH_2)_2\text{-}NH_2$ (X=NH, S), yielded similar mononuclear and dinuclear complexes. In the mononuclear complexes the ligands function as

O,N,X,N,O donors, whereas in the dinuclear complexes they function as O,N,X,N,O,N,X,N donors [263].



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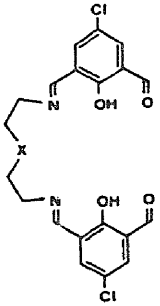


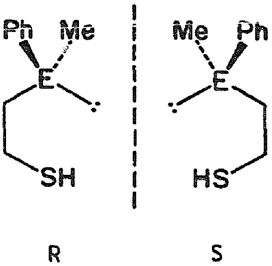
X = NH, S

(44)

The complexation of a series of acetothioacetanilides with Ni(II) has been investigated in aqueous dioxan. Comparison with the corresponding *β*-ketoanilides showed that the complexes with the *β*-ketothioanilides are less stable [264].

4.10. Complexes with arsenic - sulfur and phosphorus - sulfur donor ligands

The racemic and optically active forms of the asymmetric didentate ligand, (+)-(2-mercaptoethyl)methylphenylarsine and the racemic form of the corresponding tertiary phosphine (45) have been used to prepare a series of square planar complexes of the type [NiL_2]. It has been shown that ligand redistribution occurs in solutions of these complexes at ambient temperature [265].



E = P, As

(45)

5. Nickel(II) macrocycle complexes

Macrocyclic ligands and their complexation with Ni(II) continue to generate an abundance of interesting and novel chemistry. Areas that have attracted particular interest are the use of macrocyclic complexes in the uptake of CO_2, the effect of ring size on the coordination of axial ligands, the synthesis and characterisation of stereoisomers of variously-substituted Ni(II)-cyclam complexes, the synthesis of macrocyclic ligands with functionalised pendant side chains and their coordination with Ni(II), as well as variously-substituted porphyrin Ni(II) complexes. Where possible, in order to facilitate clarity, complexes have been dealt with in order of increasing ring size.

Interest in Ni(II) macrocyclic chemistry is manifested in the number of reviews that have been published recently. Kimura [266] has reviewed the complexation of a series of macrocyclic oxo polyamine ligands, which have the dual features of macrocyclic polyamines and oligopeptides. It was found that, due to the involvement of the imide anions in coordination, their ligand field strengths are stronger than their polyamine macrocyclic analogues. A consequence of this is their ability to stabilise the Ni(III) oxidation state more readily. The biological significance of these complexes was also discussed.

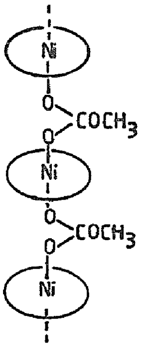
Ito et al. [267] have reviewed the chemical and structural characteristics of a series of tetraaza cycloalkane complexes, with a view to taking advantage of properties such as CO_2 uptake, effect of in-plane coordination on axial coordination, and stabilisation of high oxidation states. As part of their continuing studies in this area, they have prepared and characterised a new series of monomethyl carbonato complexes of nickel(II)-containing tetraazocycloalkanes. The complexes, $Ni(L)(O_2COCH_3)(ClO_4)$ (L=[14]ane N_4; L=[15]ane N_4; L=*iso*[14]ane N_4; L=*RSRS*-Me_4[14]ane N_4) and [Ni(*RRSS*-Me_4[14]ane N_4)$(O_2COCH_3)_2$]. $HNEt_3ClO_4$, have been obtained by CO_2 uptake reaction in basic methanol from the corresponding tetracoordinate macrocyclic complex [NiL]$(ClO_4)_2$. The first three complexes were assigned a linear chain structure (**46**), while X-ray crystal structure determinations yielded a trigonal bipyramidal structure (**47**) for the second last complex and a *trans* hexacoordinate configuration (**48**) for the last complex [268].

The electrocatalytic properties of Ni(cyclam)$^{2+}$ in the reduction of CO_2 have been investigated. Under specific experimental conditions, it has been shown that Ni(cyclam)$^{2+}$ is extremely efficient and selective for the electroreduction of CO_2 into CO, even in water. During the electrocatalytic process, a nickel(I) species, [Ni(cyclam)CO]$^+$, was generated, which may be the precursor to CO evolution [269].

New oscillating reactions, in which the macrocyclic nickel(II) complex ion, [NiL]$^{2+}$ (L=11,13-dimethyl-1,4,7,10-tetraazacyclotrideca-10,13-diene), functions as a catalyst in acidic bromate medium have been described. The [NiL]$^{2+}$ ion can undergo an irreversible oxidation reaction of Ni(II)→Ni(III) [270].

5.1. Macrocycles with nitrogen donor atoms

A kinetic study of the conversion of *cis*-[NiL$(H_2O)_2$]$^{2+}$ (L=1,4,7,10-tetraazacyclotridecane) to the planar complex, [NiL]$^{2+}$, has been reported.



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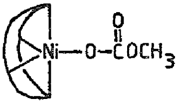

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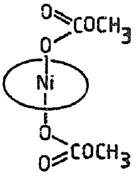


(48)

It was found that for pH values below approximately 6, the interconversion reaction exhibits biphasic first-order kinetics, with a transient configurational isomer of planar $[NiL]^{2+}$ being observed. Above pH 7, the reaction is base-catalysed and monophasic [271].

1,4,8,11-Tetraazacyclotetradecane (cyclam) and its variously-substituted analogues continue to contribute substantially to this area of Ni(II) chemistry. The single-crystal X-ray structures of two new complexes of nickel(II)-cyclam have been reported. The complexes, cis-$[NiL(OH_2)_2]Cl_2.2H_2O$ and $[NiL]ZnCl_4$ (L = cyclam), both have the *RRRR* set of nitrogen configurations. Ni-N distances average 2.10 Å in the hexa-coordinate complex and 1.9 Å in the tetra-coordinate complex [272].

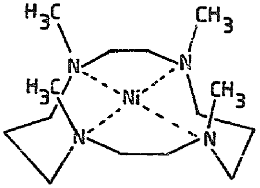
The folded *cis*-macrocyclic complexes, $[NiL(en)](ClO_4)_2$ (L = 1,4,8,11-tetraazacyclotetradecane; 1,4,7,10-tetraazacyclotridecane; C-*meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane), have been prepared and their base-catalysed conversion to planar species investigated. Kinetic studies indicate that conversion is first order in complex and hydroxide ion concentration [273].

A large number of alkyl-substituted cyclam ligands have been prepared and reacted with Ni(II). Substituents vary from methyl to benzyl groups and are located on nitrogen atoms or on carbon atoms at various positions on the chelate rings. The redox potentials for oxidation and reduction of 15 nickel(II) complexes of variously-substituted cyclam ligands that contain one to four *N*-alkyl groups, varying from methyl to benzyl, have been determined in acetonitrile solution. In addition, the single-crystal X-ray structures of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2.2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$ have been reported. Both complexes have *trans*-III stereochemistry with an average Ni-N distance of 2.142 Å in the hexa-coordinate complex and 1.990 Å in the tetra-coordinate complex [274].

Proton magnetic resonance spectroscopy has been used to investigate the effects of methyl substituents on the conformational characterisation of nickel(II)-tetraaza macrocyclic complexes in solution [275]. These studies include the characterisation of six stereoisomers of the complex (5,5,7,12,12,14-hexamethyl-1,4,8,11-

tetraazacyclotetradecane)nickel(II). The isomers arise from two asymmetric carbon centres and four asymmetric nitrogen centres [276].

The macrocyclic ligand, 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane, when coordinated to four equatorial sites of Ni(II), gives rise to a number of possible arrangements, depending on the location of the methyl groups above and below the coordination plane. The crystal structures of *R,S,R,S*-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) bis(trifluoromethane sulphonate)-acetone hydrate [277] and *R,S,R,S*-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) bisperchlorate (determined at 155 K) [278] have been reported. Both structures confirm the *R,S,R,S* conformation with all four methyl groups on the same side of the coordination plane (**49**). The crystal structure of the related complex, acetonitrile-(1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) bisperchlorate has also been reported. The geometry about the nickel atom is essentially that of a distorted square pyramid, with all the methyl groups, as well as the acetonitrile ligand, on the same side of the coordination plane (**50**) [279]. Single-crystal X-ray methods have been used to determine the structure of (1*RS*,4*RS*,7*RS*,8*SR*,11*SR*,14*SR*)-1,4,5,5,7,8,11,12,12,14-decamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) perchlorate. The complex is essentially square planar, with the methyl groups on the nitrogen atoms located equally on two opposite sides of the coordination plane (**51**) [280].



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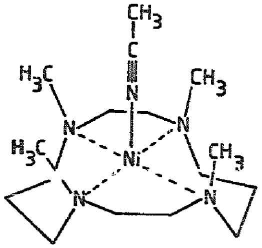

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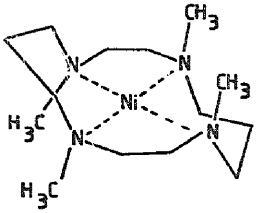


(51)

In a continuing series on macrocyclic ligands and their metal ion complexes, 5,12-dimethyl-7,14-diisopropyl-1,4,8,11-tetraazacyclotetradecane (L) has been reacted with nickel(II) diperchlorate. The resultant complexes, $[Ni(L)](ClO_4)_2$ and $[Ni(L)(ClO_4)_2]$, are square planar and tetragonal respectively. Interestingly, the Ni-$OClO_3$ distance differs by 22 pm in the two complexes [281].

5-Oxo-1,4,8,11-tetraazacyclotetradecane (HL) has been prepared and reacted with Ni(II) in aqueous solution. Only $[NiL]^+$ forms in solution, while $[NiL](ClO_4)$ has been isolated in the solid state. The $[NiL]^+$ ion is square planar with a d-d transition at 22625 cm^{-1} [282].

1,5,8,12-Tetraazacycloheptadecane (L) has been synthesised and complexed with a variety of nickel(II) salts. The complex, $[NiL](ClO_4)_2$, is square planar and does not exhibit any octahedral⇔planar equilibrium in solution. In addition, the severely distorted octahedral complexes, $[NiLCl_2]$ and $[NiL(SCN)_2]$, have been prepared, but revert to their square planar analogues, $[NiL]Cl_2$ and $[NiL](SCN)_2$, on exposure to moisture [283]. The kinetics of dissociation of $[NiL]^+$ has been studied in acidic solution and compared to that of $[Ni(cyclam)]^{2+}$. Dissociation of $[NiL]^+$ was found to be 10^{10} times faster than that of $[Ni(cyclam)]^{2+}$ [284].

