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Nickel 1987–1989

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Contents

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Introduction

This review has been written to bridge the gap between the Nickel 1986 review and the Nickel 1990 review published in this series. It overviews work published between 1987 and 1989 inclusive, and is based on a data search of the coordination complexes of nickel listed in Chemical Abstracts for these years. Independent searches for this period have been carried out in the following journals: Inorganic Chemistry; Inorganica Chimica Acta; Journal of the Chemical Society (Dalton Transactions and Chemical Communications); Journal of the American Chemical Society; Polyhedron; Journal of Coordination Chemistry; Acta Crystallographica; and Coordination Chemistry.

Material has been arranged by oxidation state, with further subdivision in terms of ligand donor type. Complexes with mixed-donor ligands have been classified, wherever possible, according to the fundamental theme of the article in which they appeared. The review does not cover organometallic complexes, although complexes containing a significant number of classical coordination chemistry ligands have generally been included.

During 1987–1989, a number of general reviews have appeared including:

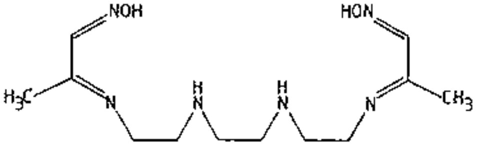
- A review of the general chemistry of iron, cobalt and nickel and their compounds. This review covers 1985 and contains 374 references [1].
- A review containing 165 references on spin equilibria in transition metal coordination compounds [2].
- An ongoing study on the thermal properties of solid nickel(II) coordination compounds. Part B of the study reports the chemical and physical factors affecting the thermal octahedral tautomerism square planar changes of Ni(II) complexes. Depending on the mode of coordination of the ligands, it was found that these transformations could be divided into two groups; octahedral monomer tautomerism square planar monomer, and octahedral polymer tautomerism square planar monomer changes [3].
- A review with 53 references entitled "Stable, two-coordinate, open shell d^0 d^9 transition metal complexes". This article examines the structural, chemistry of two-coordinate amide complexes of Cr, Mn, Fe, Co and Ni, including bulky ligands, silylamides and borylamides [4].

As in previous years, areas that have attracted considerable interest include complexes with macrocycle ligands, polynuclear complexes, complexes with ligands of a biological nature and the ubiquitous Schiff-base and related ligand complexes.

1. Nickel(IV)

A general paper has been published which looks at factors governing the stability of nickel(IV) and nickel(III) compounds. It was found that both the nature of the central atom and the ligand have an effect on the stability of the Ni(IV) and Ni(III) complexes, with polydentate ligands with a high electron density forming Ni(IV) and Ni(III) complexes, while ligands having an aromatic character tend to be preferably oxidised [5].

The kinetics and mechanism of the two-electron oxidation of the sexidentate bis(oxime-imine) ligand [H_2L = 3,14-dimethyl-4,7,10,13-tetraazahexadeca-3,13-diene-2,15-dione dioxime (**1**)] complex of nickel(II), [NiL], by bromine, have been investigated in bromide ion media over the pH range 3.1–7.6 at 25 °C and 1.0 M ionic strength. In the presence of an excess of bromine or nickel(II), oxidation is monophasic and the initial product is a formal Ni(IV) species, $[NiL]^{2+}$, which undergoes subsequent reactions to give an unknown oxidation product in the presence of excess bromine at $pH > 6$ or to give $[NIL]^+$ by comproportionation with excess nickel(II) at $pH > 5$ [6].

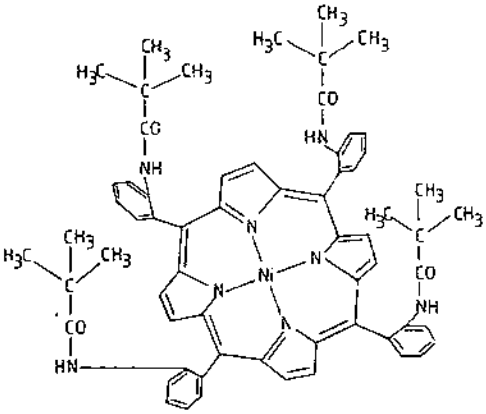


(**1**)