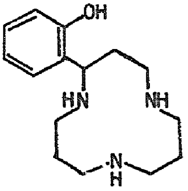
Oxygen-17 nuclear magnetic resonance has been utilised to investigate high-spin⇔low-spin equilibria in (1,4,8,11-tetraazaundecane)nickel(II). The role of ClO_4^- appears to be specific in the conversion to low-spin Ni [285].

Pendant-arm macrocyclic ligands and their Ni(II) complexes have attracted considerable interest. Ligands vary from triaza to tetraaza macrocycles with pendant arms consisting of phenol, pyridyl, carboxylic acid, amine and nitrile groups.

Kimura and co-workers have prepared the phenol-pendant macrocycles **(52)** [286], **(53)** [287] and **(54)** [288] and complexed them with Ni(II). At acidic pH, it was found that the phenolate group served as an extra donor, and that the 1:1 metal complexes were more stable than their phenol-less analogues. Crystal structures have been determined for the complexes $[NiL](ClO_4).H_2O$ {HL=**(53)**} [287] and $[NiL(H_2O)](ClO_4)$ {HL=**(54)**} [288]. In the former complex, the coordination sphere around Ni is square-pyramidal with the phenolate oxygen almost at the apex of the pyramid. In the latter complex the coordination sphere is octahedral with the phenolate oxygen and water molecules occupying *cis* positions, while the macrocycle has an unusual folded *cis* configuration.

The pyridyl analogue of **(53)**, in which the phenol pendant arm is replaced by a pyridyl arm, has been prepared by the same research group and behaves in a similar fashion when complexed with Ni(II). A crystal structure determination of the resultant complex, $[NiL](ClO_4)_2$ {L=**(55)**}, shows a square pyramidal coordination sphere around Ni with the pyridine ring above the plane of the macrocycle [289]. In addition, the three new pyridine pendant-containing ligands (**56a, b, c**), which are potentially hexadentate, have been complexed with Ni(II) [290].

Carboxylic acid pendant arms are attached to nitrogen donor atoms in the new 14-membered tetraazamacrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane- *N′*,*N″*-diacetic acid (H_2L). H_2L, when reacted with Ni(II), yielded the complex, $[NiL].HBr.H_2O$, the crystal structure of which has been determined. The complex exhibits *cis*-octahedral geometry, with the macrocycle coordinated in a folded configuration with four amine groups coordinated to adjacent sites and the two carboxylate groups occupying the two remaining sites. The



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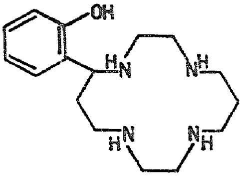

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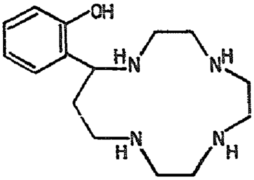

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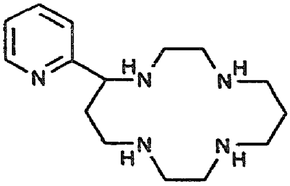
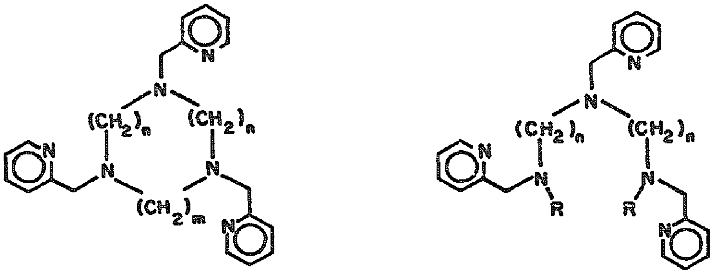


(55)

mean Ni-N distance is 2.08 Å and the average Ni-O distance is 2.13 Å [291,292].

Eight monofunctionalised, tetra-*N*-alkylated cyclam ligands have been prepared by derivatisation of the secondary amine of 1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecane. Functional groups that have been attached to the secondary amine consist of CH_2CN,CH_2CH_2CN,$CH_2CH_2NH_2$, $CH_2CH_2CH_2NH_2$, $CH_2CH_2C(O)NH_2$, $CH_2CH_2C(O)NH_2$, $CH_2CH_2C(O)OCH_3$ and $CH_2CH_2C(O)OH$. These ligands, when complexed with Ni(II) diperchlorate, yielded a variety of diasterioisomeric complexes [293].



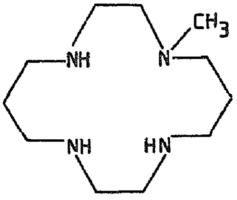
a: n = m = 2

b: n = m = 3

c: n = 2; R = CH_3

(56)

The three macrocycles (**57**), (**58a**) and (**58b**), in which a methyl group has been introduced on a nitrogen atom of cyclam or isocyclam, have been prepared and complexed with Ni(II). It was found that the presence of the methyl group substantially affects the behaviour of these complexes in solution. Apart from affecting the high spin⇔low spin conversion, *N*-methylation of the ligand made attainment of the Ni(I) state easier and attainment of the Ni(III) state more difficult [294].



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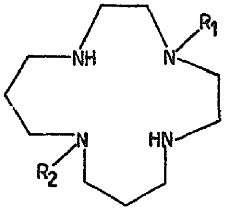


a: $R_1 = H$; $R_2 = CH_3$

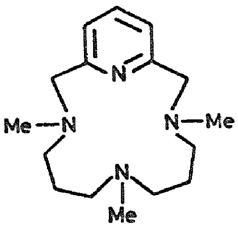
b: $R_1 = CH_3$; $R_2 = H$

(58)

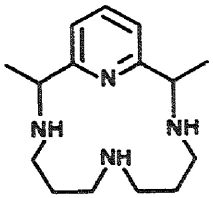
Template synthesis has been used in the preparation of a new class of nickel(II) hexaazamacrocyclic complexes of [3,10-bis(R-thio)-5,7,12,14-tetramethyl-1,2,4,8,9,11-hexaazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)N^1,N^4,N^8,N^{11}]nickel(II) (R = methyl, ethyl, propyl, butyl, benzyl) [295]. While the ligands are potentially hexacoordinate, a crystal structure of the propyl analogue revealed that Ni has square planar coordination, with bonding occurring via nitrogen atoms 1, 4, 8 and 11 [296].

A template condensation/addition reaction of $CH_3CH_2O_2C(O)CR{:}CHNHC_6H_4$-*o*-$NH_2$ (I;R = CN), (II;R = CO_2Et) and $Ni(OAc)_2$ in 2:1:1 ratio, yielded the macrocyclic complex, [NiL], where H_2L = 12-amino-6,3-di(ethoxycarbonyl)-5-methyl-dibenzo[*b*,*i*]-1,4,8,11-tetraaza[14]annulene. [NiL] was characterised using polarography and spectroscopic methods [297].

Three structurally related pyridine-containing tetraaza macrocycle ligands 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**59**), *β*-2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**60**) and 7-methyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (**61**) have been complexed with Ni(II). The three possible diastereoisomeric forms of the nickel complex of (**59**) have been isolated as $[Ni(L)](ClO_4)_2$, with one being isolated in a monoaquo form as $[Ni(L)(OH_2)](ClO_4)_2$. X-ray crystal structures of the red form of $[Ni(L)](ClO_4)_2$ and $[Ni(L)(OH_2)](ClO_4)_2$ have been determined [298]. The crystal structure of the free macrocycle ligand (**60**) has also been reported. Empirical force-field methods have been used to calculate the steric energies of the various conformations of this ligand, in the free state, and in a series of nickel(II) complexes, $[NiL]^{2+}$, $[NiL(NO_2)(ONO)]$ and $[NiL(en)]^{2+}$ [299]. (**61**), when reacted with a variety of nickel(II) salts, yielded the complexes $[Ni(L)]X_2$ ($X = ClO_4$ or NO_3). Reaction of $[Ni(L)](ClO_4)_2$ with NCS^- NO_2^- or oxalate (ox) yielded $[Ni(L)(NCS)_2]$, $[Ni(L)(NO_2)(ClO_4)]$ and $[LNi(\mu\text{-ox})NiL](ClO_4)_2$ respectively. Interestingly, reduction of the pyridine ring of $[Ni(L)](ClO_4)_2$ gives a symmetric diamagnetic square planar complex, $[Ni(L')](ClO_4)_2$ {L′ = (**62**)}, the crystal structure of which has been determined. Coordination still occurs via the same four nitrogen atoms in this complex [300].



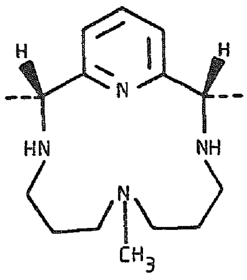
(**59**)



(**60**)

The tropocoronand ligands (**63**) have been prepared and complexed with Ni(II). Spectral data and single-crystal X-ray diffraction studies revealed an interesting structural transition from nearly planar to nearly tetrahedral coordination geometry as the length of the linker chain was increased [301].

A detailed study of the host-guest complexing behaviour of vaulted cyclidene complexes has been reported. To this end, the crystal structure of (2,17,19,25-tetramethyl-3,6,13,16,20,24,27,31-octaazapentacyclo[$16.7.7.2^{8,11}.2^{3,6}.2^{13,16}$]octatriconta-1,8,10,17,19,24,26,31,33-nonaene-K^4N)nickel(II) hexafluorophosphate has been determined. The benzene cap is essentially parallel to the NiN_4 floor and no solvent molecule is associated within the confines of the crystal lattice. In the analogous anthracene complex, a molecule of acetonitrile solvent is in the cavity,



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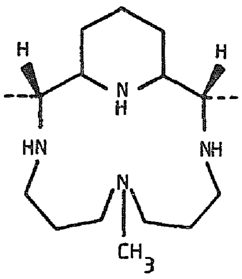

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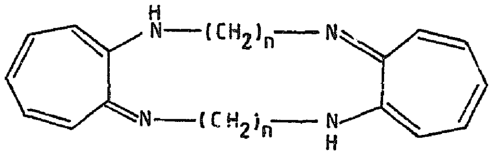


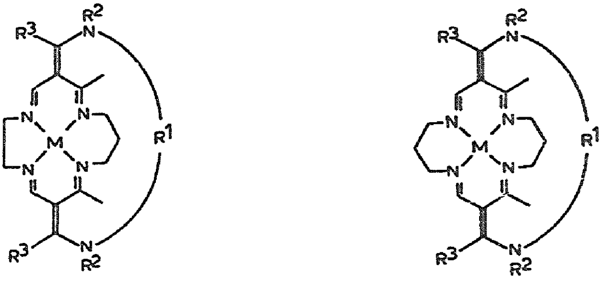
n = 2 - 6

(63)

while the data were indecisive for the 3,6-durene analogue [302]. In further studies, the same group have examined the one-electron oxidation of the lacunar cyclidene complexes of nickel(II), $[NiL]^{2+}$ (**64**) to $[NiL]^{3+}$, in acetonitrile solution. The stability of the Ni(III) complexes is a function of the extent of axial ligation which, in turn, depends on the size of the lacuna [303]. In addition, Busch and co-workers have prepared and characterised a series of dinickel(II) complexes containing macrotricyclic bis(cyclidene) ligands [304].

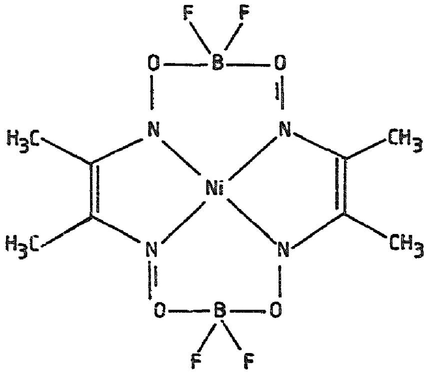
The square planar macrocyclic complex (**65**) has been prepared and characterised by elemental analysis and IR spectroscopy. The complex exhibits interesting fragmentation patterns in its mass spectrum, with B-F and B-O bond fission, followed by N-O and C-N bond cleavage. The F atom formed during the first fragmentation coordinates in an axial position to the parent molecule, forming the $[NiL_2F]^+$ ion [305].

Porphyrin and variously-substituted porphyrin complexes of Ni(II) have been examined using a number of analytical techniques. Resonance Raman spectroscopy has been used to examine the core size in the Ni(II) complexes of octaethylporphyrin, protoporphyrin IX dimethyl ester and *meso*-tetraphenylporphine in methylene chloride and piperidine. The high frequency porphyrin skeletal modes were found to be extremely sensitive to core size expansion [306]. Similarly, a normal coordinate analysis of the Ni(II) complex of octaethylporphyrin has been undertaken, with isotopic labelling being employed in the interpretation of the vibrational spectra



$R^1 = (CH_2)_{3-8,12}$; $R^2 = CH_3$; $R^3 = CH_3, C_6H_5$

(64)



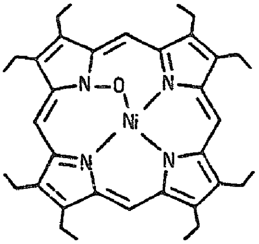
(65)

[307]. In addition, laser photolysis has been used to study the behaviour of nickel(II) tetraphenylporphyrin, Ni(II)L, in a mixed solvent of pyridine and toluene. Results showed that only one pyridine molecule was responsible for the photochemistry of Ni(II)L in this mixed solvent [308].

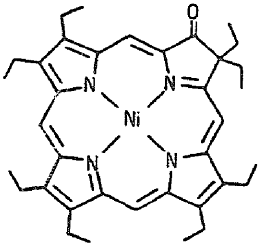
The coordination-hole contraction in hexahydro- and tetrahydroporphiniod ligands coordinated to low-spin Ni(II) has been investigated by the examination of the crystal structures of thirteen of these complexes. The contraction is characterised by a deformation of the ligand system towards a saddle-shaped, ruffled conformation of approximate S_4 symmetry. Ni is essentially co-planar with the four coordinating N atoms. The Ni-N distances were found to decrease with increasing saddle steepness [309].

Octabutyl- (H_2L) and octaoctylporphyrin (H_2L') have been prepared and complexed with Ni(II). The resultant complexes, [NiL] and [NiL′], were isolated and found to be highly lipophilic [310].

Nickel(II) octaethylporphyrin *N*-oxide (**66**) undergoes a novel oxygen atom transfer when refluxed in xylene under inert atmosphere. The resultant complex, nickel(II) octaethyloxochlorin (**67**), has been identified on the basis of spectroscopic evidence and independent synthesis [311]. In an independent study on the structure of metallo-β-oxoporphyrins, the structure of the related complex, [3,3,7,8,12,13,17,18-octaethyl-2(3*H*)-porphinonato(2-)]nickel(II), has been reported. The coordination sphere about nickel is essentially square planar [312].



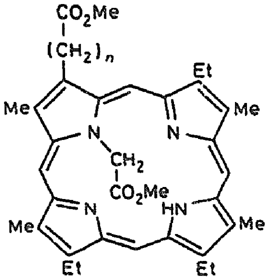
(**66**)



(**67**)

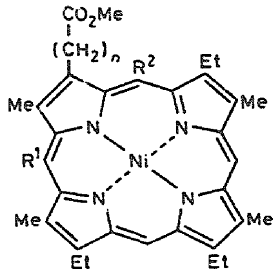
Similar behaviour has been observed when the (*N*-methoxycarbonylmethyl)-substituted porphyrin (**68**) is refluxed in benezene in the presence of $[Ni(acac)_2]$. The (*meso*-methoxycarbonylmethylporphyrin) nickel(II) complexes (**69**) are produced by intramolecular migration of the *N*-substituent to carbon, in what is thought to be the first definitive demonstration of this fact [313].

(Phthalocyaninato)nickel(II) bromide has been synthesised, by the oxidation of



n = 1, 2

(**68**)



n =2: $R^1 = R^2 = H$; $R^1 = H$, $R^2 = CH_2CO_2Me$; $R^1 = CH_2CO^2Me$, $R^2 = H$
n = 1: $R^1 = R^2 = H$

(69)

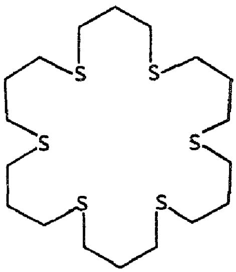
(phthalocyaninato) nickel(II) with Br_2, and its crystal structure determined. Comparison with its iodide analogue reveals that the structures are very similar. However, their electrical conductivity and magnetic properties differ significantly at room temperature, showing that anion effects should also be taken into account when investigating these systems [314]. This view is strengthened by the synthesis and crystal structure determination of the highly conducting complex (phthalocyaninato)nickel(II) hexafluoroantimonate, which is also isostructural with the iodide analogue [315]. To conclude this section, the high resolution powder diffraction diagram of the β-form of (phthalocyaninato)nickel(II) has been determined [316].

5.2. Macrocycles with oxygen donor atoms

The infrared, Raman and electronic spectra of the complexes, $2(NiCl_2).L.2H_2O$, $NiBr_2.L.4H_2O$ and $Ni(NO_3)_2.L.2H_2O$ (L = 18-crown-6), have been studied. It was found that the conformational changes of L depend on the type of anion, the composition of the complex, and the degree of hydration. The nitrate complex was assigned octahedral coordination, while the halide complexes were found to have C_{3v} symmetry [317].

5.3. Macrocycles with sulfur donor atoms

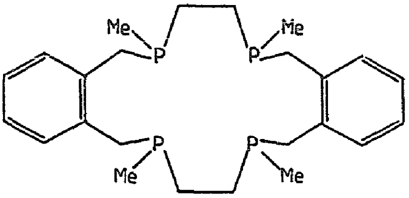
The hexadentate ligand, hexathia-24-crown-6 {L = **(70)**}, has been prepared and complexed with Ni(II). The resultant complex, $[NiL](BF_4)_2$, is essentially octahedral, in which the Ni atom is enveloped by the ligand, yielding meridional stereochemistry. Ni-S bond lengths vary from 2.415(1) to 2.445(1) Å [318].



(70)

5.4. *Macrocycles with phosphorus donor atoms*

The template synthesis of the tetradentate macrocyclic ligand, L=(71), yielded three stereoisomers. Reaction with $NiBr_2$ afforded the complex $NiLBr_2$ [319].



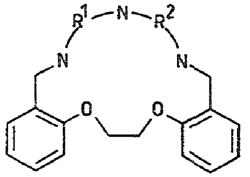
(71)

5.5. *Macrocycles with mixed donor atoms*

1-Thia-4,7-diazacyclononane-*S*-oxide (L) has been prepared and reacted with Ni(II). L functions as a tridentate N_2O donor macrocyclic ligand in the hexacoordinate complex, $[NiL_2](PF_6)_2$. This complex, which has *trans-O,O* geometry, has been compared with the Ni(II) complex of bis(2-aminoethyl)sulphoxide [320].

In a template synthesis, the complex NiL ($H_2L=CH_3C(O)CH_2C(CH_3)$: NCH_2CH_2N: CHCH{C(O)R} $C(O)CH_3$; R=CH_3, C_6H_4, OEt), when reacted with ethylenediamine, yielded Ni complexes with tetraaza 14-membered macrocyclic ligands. However, reaction with 1,3-propanediamine afforded acyclic complexes of the type [NiL′] ($H_2L'=CH_3C(O)CH_2C(CH_3)$: NCH_2CH_2N: CHCH{C(O)R}$C(CH_3)$: $NCH_2CH_2CH_2NH_2$) [321].

A series of N_3O_2 donor macrocycles incorporating 17- to 19-membered macrocyclic rings {L=(72)}, has been prepared. The complexes were assigned the stoichiometry $NiLX_2.nH_2O$ (X=Cl, Br, I, NCS, NO_3; n=0, 1/2, 1). L functions in a tetradentate fashion when X=NCS, and in a pentadentate manner when X=I. It was found that the coordinating behaviour of the ligands is affected by the coordinating ability of the accompanying anion [322].



$R^1 = R^2 = CH_2CH_2$

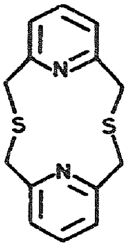
$R^1 = CH_2CH_2$, $R^2 = CH_2CH_2CH_2$

$R^1 = R^2 = CH_2CH_2CH_2$

(72)

The complex formation of Ni^{2+} with a number of aza crown ethers has been investigated in methanol, using calorimetry and potentiometry. Surprisingly, the reactions of Ni(II) with the aza crown ethers were endothermic. This effect was explained in terms of a two-step reaction mechanism [323]. While on the subject of aza crown ethers, Ni(II), when reacted with 1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (L), yielded the complexes $NiLCl_2$ and $NiL(ClO_4)_2.2H_2O$ [324].

Template synthesis has been employed in the preparation of a novel N_2S_2 pyridinophane macrocycle, L=(73). The crystal and molecular structure of the nickel(II) complex of this ligand, $[NiLCl_2]$, have been determined. The complex possesses distorted octahedral geometry, with the chlorine atoms occupying *cis* equatorial positions. L is folded in such a way that the S atoms are *trans* diaxial and the N atoms of the pyridine rings are *trans* to the chlorine atoms [325].