Variously substituted analogues of (**1**) have been prepared in which the methyl groups on the oxime-imine chromophores have been replaced by more bulky phenyl groups. The nickel(II) complexes of these ligands, [NiL], have been oxidised to their corresponding Ni(IV) and Ni(III) complexes. It was found that variation of the ligand structure had little effect on the reduction potentials of the complexes [7]. In addition, the kinetics and mechanisms of oxidation of $[Co(phen)_3]^{2+}$, $[Co(bpy)_3]^{2+}$, $[Co(4,7\text{-}Me_2phen)_3]^{2+}$ and $[Co(5,6\text{-}Me_2phen)_3]^{2+}$, using the nickel(IV) complexes, $[NiL]^{2+}$, have been investigated at 25 °C and 0.10 M ionic strength, using stopped flow spectrophotometry [8].

Rate studies have been carried out on the reduction of the nickel(IV) bis-oxime complex, bis(6-amino-3-methyl-4-azahex-3-en-2-one oximato)nickel(IV), $[NiL_2]^{2+}$, and on the reduction of the nickel(III) mono-oxime complex, 15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oximato)nickel(III), $[NiL^1]^{2+}$, using $[Co(phen)_3]^{2+}$ and hydroquinone as reductants. In addition, the kinetics of the oxidation of the nickel complex, $[Ni(HL^1)]^{2+}$, using the nickel(III) complex, $[NiL^2]^{3+}$ (L^2 = 1,4,7-triazacyclononane), as oxidant have been investigated [9].

The electrochemical and spectroelectrochemical characterisation of nickel(II) *meso*-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrin, (TpivPP)Ni = (**2**), in dichloromethane, benzonitrile and tetrahydrofuran, has been reported. The oxidative behaviour of this complex was found to be different from that of all previously studied porphyrins, and is reversibly oxidised by three electrons in two steps and generates as final product, $[(Tipvv)Ni]^{3+}$, which was characterised as a Ni(IV) cation radical in solution by both UV–VIS and ESR spectroscopy [10].



(2)

Metal and halogen absorption edge extended X-ray absorption fine structure (EXAFS) have been used to establish the structural parameters for Ni(II)–Ni(IV) mixed valence compounds [11].

2. Nickel(III)

The nickel(III) complex anion, *trans*-$[Ni(CN)_4(H_2O)_2]^-$, which has labile axial water molecules that are readily replaced by other ligands, has been prepared by the oxidation of $[Ni(CN)_4]^{2-}$ in aqueous solution. Nickel(III) complexes that have been prepared via this intermediate include $[Ni(CN)_4(NCO)_2]^{3-}$, $[Ni(CN)_4(Cl)_2]^{3-}$, $[Ni(CN)_4(NCCH_3)_2]^-$, $[Ni(CN)_4(py)_2]^-$, $[Ni(CN)_4(N_3)_2]^{3-}$, $[Ni(CN)_4(\text{imidazole})_2]^-$, $[Ni(CN)_4(NH_3)_2]^-$, $[Ni(CN)_6]^{3-}$ and $[Ni(CN)_4(bpy)]^-$. EPR spectra of the frozen aqueous solutions containing these complexes indicated a variety of tetragonally elongated complexes with two equivalent axial donor ligands [12].

2.1. Complexes with nitrogen donor ligands

Tetraaza macrocycle ligands have been used to great effect in the stabilisation of the nickel(III) oxidation state. The crystal structure of the nickel(III) complex with *meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L) has been determined as a mixed chloride, perchlorate salt, $[NiLCl_2]ClO_4$. The nickel atom essentially has an octahedral configuration surrounded by four N atoms of the macrocycle and two chloride ions in the *trans* axial positions. The coordination bond lengths are considerably shorter than the analogous nickel(II) complex [Ni–N = 2.011(2) and 1.983(2) Å, Ni–Cl = 2.4721(6) Å] [13].