(73)

6. Nickel(II) complexes with biological ligands

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

Table 7 lists amino acids that have been complexed with Ni(II). These consist of glycine [326–332], α-alanine [329,331,335], β-alanine [329,332], L-phenylalanine [329], L-valine [329,332], proline [331], serine [333,334], histidine [332,334,336], tryptophan [332], L-tyrosine [337], aspartic acid [336], benzyl aspartic acid [340], glutamic acid [336,341] and α-aminoisobutyric acid [342,343]. As expected, the bulk of these studies have been undertaken in aqueous and mixed solutions.

Turning to ligands derived from amino acids, the barium dithiocarbamate derivatives of the α-amino acids, glycine, DL-alanine, DL-2-aminobutyric acid, DL-norvaline and DL-norleucine have been prepared and the anions complexed with Ni(II). The complexes are essentially square planar, with coordination occurring via the sulfur atoms of the dithiocarbamate moiety [344].

Complex formation between Ni(II) and a series of phosphorus derivatives of amino acids has been studied in aqueous solution over a broad pH range. Ligands investigated include $RNHCHR^1PO_3H_2$ (R=H, Me, Bu, *iso*-Bu, isopentyl, octyl; $R^1=\beta$-pyridyl), as well as 6-methylpyridine-2-phosphonic acid [345].

In an ongoing study, the formation constants of the binary complexes of Ni(II) with glycinehydroxamic acid have been determined in aqueous solution. In addition, the reaction of the Ni(II)-glycinehydroxamate complexes with pyridoxal was investigated at pH>7. Evidence suggests that ternary complex formation occurs prior to the possible formation of the Schiff base metal complex [346]. Similarly, the interaction of pimelodihydroxamic acid with Ni(II) has been studied using analytical potentiometry. The complex was assigned octahedral coordination in solution, on the basis of isolated complexes [347].

The crystal and molecular structure of the histamine complex, $[NiL_2(NCS)_2]$ {L= 4-(2-aminoethyl)imidazole}, have been reported. Both histamine ligands coordinate to Ni^{2+} via their N^π atoms and the nitrogen atoms of the side chains, while the coordination sphere about Ni^{2+} is a distorted octahedron [348]. The related ligand, *N*-isopropylidene-1*H*-imidazole-4-ethylamine (L′), a Schiff base derived from histamine and acetone, has been complexed with Ni(II). A single-crystal X-ray structure of the resultant complex, $[Ni(L')_2](ClO_4)_2$, revealed square planar geometry, with coordination occurring via two imidazole and two imine N donor atoms [349].

Turning to peptides, the tripeptide analogues of the Cu(II) binding site of human serum albumin, Gly-Gly-His derivatives of poly(L-lysine), have been investigated using CD spectroscopy. Spectral characteristics indicate that the coordination sphere of the metal ion is square planar [350]. Similarly, the complexation of the NH_2-terminal 24 residues peptide fragment from dog serum albumin has been studied using NMR and CD spectroscopy. The Ni ion was assigned a square planar geometry with coordination occurring via four N donor atoms [351].

The interaction of the *N*-terminal tetrapeptide fragment of fibrinopeptide A with Ni(II) has been investigated. A combined approach of potentiometry and spectro-

Table 7
Amino acids that have been complexed with Ni(II)

Ligand	Comments	Ref.
Glycine (HL)	Potentiometric and calorimetric study of complexation in H_2O and H_2O/dioxane.	[326]
	Thermodynamic study of complex formation in aqueous KNO_3 solution.	[327]
	Thermodynamics of mixed-ligand complex formation with HL and $Ni(edta)^{2-}$.	[328]
	Kinetic study on ternary complex formation of HL with diaquonitrilotriacetato-nickelate(II).	[329]
	Thermodynamic parameters associated with mixed ligand complexes of Ni(II) with HL and 4-methoxypicolinic acid N-oxide.	[331]
	Complexation of Ni(II) with HL and nitrilotris(methylenephosphonic acid).	[332]
α-Alanine (HL)	Kinetic study on ternary complex formation of HL with diaquonitrilotriacetato-nickelate(II).	[329]
	Thermodynamic parameters associated with mixed ligand complexes of Ni(II) with HL and 4-methoxypicolinic acid N-oxide.	[331]
	X-ray crystal structure of bis(alaninato) nickel(II) tetrahydrate.	[335]
β-Alanine (HL)	Kinetic study on ternary complex formation of HL with diaquonitrilotriacetato-nickelate(II).	[329]
	Complexation of Ni(II) with HL and nitrilotris(methylenephosphonic acid).	[332]
L-Phenylalanine (HL)	Kinetic study on ternary complex formation of HL with diaquonitrilotriacetato-nickelate(II).	[329]
L-3,4-Dihydroxyphenylalanine (H_3L)	Stability constants determined pH-metrically.	[330]
L-Valine (HL)	Kinetic study on ternary complex formation of HL with diaquonitrilotriacetato-nickelate(II).	[329]
	Complexation of Ni(II) with HL and nitrilotris(methylenephosphonic acid).	[332]
Proline (HL)	Thermodynamic parameters assosciated with mixed ligand complexes of Ni(II) with HL and 4-methoxypicolinic acid N-oxide.	[331]
Hydroxyproline (HL)		
Histidine (HL)	Complexation of Ni(II) with HL and nitrilotris(methylenephosphonic acid).	[332]
	Mixed-ligand complexes of Ni(II) with HL and ATP.	[336]
	Calculation of coordination geometry of Ni(II) with L-histidine in H_2O using proton NMR.	[337]
	Kinetic study of complex formation with Ni(II).	[338]
Serine (HL)	Complex formation in aqueous medium. Stability constants follow the order $NiL > NiL_2 > NiL_3$.	[333]
	Complex formation of Ni(II) with DL-(HL), D-(HL) and L-(HL) in aqueous medium.	[334]
Tryptophan (HL)	Complexation of Ni(II) with HL and nitrilotris(methylenephosphonic acid).	[332]
L-Tyrosine (HL)	Stopped-flow kinetic study. Initial complexation occurs via the carboxylate group.	[339]

Table 7 (*continued*)

Ligand	Comments	Ref.
Aspartic acid (H_2L)	Mixed-ligand complexes of Ni(II) with H_2L and ATP.	[336]
Benzyl aspartic acid (H_2L)	Stability constants were determined for both 1:1 and 1:2 complexes.	[340]
Glutamic acid (H_2L)	Mixed ligand complexes of Ni(II) with H_2L and ATP.	[336]
	Mixed-ligand complexes of Ni(II) with H_2L and uracil or thymine as a secondary ligand.	[341]
α-Aminoisobutyric acid (HL)	Kinetic, thermodynamic and structural studies.	[342]
	X-ray crystal structure of $[Ni(L)_2(H_2O)_2].3H_2O$.	[343]

scopic techniques has been used to study the complexation of Ala-Asp-Ser-Gly with Ni(II). The stability constants of the nickel(II) complexes of Ala-Ala-Ala-Ala have also been determined [352]. Similarly, infrared spectroscopy has been used to study the interaction between Ni(II) and the aspartate-containing tetrapeptide Ac-Asp-Val-Asp-Ala-OH. It was concluded that in the 1:1 complex, Ni(II) is bound simultaneously with the carboxylate groups of the two aspartyl residues [353].

Ni(II) coordination in nickel reconstituted hemoglobins has been studied using visible spectroscopy and ESR. It has been shown that two distinct metal environments exist, comprising a penta-coordinated complex with a strong proximal histidine bond and a complex with much weaker axial ligation. Comparison with isolated subunit complexes showed that the penta-coordinated complex is associated with myoglobin, while the second complex is found with isolated α-chains [354]. In addition, the transient photoligation behaviour of nickel(II) protoporphyrin reconstituted myoglobin and hemoglobin has been studied using time-resolved resonance Raman scattering [355]. Soret-resonance Raman difference spectroscopy has been used to identify the Ni-histidine stretching mode in these complexes [356].

Nickel metalloenzymes and co-enzymes have been the subject of some study. A nickel X-ray absorption spectroscopic study has been utilised in determining the structural characteristics of F_{430} isolated from *Methanobacterium thermoautotrophicum*. Results indicated that "free" F_{430} is different in structure to F_{430}-containing protein [357].

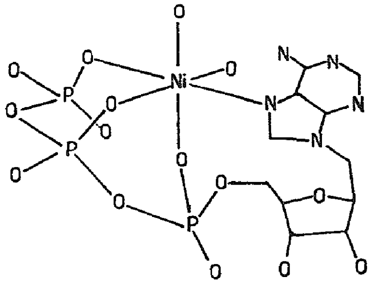
The oxidation potentials of 15 nickel thiolates were investigated in aprotic media using differential pulse polarography and cyclic voltammetry, in an attempt to ellucidate the Ni(III) site of hydrogenases of hydrogen uptake bacteria. The potential distribution of the thiolates in relation to the RS^-/Ni ratio suggests that four cysteinyl residues are coordinated to the Ni(III) ion, provided that no other anionic residues are present about the metal [358].

EPR has been used to detect two new nickel species produced by the exposure of reduced hydrogenase from *Chromatium vinosum* to carbon monoxide. It was concluded that both hydrogen, possibly as a hydride, and CO are able to bind to nickel at the same coordination position. This explains the fact that CO is a competitive inhibitor of the enzyme [359].

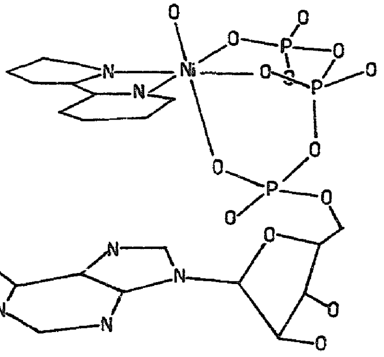
The interaction of the co-enzyme, thiamine, with Ni(II) in aqueous solution has been examined using proton NMR. The results indicate a prevailing aspecific interaction in solution involving the thiamine [360].

A thermodynamic and temperature-jump kinetic study has been undertaken of the complexation of the co-enzymes flavin adenine mononucleotide (FMN) and flavin adenine dinucleotide (FAD) with Ni(II). FMN exhibits two distinct relaxation times, attributed to two distinct complexes, while FAD exhibits four relaxation times, attributed to a series of complexes forming the basis of a multistep reaction mechanism [361].

Stopped-flow spectroscopy has been used to study the kinetics of formation of mixed-ligand complexes containing Ni(II), 2,2′-bipyridine and adenosine 5′-triphosphate. The kinetics were explained in terms of three interconnected ternary formation steps, which correspond to the formation of Ni(ATPH)(bipy), Ni(ATP)(bipy) and HONi(ATP)(bipy). Proposed structures for Ni(ATP) (**74**) and Ni(ATP)(bipy) (**75**) have also been suggested [362].



(**74**)



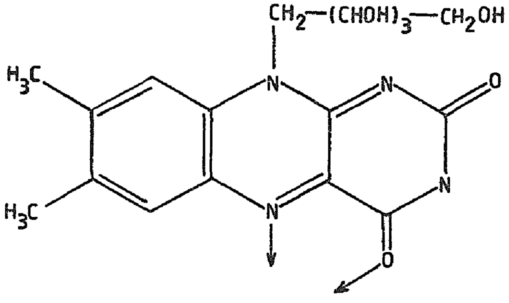
(**75**)

Adenosine 3′-monophosphoric acid (3′AMP) and adenosine 2′-monophosphoric acid (2′AMP), analogues of ATP, were complexed with Ni(II) yielding the complexes, Ni(3′AMP).5H_2O and Ni(2′AMP).6H_2O, respectively. Spectroscopy indicated that coordination takes place via the phosphate group and the adenine ring, possibly through N(7) [363].

A potentiometric study of the complexation of 5′-cytidine monophosphate with Ni(II) has been undertaken in aqueous solution. Stability constants were determined assuming the formation of 1:1 complexes and were compared to the corresponding values of the component base and nucleoside [364].

The complexation of riboflavine {L=(**76**)} with Ni(II) has been investigated in acetonitrile solution. Spectral and solubility data indicate that complexation occurs via the O(4) atom. Higher complexes, having the formula $[Ni(L)]_2^{4+}$, have also been observed [365].

Pyrimidines and purines are essential constituents of nucleic acids, and have



(76)

attracted considerable interest, particularly in terms of their complexing properties in aqueous media. The interaction of Ni(II) with the substituted pyrimidines, 2-mercaptopyrimidine, 4,5-diamino-6-hydroxypyrimidine and 2,4-diamino-6-hydroxypyrimidine [366], as well as with a number of 9-methylpurines [367], has been investigated.

The reactions of Ni(II) with carbohydrates and their derivatives continue to attract interest. This is manifested by an ongoing research effort in the binding of metal ions to polysaccharides, in which spectroscopic and potentiometric studies of the binding of Ni(II) to some monosaccharide units have been undertaken. This study investigates the bonding of Ni^{2+} to glucosamine, *N*-acetylglucosamine and other derivatives of glucose in acidic, neutral and alkaline aqueous media [368].

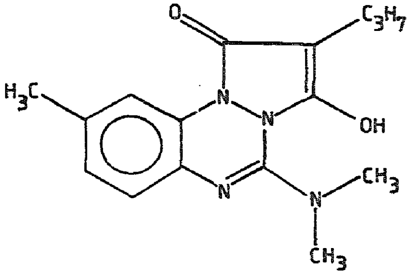
In addition, Yano and co-workers have shown that glucose-type aldoses react with $[Ni(\beta\text{-alanine})_2(H_2O)_2]$, yielding novel nickel(II) complexes that contain *N*-glycosides [369]. Similarly, they have shown that the Ni(II) complex, $[Ni(H_2O)_2L_2]Cl_2$ (L = *N,N,N'*-trimethylethylenediamine), is able to epimerise aldoses at C-2, and that of the two C-2 epimers, only the mannose-type epimers complex with Ni(II) stereoselectively [370].

The benzoate complex, NiQ_2 (HQ = benzoic acid), when reacted with ascorbic acid (L) in aqueous solution, yielded the mixed-ligand complex, $NiQ_2L.4H_2O$. IR spectra and thermogravimetry indicated that L is coordinated to Ni via an OH group, while the H_2O molecules are hydrogen-bonded to L [371].

DTA, TGA and DTGA have been used to study the thermal decomposition of Ni(II) complexes of barbituric acid, 5,5-dihydroxybarbituric acid and barbital. The 5,5-dihydroxybarbituric acid complex is more stable than the barbituric acid complex, which in turn is more stable than the barbital complex [372]. Solution studies of the complexation of a number of 5-(2-substituted phenylazo)barbituric acids with Ni(II) have also been undertaken. The resultant complexes, determined in a dioxane-water medium, exhibited 1:1 and 1:2 (Ni:ligand) stoichiometry [373].

To conclude, a number of ligands that are utilised as drugs, have been complexed with Ni(II). These include bromazepam, an anxiolytic drug [374], 6-acetyldihydrohomopterin, a pyrimidodiazepine isolated from *Drosophila melano-*

gaster [375], sulphadimidine [376] and the antibiotic drugs, nystatin and amphotericin B [377]. In addition, the anti-inflammatory drug, 5-dimethylamino-9-methyl-2-propyl-1*H*-pyrazolo[1,2-α][1,2,4]benzotriazine-1,3(2*H*)-dione {azapropazone = (77)} has been complexed with Ni(II). The resultant complex, $NiL_2.5H_2O$ (HL = azapropazone), has been assigned pseudo-octahedral stereochemistry with two of the five water molecules coordinated and the two didentate N,O donor atoms of L completing the coordination sphere [378].



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7. Nickel(II) polynuclear complexes

Polynuclear nickel-containing complexes continue to attract substantial interest. As in previous articles in this series, the complexes have been divided into those that contain Ni-Ni or Ni-metal interactions (clusters) and those that do not.

7.1. Cluster complexes

Homonuclear [379–383] and heteronuclear [384–393] Ni-containing clusters have been synthesised and characterised. Single-crystal X-ray methods remain the most reliable method of characterisation, and Table 8 lists relevant structural data for a number of Ni-containing cluster complexes. Homonuclear clusters vary from those containing a Ni_2 core to one containing a Ni_{38} framework. Ni-Ni interactions range from 2.429 to 2.94 Å. Heteronuclear clusters containing Ni with Os [384], with Ru [387] and with Rh [388] have been isolated and their structures determined. In addition, the catalytic activity of the Ni-Os complex, $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_8(PPh_2H)]$ [384], for the isomerisation and selective hydrogenation of dienes, alkenes and alkynes has been reported, together with that of its related complex, $[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(CO)_9]$ [385].

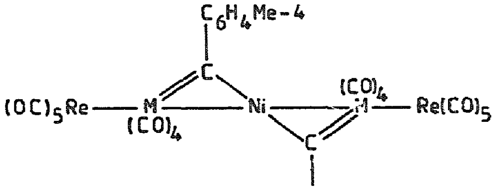
IR and ^1H NMR have been used to characterise a number of heterometallic carbidocarbonyl cluster complexes. These include $(Et_4N)_2[Fe_5NiC(CO)_{15}]$, $(Et_4N)[Fe_3NiH(CO)_{12}]$ and $[Fe_5NiC(CO)_{16}]$ [389], as well as $(Et_4N)[Fe_4MNiC(CO)_{15}]$ (M = Rh, Co) and $(Et_4N)[Fe_3Ni_3C(CO)_{15}]$ [390]. In $(Et_4N)[Fe_4MNiC(CO)_{15}]$ the

Table 8

Complex	Structural Data (Å)	Comments	Ref.
Homonuclear			
$[Ni(\mu\text{-}t\text{-}Bu_2As)(PMe_3)]_2$	Ni-Ni=2.429(1)	Planar symmetrical Ni_2As_2 core.	[379]
$[Ni(\mu\text{-}t\text{-}Bu_2As)(CN\text{-}p\text{-}tol)_2]_2$	Ni-Ni=2.693(2)	Ni atoms have psuedotetrahedral geometry.	[379]
$[Ni_9(CO)_{18}]^{2-}$	Ni-Ni(av.)=2.77 Ni-Ni(av.)=2.94	Three short and six long Ni-Ni interactions.	[380]
$[Ni_9(AsPh)_3(CO)_{15}]^{2-}$	Ni-Ni(av.)=2.519 Ni-Ni(av.)=2.680	Ten short and eight long independent Ni-Ni interactions	[381]
$[Ni_{10}(AsMe)_2(CO)_{18}]^{2-}$	Ni-Ni(av.)=2.490 Ni-Ni(av.)=2.686	Five short and five long independent Ni-Ni interactions.	[381]
$[HNi_{34}(CO)_{38}C_4]^{5-}$	Ni-Ni(av.)=2.663(2)	Isolated as $[NMe_3CH_2Ph]^+$ salt.	[382]
$[Ni_{35}(CO)_{39}C_4]^{6-}$	Ni-Ni(av.)=2.663(2)	Isolated as $[NEt_4]^+$ salt.	[382]
$[Ni_{38}(CO)_{42}C_6]^{5-}$	Ni-Ni(av.)*c*=2.488 Ni-Ni(av.)*i*=2.633	Isolated as $[NBu_4]^+$ salt. *c*=μ-capping, *i*=interlayer Ni distances.	[383]
Heteronuclear			
$[(\eta\text{-}C_5H_5)NiOs_3(\mu\text{-}H)_3(C)_8(PPh_2H)]$	Ni-Os(av.)=2.557(3) Os-Os(av.)=2.865(2)	Tetrahedral cluster of three Os atoms and one Ni atom. H atoms are Os-Os edge bridging.	[384]
$[(CH_3C_5H_4)_2V_2S_3]Ni$	Ni-V(av.)=2.813 V-V(av.)=2.484	Tetrahedral Ni bound via two μ_3-S atoms.	[386]
$[Ni_2Ru_3(\eta\text{-}C_5H_5)_2(CO)_9(\mu_5\text{-}PPh)]$	Ni-Ru(av.)=2.612(3) Ru-Ru(av.)=2.817(3)	Pentanuclear cluster with two edges of the Ru_3 triangle bridged by two Ni atoms.	[387]
$[Rh_5Ni_6(CO)_{21}H_x]^{3-}$	Ni-Ni(av.)=2.702 Ni-Rh(av.)=2.629 Rh-Rh(av.)=2.900	Isolated as $[PPh_3Me]^+$ salt. Rh_5Ni_6 core exists as an unprecedented D_{3h} polyhedron rather than a pentacapped trigonal-prismatic D_{3h} polyhedron.	[388]

Ni and M atoms are *cis* to each other in an octahedral arrangement of the Fe_4MNi framework.