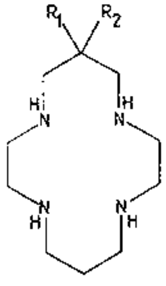
Pulse radiolysis has been used to generate Ni(III) and Ni(I) complexes of substituted tetraaza macrocycles from their corresponding nickel(II) precursors. Macrocycles employed in this study include 8-methyl-8-nitro-1,3,6,10,13,15-hexaazatricyclo[13.1.1.1^{13,15}]octadecane, 8-amino-8-methyl-1,3,6,10,13,15-hexaazatri-cyclo[13.1.1.1^{13,15}]octadecane, 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane and 9-methyl-9-nitro-1,4,7,11-tetraazacyclotridecane [14].

Hexakis(urea)manganese(III) has been used to oxidise a number of nickel(II) macrocyclic complexes to their corresponding nickel(III) complexes. The kinetics of the outer-sphere reduction of the hexakis(urea)manganese(III) ion by the nickel(II) macrocyclic compounds, [NiL]$(ClO_4)_2$ (L = 1,4,8,11-tetrazacyclotetradecane), [NiL_2]$(ClO_4)_2$ (L = 1,4,7-triazacyclononane) and [NiL]$(ClO_4)_2$ (L = 5,12-dimethyl-1,4,8,11-tetrazacyclodeca-4,11-diene) were determined in acetonitrile at 25 °C [15]. Similarly, the outer-sphere electron transfer between the nickel(II) complex ion, [Ni(cyclam)]$^{2+}$, and a number of copper(III) imine–oxime complexes has been investigated. The results of the kinetic studies of the oxidation of [Ni(cyclam)]$^{2+}$ by the CU(III) complexes revealed an outer-sphere electron-transfer process for the square planar oxidant and reluctant complexes [16].

The synthesis of (*R*)-2-methyl-1,4,7-triazacyclononane and the preparation of its nickel(II) and nickel(III) complexes, bis[(-)-(*R*)-2-methyl-1,4,7-triazacyclononane]nickel(II) and -nickel(III), have been reported. It was found that the NiN_6 chromophore was retained in both oxidation states.

The nickel(II) species was found to be very stable in aqueous media with a slow, acid-catalysed hydrolysis, while the nickel(III) ion showed only slight decomposition at pH 3, and was indefinitely stable in acetonitrile [17].

Fluorine-containing cyclams (**3**) have been prepared for the first time. Nickel(II) complexes of (**3**) have been prepared and isolated. In addition, the effect of F substitution on their electrochemical properties has been investigated. It was found that upon fluorination, the higher oxidation state of nickel(III) became successively destabilised with respect to nickel(II), while the lower oxidation state of nickel(I) became successively stabilised with respect to nickel(II) [18].



R_1 = H, F; R_2 = H, Me, F

(**3**)

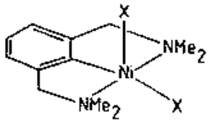
Studies have been carried out on the methyl(cyclam)nickel(III) dication in aqueous solution. The kinetics of reactions involving homolysis, O_2 insertion and methyl transfer to Cr(II)(aq) have been determined, and the properties of new intermediates discussed. In addition, the biological relevance of these intermediates has been pointed out [19].

The kinetics and mechanism of reduction of several nickel(III) tetraaza macrocyclic complexes by iodide ion have been determined in perchlorate media. Complexes studied included $[NiL](ClO_4)_2$ (L = α-*C-meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetra-decane, *C-rac*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane, *C-meso*-5,12-diethyl-1,4,8,11-tetraazacyclotetra-decane, *C-rac*-5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). The reaction order was found to be unity with respect to both $[Ni^{III}L]$ and $[I^-]$ over a large range of I ion concentration [20].

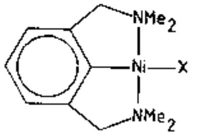
The complexes $NiLX_2$ (L = *N*-cetylcyclam; X = Cl, ClO_4) have been synthesized as potential carriers for the transport of electrons across a CH_2Cl_2 bulk liquid membrane via the Ni^{II}/Ni^{III} redox change. Two-phase (water/dichloromethane) experiments have shown that aqueous peroxydisulphate ion is able to oxidise $Ni^{II}LCl_2$, but not $Ni^{II}L(ClO_4)_2$, due to the very large difference in the Ni^{II}/Ni^{III} redox potentials. However, the $[Ni^{III}LCl_2]Cl$ complex in the organic layer can be reduced by a series of aqueous cationic reducing agents [21].