In an ongoing investigation of the chemistry of di- and tri-metal complexes with bridging carbene or carbyne ligands, the syntheses of the pentanuclear metal complexes, $[NiM_2Re_2(\mu CC_6H_4Me\text{-}4)_2(CO)_{18}]$ (M=Cr or W), have been reported. The structures (**78**) have been characterised using microanalysis, IR and ^1H- and ^{13}C-NMR [391]. In a continuation of this study, the related complexes, $[NiW_2(\mu\text{-}CR)_2(CO)_4L_2]$ ($L=\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$; R=Me, Ph or $C_6H_4Me\text{-}4$) (**79**) and $[NiPtW_2(\mu\text{-}CR)(\mu_3\text{-}CR)(CO)_4(cod)L_2]$ ($L=\eta\text{-}C_5H_5$, $\eta\text{-}C_5Me_5$; R=Me, Ph or $C_6H_4Me\text{-}4$) (**80**) have been prepared and characterised in a similar fashion [392].



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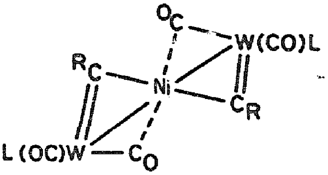
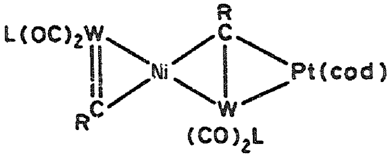




(79) (80)

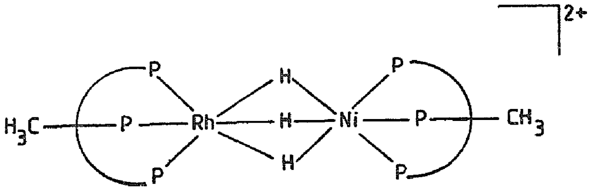
The NiMo and NiW mixed-metal complexes, $(CO)_4M(\mu\text{-}PCy_2)_2Ni(PPh_3)$ (M = Mo, W), have been prepared and characterised using $^{31}P\{^1H\}$-NMR and IR spectroscopy. The Mo-Pd analogues of these complexes exhibit metal-metal bonding as verified by a crystal structure determination [393].

7.2. General polynuclear complexes

As has been the trend recently, a vast number of polynuclear nickel-containing complexes have been prepared, ranging from dinuclear to polynuclear species. Bridging ligands and functional groups that have been utilised include Schiff base and related ligands, halides and pseudo-halides, polyfunctional acids, alkoxides, azines and phosphorus- and sulfur-containing ligands.

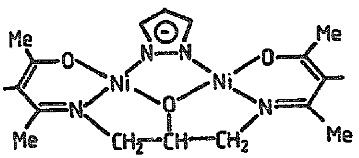
By way of introduction, two interesting bridging complexes have been reported. The first, $[\{MeC(CH_2PPh_2)_3\}Ni(Te_2)NiMeC(CH_2PPh_2)_3].2C_4H_8O$, contains a bridging Te_2 unit which bridges side-on between two Ni(triphos) moieties [394]. The second, $\{[MeC(CH_2PPh_2)_3]Rh(\mu\text{-}H)_3NiMeC(CH_2PPh_2)_3\}^{2+}$, has three bridging hydride ligands (**81**). The electrochemistry of the latter complex has been investigated in dichloromethane [395].

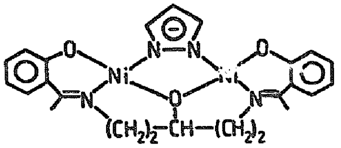
A large variety of Schiff base ligands have been employed in the synthesis of homo- and heteropolynuclear nickel(II) complexes. Table 9 lists some of these ligands and their associated complexes [396–404]. Of particular interest are the series of complexes (**82**) where the ligands have been derived from the condensation of

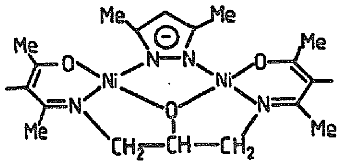


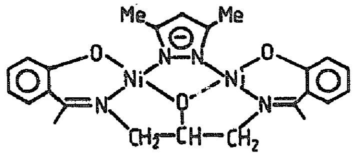
(81)

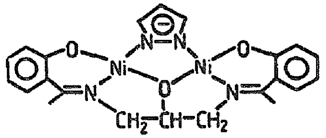
acetylacetone or salicylaldehyde with 1,3-diaminopropan-2-ol or 1,5-diaminopentan-3-ol and an exogenous two-atom bridge between the two metal centres consisting of deprotonated pyrazole or related ligands. The electrochemistry of these complexes revealed two nearly reversible electrode processes observed at very negative potentials [401].

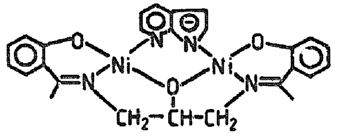










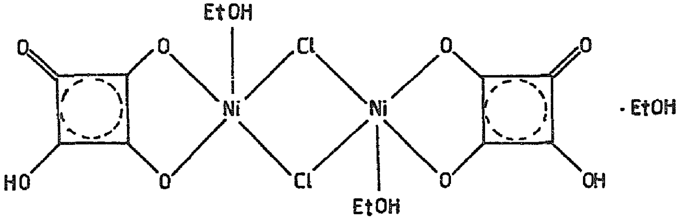


In addition to the mixed-metal complexes incorporating Sn and Te with Schiff base ligands [403], the oxime ligands, HL = 2-OH-R-substituted-$C_6H_3CH(:NOH)$ (R = H, 4-Me, 5-Me, 5-Cl) and 2-hydroxy-1-naphthaldehyde oxime, have been used to prepare the complexes NiL_2MCl_4 (M = Sn, Te). Spectral data indicated that Ni(II) changes its configuration from square planar to octahedral on forming the bimetallic complexes [405].

Table 9
Homo- and heteropolynuclear Ni(II)-Schiff base complexes

Ligand	Complex	Comments	Ref.
2-(2′-Hydroxyacetophenone)imino-5-mercapto-1,3,4-thiadiazole (H_2L)	$[NiL]_n$	Coordination via azomethine N, phenolic O, ring S and thiol S atoms.	[396]
3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione′-iminoglycine (H_2L)	$[NiL(H_2O)_2]_n$	Ligand functions in a dibasic tridentate fashion.	[397]
N,N′-m-Phenylenediiminebis (3-formyl-salicylic acid) (H_4L)	$Ni(H_2L)(H_2O)_2.H_2O$ $Ni(H_2L)(H_2O)py$ $Ni_2L(H_2O)_4$ $Ni_2L(H_2O)_3py.2H_2O$	Pseudooctahedral coordination for Ni in all complexes, with Schiff base coordinating in the equatorial plane, and H_2O and py in axial positions.	[398]
Acetylacetonebisimino(S-H-S′-benzyldithio-carbazate) (HL)	NiL	Thiol S-bridged dimeric structure. Formed from reaction of NiL_2 with acetylacetonebisimino-(*S*-methyl-S′-benzyldithiocarbazate).	[399]
N,N′-Malonic dihydrazidediimine-bis(acetone) (L)	$[NiLCl_2]_2$	Ligand functions in a tetradentate fashion, coordinating via two azomethine N atoms and two O atoms.	[400]
1,3(5)-Diaminopropran-2(3)-oldiimine-bis(R) (R = acetylacetone, salicylaldehyde) (H_3L)	$[Ni_2LL']$	HL′ = pyrazole or related species. Electrochemical investigation.	[401]
N,N′-Ethylenediiminebis(acetylacetone) (H_2L)	NiL Ni_2LCl_2 $NiCuLCl_2$	In the binuclear complexes, the inside Ni atom has a planar environment, while the outer Ni atom has a tetrahedral environment.	[402]
N,N′-R-diiminebis(salicylaldehyde) (R = ethylene, propylene, phenylene) (H_2L)	$NiLMCl_3$	M = Sn,Se,Te,Zr. Prepared by reaction of NiL with MCl_4.	[403]
Bis(salicylidene)ethylenediamine (H_2L)	$NiLMX_2$	MX_2 = alkaline earth salts. O-bridged polynuclear structure.	[404]

A number of polynuclear complexes containing halide or pseudo-halide bridging moeities have been reported. The divalent chloride of nickel has been reacted with squaric acid (1,2-dihydroxy-3,4-diketocyclobutene). The resultant complex, $[Ni(HC_4O_4)(Cl)(C_2H_5OH)]_2$, is dinuclear (**83**), with bridging chloride atoms and the coordination environment of the Ni atoms is postulated as being trigonal-bipyramidal [406].



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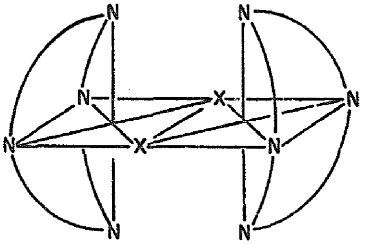
Other polynuclear nickel complexes with chloride-containing bridging groups that have been reported include, $[NiCl_2L_2]$ (L = 2-pyridylphenylacetonitrile) [413], and the macrocycle complexes, $Ni(L)MCl_4$ (L = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; M = Zn, Cu, Co, Mn). The crystal structure of the Zn analogue has been determined, revealing that the Ni(II) ion is octahedrally coordinated by four N atoms of the macrocycle ligand and by two bridging chloride atoms [407]. The Zn(II) ion is tetrahedrally coordinated by the two bridging chloride atoms, as well as by two non-bridging chloride atoms [408].

^1H NMR has been used to investigate the dinuclear Ni(II) complexes formed by the macrocyclic ligand, L = *dl*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, and a variety of bridging halides and pseudo-halides. The complexes have the general formula $[NiLX]_2(ClO_4)_2$ (X = Cl, SH, $C_2O_4/2$), and were postulated to contain dinuclear $[NiLX]_2^{2+}$ cations (**84**) [409].



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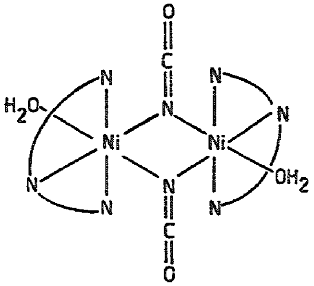
Chloride- and bromide-bridging groups have also been observed in the direct transmetallation reactions of the tetranuclear copper(II) complexes, $(\mu_4\text{-}O)[NCu]_2X_6$ (N = *N*,*N*-diethylnicotinamide, pyridine; X = Cl, Br), with $Ni(NS)_2$ reagents, where NS is a monoanionic *S*-methyl hydrazinecarbodithioate ligand. The resultant products, $(\mu_4\text{-}O)[N_4Cu_3Ni]X_6$, contain one water molecule at each new hexa-coordinate Ni centre [410]. In addition, the rate laws for the transmetallation reactions have been determined in nitrobenzene [411].

Two new dinuclear complexes with bridging μ-cyano ligands have been prepared by solid state reaction of the tetracyanonickellate(II) of aquopentaamminerhodium(III) and iridium(III) respectively. The complexes have been characterised using chemical analysis, electronic and IR spectroscopy and TG analysis [412].

A novel μ-*N*-cyanate-bridged nickel dimer, exhibiting ferromagnetic coupling, has been reported. The crystal and molecular structure of $[Ni_2(terpy)_2(NCO)_2(H_2O)_2](PF_6)_2$ have been determined, revealing one-end N-cyanto-bridging (**85**), thought to be the first example of this type of bridging in nickel dimers. The coordination sphere about each Ni atom is a distorted octahedron [413].



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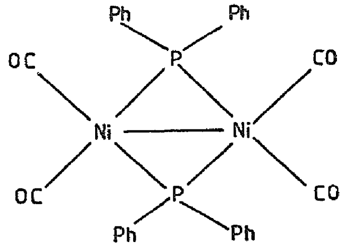
Two new series of polynuclear nickel complexes have been prepared using octahedral dinitrobis(diamine)nickel(II) complexes (diamine = ethylenediamine, 1,2-diaminopropane, 1,3-diaminopropane and 1,2-diaminocyclohexane) as starting materials. One series has the general formula, $[Ni_5(diamine)_4(NO_2)_8(OH)_2]$, and is pentanuclear, while the other has the general formula, $Ni(diamine)_2(NO_2)X$ (X = halide or pseudo-halide), and is polymeric [414].

Turning to phosphorus bridging moieties, the PPh_2-bridged dinuclear nickel complex, $[Ni_2(\mu\text{-}PPh_2)_2(CO)_4]$ (**86**), has been prepared from $Ni(CO)_4$ and Ph_2PLi. A Ni-Ni interaction was proposed for this complex, facilitated by the inclusion of a second PPh_2 bridge into the intermediate mono-bridged complex, $[Ni_2(\mu\text{-}PPh_2)(CO)_6][(Ph_3P)_2N]$ [415]. The structurally related heterobinuclear complexes, $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2NiPPh_3$ (**87a**) and $(C_5H_5)_2Zr(\mu\text{-}PPh_2)_2NiCO_2$ (**87b**), have also been reported, and the presence of a Zr-Ni interaction was suggested [416].

The crystal and molecular structure of the trinuclear Ni complex, $[\{(C_5H_5)Ni[P(S)(OCH_3)_2]_2\}_2Ni]$, have been determined. The coordination geometry of the central Ni atom is distorted tetrahedral with the mean bond length of the four Ni-S bonds being 2.31(4) Å. The two terminal $(C_5H_5)Ni$ fragments are coordinated to the P atoms of the $P(S)(OCH_3)_2$ bridging ligands, with an average Ni-P bond length of 2.1363(4) Å [417].

The tetranuclear complex, $[Ni_4(S_2)(SCH_2CH_2S)_4]^{2-}$, has been prepared and iso-



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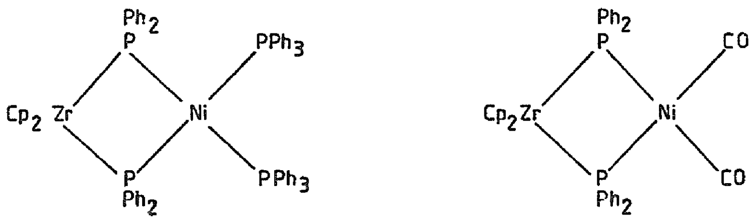


(a)

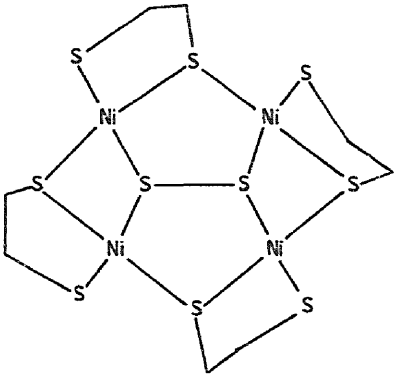
(b)

(87)

lated as its [Ph_4P] salt. A crystal structure determination revealed a Ni_4 complex with the Ni atoms in a rectangular arrangement, coordinated to polysulphide and thiolate ligands simultaneously (**88**). The coordination geometry about each Ni atom is essentially square planar. The crystal structure of the related trinuclear complex, [$Ni_3(SCH_2CH_2S)_4]^{2-}$, isolated as its [Ph_4P] salt, has also been determined. This latter complex has a linear metal framework, with square planar coordination for each of the Ni atoms [418].

The potentially binucleating ligand, $C_2S_2(NH(CH_2)_2SCH_2CH_2OH)_2$, has been prepared from dithiooxamide and complexed with a variety of Ni(II) salts. The complex, $[Ni_3\{C_2S_2(NH(CH_2)_2SCH_2CH_2OH)_2\}_2](NO_3)_2$, is trinuclear with the central Ni(II) ion being diamagnetic and the terminal Ni(II) ions exhibiting paramagnetic properties [419].

Polyfunctional carboxylic acid ligands have been used to great effect in the preparation and study of polynuclear Ni complexes. These include binuclear Ni complexes prepared using 2-carboxy-phenylazosalicylaldehyde [420] and triethylenetetraaminehexaacetic acid [421], polymeric complexes using salicylic acid [422], mixed ligand complexes using aminobenzoic acid and orotic acid [423], as well as polynuclear complexes of fumaric acid dihydrazide [424]. In addition, the crystal



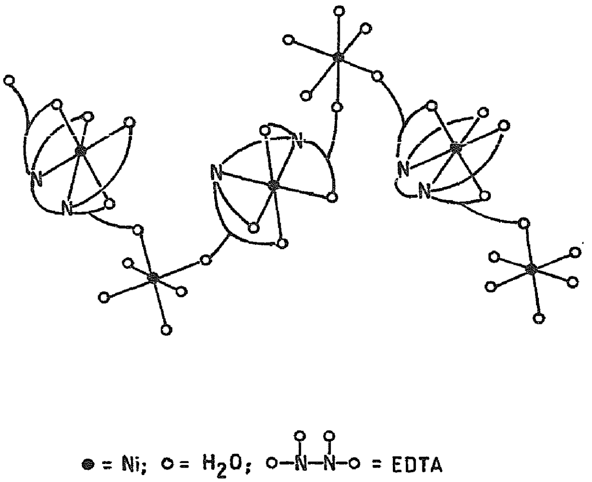
(88)

structure of the polymeric complex, $[NiL(H_2O)_2(NH_3)]_n$ (H_2L = orotic acid), has been reported. The primary coordination sphere about the Ni ion is octahedral with the oratato anion coordinating via the heterocyclic N and adjacent carboxylate group. The remaining coordination sites are occupied by NH_3 and H_2O molecules with the sixth coordination site occupied by the exocyclic keto O of another oratato anion, which is functioning as the bridging moiety [425].

The structure and magnetic behaviour of the chain complex, $Ni_2(edta)(H_2O)_4.2H_2O$, have been reported. Two different sites for the Ni(II) ions were observed, one coordinated to the edta ligand and the other coordinated to oxygen atoms belonging to the carboxylate groups of the edta ligand and four water molecules. Both Ni centres are octahedral, with the edta-coordinated centre being highly distorted. The Ni subunits are linked in an alternating Ni(Edta)-$Ni(H_2O)_4$ zig-zag chain (**89**) [426]. The mixed-metal analogues of the preceding complex, $Co_xNi_{2-x}(Edta).2H_2O$, have also been prepared. These solids are crystalline polymers with three crystallographically independent metal centres corresponding to the subunits MN_2O_4, MO_4 and MO_6, bridged via the carboxylate groups belonging to the edta ligand [427]. In addition, the same group have reported the synthesis and molecular structure of the Ni-Cu bimetallic complex with the edta-type ligand, glycine *N*,*N*′-1,2-cyclohexanedylbis[*N*-carboxymethyl] [428].

Turning to oxygen-bridging ligands, a new class of bimetallic isopropoxides of nickel(II) with niobium and tantalum, having the general formula, $Ni[M(OPr^i)_6]_2$ (M = Nb, Ta), has been reported. On the basis of a number of analytical, magnetic and spectroscopic studies, octahedral geometry has been assigned to the Ni(II) ion, while the secondary metallate derivatives alternate between octahedral and tetrahedral geometry [429].

The crystal structure of the mixed ligand tetranuclear nickel(II) complex, $[Ni(ex\text{-}a)(pym)]_4.Me_2CO$ (exa = *O*-ethylxanthate;pym = pyridine-2-methoxide), has



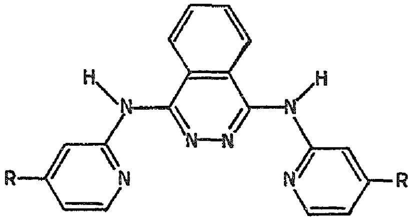
(89)

been determined using X-ray diffraction methods. The structure consists of a cubane-like cluster with four Ni and four bridging O atoms arranged at alternate corners of a distorted cube. The coordination geometry about each Ni atom is essentially distorted octahedral, consisting of a chelating xanthate ligand, three bridging oxygen atoms, and a nitrogen atom from the pyridine-2-methoxide ligand [430].

Polyketonate ligands and their ability to form polynuclear complexes continue to attract interest. The Ni(II) complexes of diethyl(2-oxocyclopentane-1,3-diyl)bisglyoxalate (H_2ecg) and diethyl-2,4,6-trioxoheptanediote (H_2decg) have been prepared and their bulk magnetic susceptibilities determined. Antiferromagnetic spin-spin coupling was observed for both complexes. In addition, the X-ray crystal structure of $[Ni(ecg)(py)_2]_2$ revealed a binuclear complex, with two coplanar triketonate dianions bridging two Ni atoms via a di-μ-oxo linkage. The Ni atoms are octahedrally coordinated by two pyridine molecules and four triketonate oxygen atoms [431].

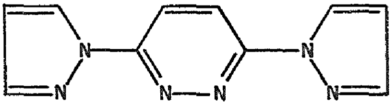
The bis-*N*-acylthiourea ligands, $[R_2NC(S)NHC(O)]_2C_6H_4$-*p* (H_2L), commonly function as bis-didentate chelating ligands forming dinuclear complexes. However, with deprotonation, they form the trinuclear Ni complexes, Ni_3L_3. In these complexes the oxygen atoms form part of the internal metalamacrocycles, while the S atoms constitute part of the external metalamacrocycles, as verified by an X-ray study of Ni_3L_3 (R = Et) [432].