The one-electron reduction of the NI(III) ion by hydroxylamine and hydrazine has been investigated in aqueous solution using iodometric methods in the presence and absence of 2,2′-bipyridine. The order in Ni(III) ion concentration was found to be unity in all cases, while the order in hydroxylamine and hydrazine concentration was found to be fractional in the absence of 2,2′bipyridine, changing to unity in the presence of 2,2′-bipyridine [22]. This work has been extended by the same group to include ethanolamine, diethanolamine and triethanolamine. The order with respect to [Ni(III)] was again found to be one, while the order with respect to amine was fractional [23].

Oxidation of the Ni(II) species (**4a–e**) by CuX_2 (X = Cl, Br) and I_2 (X = I) has resulted in formation of the Ni(III) species (**5a–e**). ESR spectroscopic data for (**5a–e**) indicate a d^7 electronic configuration. In addition, a crystal structure determination of the iodo analogue (**5c**) has verified a square-pyramidal coordination geometry for the Ni(III) centre [24].



X = Cl, Br, I, NO_3, NO_2
(4)



X = Cl, Br, I, NO_3, NO_2
(5)

2.2. *Complexes with phosphorus donor ligands*

The electronic spectrum of the nickel(III) complex, dichlorobis[*o*-phenylenebis-(dimethylphosphine)]nickel(III) hexafluorophosphate, has been determined at 19 and 298 K. Results obtained were found to be in agreement with a previously determined crystal structure which showed the four phosphorus atoms of the bidentate ligands occupying the equatorial plane and two chloride atoms occupying *trans*-axial positions [25].

2.3. *Complexes with sulphur donor ligands*

Various dithiolene nickel(III) complexes have been prepared. The synthesis of the 1,2-dithiolene dianion, bis(methylthio)-1,2-dithiolate, together with its bis complexes with Ni(III), PD(III) and Pt(III) have been reported. In addition, the reduced M(II) species were also isolated in an oxygen-free environment [26].

X-ray crystallography has been used to determine the structure of the tetramethylammonium salt of $Ni(DDDT)_2^-$, where $DDDT^{2-}$ is the dithiolato ligand, 5,6-dihydro-1,4-dithiin-2,3-dithiolato. The Ni(III) complex was found to possess square planar coordination with an average Ni–S bond length of 2.146(2) Å [27].

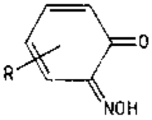
A series of mixed-valence compounds of general formula Ni(OAc)(LLLL)Ni(tdt)$_2$ (tdt = toluene-3,4-dithiolate, LLLL = tetradentate N_2S_2 donor ligand with two benzimidazole groups and two thioether groups) has been prepared. Spectroscopic data indicate that the compounds consist of octahedral $[Ni(LLLL)(OAc)]^+$ cations in which nickel is divalent, and square planar $[Ni(tdt)_2]^-$ anions in which nickel is trivalent. The crystal structure of the analogue in which LLLL = 1,6-bis(benzimidazol-2-yl)-2,5-dithiahexane (bbdh) has been determined. Two anions, $[Ni(tdt)_2]^-$, with Ni–S distances of 2.140(2)–2.153(2) Å, lie on centres of symmetry. The cation, $[Ni(OAc)(bbdh)]^+$, was found to be hexacoordinate via coordination by two oxygens of acetate [Ni–O = 2.108(4) and 2.137(4) Å], two nitrogen atoms of the benzimidazoles [Ni–N = 2.026(5) and 2.047(5) Å[, and two sulphur atoms of the thioethers [Ni–S = 2.415(2) and 2.416(2) Å] [28].