Azine ligands have the potential to form both mononuclear and polynuclear complexes, depending on steric factors, the metal ion, and the reaction conditions employed. The tetradentate pyridyl phthalazine ligands {L = (**90**)} have been complexed with a variety of nickel(II) salts. Binuclear derivatives were obtained, except for the 6-methyl derivative where, due to steric factors, only a mononuclear complex was obtained. The single-crystal X-ray structure of the unsubstituted derivative, $[L_3Ni_2(H_2O)_2]Br_4.6H_2O$, was determined, revealing a binuclear Ni structure involving two bridging water molecules, a tetradentate bridging ligand (L) and two didentate ligands (L) [433]. The structurally related ligand 3,6-bis(1′-pyrazolyl)-pyridazine {ppd = (**91**)} has also been reacted with nickel(II) chloride. The resultant complex, $[Ni_2(ppd)_2(H_2O)_4]Cl_4.2H_2O$, is binuclear, in which the two pseudooctahedral Ni centres are bound simultaneously between two adjacent ppd ligands in a doubly-bridged structure. Significant antiferromagnetic exchange between the Ni(II) centres was observed [434].



R = H, 3-Me, 4-Me, 5-Me, 6-Me

(**90**)



(**91**)

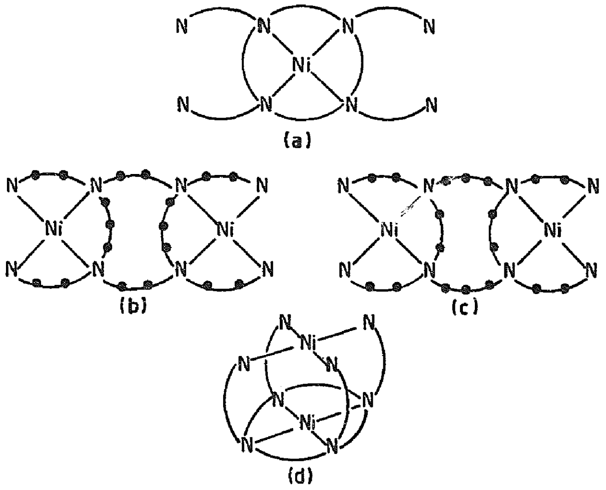
Triazoles, like the azine ligands described above, also have a tendency to form polynuclear complexes. Variously-substituted 1,2,4-triazoles have been complexed with nickel(II) fluoride. The resultant complexes have the general formula $Ni_3L_4F_2(NCS)_4(H_2O)_x$, in which the adjacent Ni ions are linked by two triazole ligands (L) and one fluoride anion [435]. In addition, the preparation of the two-dimensional polymeric triazole complex, $[Ni(NCS)_2(L)_2]_n$ (L = 1*H*-1,2,4-triazole), as well as the linear complex $[Ni(NCS)_2(L)_2]_3$ (L = 4*H*-1,2,4-triazole), have been reported [436].

Tetrazole has been reacted with Ni(II) chloride, yielding an amorphous compound with the general formula, $NiL_{1.5}Cl_20.5H_2O$ (L = tetrazole). X-ray diffraction indicates polymeric chains with bridging Cl atoms and tetrazole ligands, possibly in a similar fashion to compounds described earlier. Each Ni atom was assigned a coordination number of six [437].

The metal complexes of 2,5-di(2-pyridyl)-3,4-diazahexa-2,4-diene (PMK), with composition $NiM(PMK)_3$ (M = Ni, Zn, Cu), have been investigated using magnetic susceptibility, EPR and ^1H NMR. Magnetic coupling has been observed for the complex, $Ni_2(PMK)_3^{4+}$ [438].

The synthesis and structure of the heterodinuclear complex, (μ-imidazolato)bis(7-amino-4-methyl-5-aza-3-hepten-2-anato(1-)copper(II)nickel(II)perchlorate, have been reported. Each metal exhibits square planar coordination by two N atoms and one O atom of the terdentate Schiff base and one N atom of the deprotonated imidazole ligand, which functions as the bridging moiety [439].

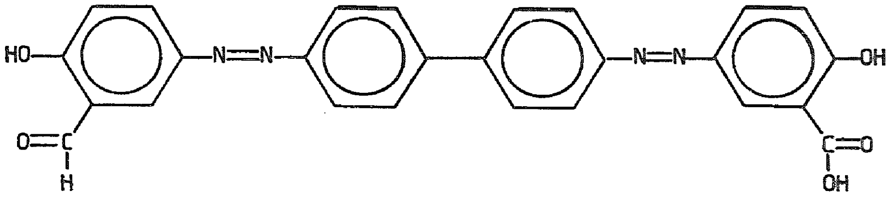
N,N′,N″,N‴-Tetrakis(2-aminoethyl)-1,4,8,11-tetraazacyclotetradecane (taec) and its binuclear nickel(II) complex, $Ni_2(taec)(ClO_4)_4$, have been synthesised and characterised. The pendant arm macrocycle (taec) has the capability of adopting a number of coordination modes (92) depending on the metal salt utilised. The crystal structure of $Ni_2(taec)(ClO_4)_4$ revealed essentially square planar coordination as shown in (b) [440].



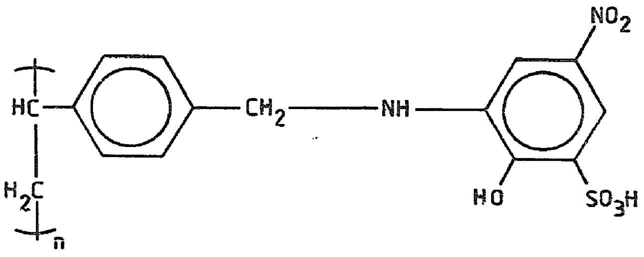
(92)

The Hoffman type inclusion compounds, $ML_2Ni(CN)_4$ (M = Ni, Cd; L = 2-methylpyridine), have been prepared and characterised using spectroscopic methods. The structures consist of corrugated polymeric layers of {M-Ni(CN)$_4$}$_\infty$, with 2-methylpyridine molecules bound directly to M. These compounds have the capability to act as host lattices in the formation of inclusion compounds with dioxane guest molecules [441].

To conclude, a number of Ni-containing polymeric complexes have been reported. These include the coordination complexes of monoarylthioureas [442], *o*- and *p*-tolylthioureas [443], polychelates of 4,4′-(4,4′-biphenylenebisazo)salicylaldehyde-salicylic acid (**93**) [444] and the mixed-ligand complexes of polystyrenemethyleneimino-4-nitrophenol-6-sulphonic acid and variously-substituted analine ligands (**94**) [445].



(**93**)

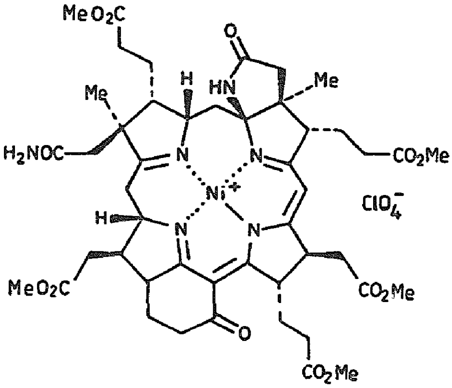


(**94**)

8. Nickel(I)

The pentamethyl ester of coenzyme F430 has been reversibly reduced from the Ni(II) form to the Ni(I) form (**95**). UV-visible and ESR spectra indicate that the Ni(I) complex is approximately square-planar with the unpaired electron in an orbital of $d_{x^2-y^2}$ character [446].

The cationic nickel(I) macrocycle complex, NiL$^+$=(1*R*,4*S*,8*R*,11*S*-1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(I), has been prepared

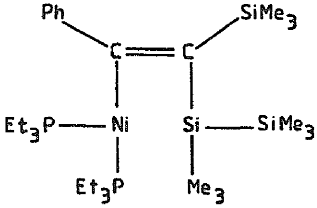


(95)

and reacted with a series of alkyl halides in aqueous alkaline solution. Alkylnickel(II) macrocycle complexes of the type $RNiL^+$ were formed. Kinetic data indicate that the reaction occurs in two steps, the first being a one electron transfer from NiL^+ to RX (X = halide), yielding an alkyl radical R. The second step involves rapid capture of the alkyl radical by NiL^+ [447,448].

9. Nickel(0)

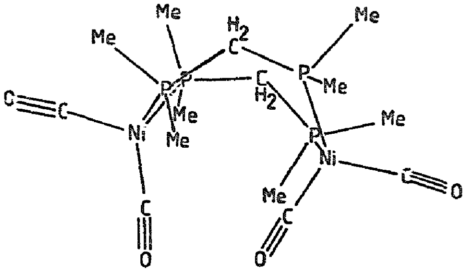
The nickelasilacyclobutene complex (96) has been prepared in solution, with its formation being followed using ^1H NMR spectroscopy. Apart from characterisation by ^1H, ^{13}C, ^{29}Si and ^{31}P NMR, a number of chemical reactions also support the proposed structure for (96) [449].



(96)

Ab initio MO calculations have been carried out on the terminal-phosphinidine complex $HPNi(CO)_3$. For the calculation, an idealized tetrahedral geometry was employed, as well as Ni-C and C-O bond lengths based on the well characterised $Ni(CO)_4$ complex. The P-H bond length was assumed to be 1.42 Å. Using these assumptions, the geometric optimisation yielded a staggered conformation, which was ascribed to the phosphorus lone pair [450].

A single-crystal X-ray determination of the reaction product of $Ni(CO)_4$ with the small-bite didentate ligand, bis(dimethylphosphino)methane, has revealed a dimeric structure, $[\mu\text{-}(CH_3)_2PCH_2P(CH_3)_2]_2Ni_2(CO)_4$, for what was previously assumed to be the monomeric complex, $[(CH_3)_2PCH_2P(CH_3)_2]Ni(CO)_2$. The coordination geometry about the two Ni atoms is essentially tetrahedral with a nonbonded Ni-Ni distance of 4.39 Å (97) [451].



(97)

The novel nickel(0) complex, $LiAlH_2(THF)_n.C_{10}H_8N_2.Ni$, has been prepared from (2,2′-bipyridyl)(1,5-cyclooctadiene)nickel. Both complexes are active as hydrodesulphurisation agents for aromatic sulfur heterocycles such as dibenzothiophene, phenoxathiin, phenothiazine and thianthrene, but give rise to different products. Ring opening generally accompanies desulphurisation using the former complex, while ring contraction occurs during desulphurisation with the latter complex. It has been concluded that these complexes desulphurise via single-electron-transfer mechanisms and that radical anions are crucial reactive intermediates [452].

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