2.4. *Complexes with nitrogen–oxygen and nitrogen–sulphur donor ligands*

Cyclic terdentate ligands have been used to stabilise the nickel(III) oxidation state via 1:2 coordination. The octahedral six coordinate complex cations, $[Ni(L^2)_2]^{2+}$ (l^2 = 1-oxa-4,7-diazacyclononane) and $[Ni(L^3)_2]^{2+}$ (L^3 = 1-thia-4,7-diazacyclononane), have been oxidised in acetonitrile and dmso solution to their corresponding Ni(III) species. These species were found to exhibit a distorted stereochemical arrangement with the O and S heteroatoms occupying the axial sites of an elongated octahedron [29]. In addition, the same group has determined the entropy changes associated with the two half reactions: (i) $[Ni^{III}L_2]^{3+} + e^- \rightleftharpoons [Ni^{II}L_2]^{2+}$ (L = 1,4,7-triazacyclononane); and (ii) $[Ni^{III}Y]^0 + e^- \rightleftharpoons [Ni^{II}Y]^-$ (Y = 1,4,7-triazacyclononane-*N*,*N'*,*N''*-tri-acetate) through investigation of the temperature dependence of the $E_{1/2}(Ni^{III}/Ni^{II})$ parameter over the 0.1–3.5 M concentration range of the background electrolyte (NaCl) [30].

The oxidation of a series of nickel(II) bis(salicylaldimine) complexes has been examined using cyclic voltammetry. Reversible oxidation was observed in strong donor solvents, but in weak donor solvents the complexes were found to undergo oxidative polymerisation at the electrode surface. A ligand radical coupling mechanism involving the phenolic portion of the salicylaldemine chelate has been proposed, while the solvent dependence was explained in terms of the ability of the solvent to stabilise the Ni(III) oxidation state relative to ligand-localised oxidation [31].

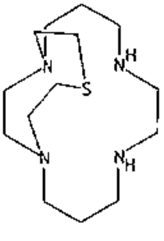
A series of tris chelate complex anions, $[Ni^{II}(RQ)_3]^-$, derived from the 1,2-quinone 2-oximes [HRQ=(**6**)], has been studied in acetonitrile solution using ^1H NMR spectroscopy and cyclic voltammetry. The complexes occur as equilibrium mixtures of *fac* and *mer* isomers and display the reversible nickel(III)–nickel(II) couples, *fac*-$Ni(RQ)_3$–*fac*-$[Ni(RQ)_3]^-$ and *mer*-$Ni(RQ)_3$–*mer*$[Ni(RQ)_3]^-$ [32].



R = 4-Me, 4-Bu^t, 4-Cl, 3,4-benzo
(6)

The dipeptide of α-aminoisobutyric acid (HL) has been complexed with Ni(II), yielding a high-spin complex, $[Ni^{II}(HL)(L)]^-$, which changes with pH to a low-spin complex, $[Ni^{II}(L)_2]^{2-}$, with loss of a proton and formation of a second Ni(II)–N(peptide) bond. Other dipeptides were found to form tetragonally compressed six-coordinate bis complexes, but change of spin with pH was only observed when α-aminoisobutyric acid was the second residue. This was attributed to the electrondonating effect of the α-carbon methyl groups on the ligand field strength. Oxidation of the low-spin complex produced a tetragonally compressed nickel(III) complex, $Ni^{III}(L)_2^-$, that was found to be very stable in neutral and basic solutions [33]. The same group have used a novel method, based on the influence of ^{61}Ni on the room-temperature EPR spectra of Ni(III) complexes, to measure the electron-transfer self-exchange rate constants of Ni(III,II) complexes. This technique was applied to the nickel/α-aminoisobutyric acid system described earlier [34].

15-Thia-1,5,8,12-tetraazbicyclo[10.5.2]nonadecane [L=(**7**)] has been prepared and completed with nickel(II). The X-ray crystal structure of the resultant complex cation, $[Ni(L)(ClO_4)]^+$, isolated as its perchlorate salt, has been determined. The complex is pseudo-octahedral with Ni–N varying from 2.0559(5) to 2.087(5) Å, Ni–S=2.385(2) Å, and Ni–$OClO_3$=2.563(6) Å. The nickel complex was oxidised in acetonitrile via cyclic voltammetry to the corresponding nickel(III) complex. In



(7)

aqueous solution, the Ni(III) complex can be generated chemically. Both the Ni(II) and Ni(III) complexes were found to be six-coordinate in solution [35].

3. Nickel(II)

3.1. *Complexes with nitrogen donor ligands*

By way of introduction to this section, two interesting reviews have appeared. The first, which contains 37 references, looks at the reactions of coordinated ethylenimine in nickel complexes [36], while the second, which contains 106 references, examines the coordination chemistry of a potentially heptadentate ligand, $L = N\{CH_2CH_2N{=}C(H)(C_5H_4N)\}_3$, with a series of 3d transition metal ions [37]. In addition, a general paper has appeared that investigates the metal–ligand bonding parameters and magnetic properties of some previously reported tetragonal nickel(II) complexes. Complexes studied include $[Ni(py)_4X_2]$ (py = pyridine), $[Ni(Hpz)_4X_2]$ (Hpz = pyrazole), $[Ni(mim)_4X_2]$ (mim = 2-methylimidazole) (X = Cl or Br) and $[Ni(en)_2(NO_2)_2]$ (en = 1,2-diaminoethane) [38].

Numerous monodentate amine ligands have been completed with nickel(II). These include ammonia [39], tetrahydrothiamine and its phosphate esters [40], bis(sulphuryl fluoride)amine [41] and bis(benzylidene)benzidine [42]. Crystal structures have also been reported for tetrakis(methoxyamine)bis(isothiocyanato)nickel [43], tetrakis(benzylamine)diisothiocyanato-nickel(II) and tris(benzylamine)diisothiocyanato(1-phenyl-1-ethylamine)nickel(II) [44], while host complexes of $Ni(NCS)_2$(1-phenyl-1-ethylamine)$_4$, prepared from racemic and enantiomerically pure amine and its clathrates with *sec*-butylbenzene and *o*-xylene have been examined by X-ray diffraction [45].

The complexation of a series of alcoholamine ligands with nickel(II) has been investigated in aqueous solution via potentiometric titration. Ligands investigated consisted of $HOCH_2CH_2NR_1R_2$ (R_1 and $R_2 = CH_3$ or CH_2CH_3) [46]. In addition, the formation constants and associated thermodynamic parameters have been determined by spectrophotometric and calorimetric methods for Ni(II) complexes with mono-, di-, and triethanolamine in methanol and dmf. The stabilities of the complexes were found to be controlled by the nature of the solvent [47].

1,2-Diaminoethane and related ligands constitute a large class of didentate-functioning diamine ligands that have been complexed with nickel(II). Table 1 summarises some of the studies that have been carried out with these ligands [48–68]. Of interest are the number of thermal studies in which solid-state square planar⇔octahedral isomerisation has been observed. This is further exemplified in work in which the thermal reactions of the penta-coordinated nickel(II) complexes, $[NiX(NH_3)L]X \cdot nH_2O$ [$L = (Me_2NCH_2CH_2)_2NMe$; X = Cl, Br, I; $n = 0, 1$] and $[NiQL]X_2$ ($Q = NH_3$, CH_3CN; $X = ClO_4$, BF_4), have been reported. In the solid-state thermal reaction, the first series of complexes evolved 1 mol of NH_3 to undergo anation, while the second series evolved 1 mol of Q to convert into square planar complexes [69].

Table 1
Nickel(II) complexes with 1,2-diaminoethane and related ligands

Ligand	Complex	Comments	Ref.
1,2-Diaminoethane (en)		$Ni(en)_3^{2-} \rightarrow Ni(en)_2(H_2O)_2^{2-} \rightarrow Ni(en)(H_2O)_4^{2-} \rightarrow Ni(H_2O)_6^{2-}$. Visible spectra of the the complex species from kinetic studies.	[48]
		Thermometric study.	[49]
		Thermochemical study in aqueous solution at 25 and 35 C.	[50]
		Thermodynamic study in aqueous ethanol solution. The influence of solvent on complexation was studied.	
		Use of Österberg's method to study the formation of nickel(II) complexes in en-water as a function of pH.	
		Calorimetric study of the formation of mixed-ligand complexes of Ni(II) with en and iminodiacetate.	
		Stepwise stability constants determined for mixed ligand complexes of Ni(II) with en and thiosalicylic acid.	[54]
	$[Ni(en)_3]WO_4$	Octahedral complex. Spectroscopic and X-ray powder study.	[55]
N,N'-Dimethyl-1,2-diamine (L)	$[NiL_2(NCS)_2]$	X-ray crystal structure determination. Octahedral coordination with NCS ligands in *trans*-axial positions.	[56]
N,N'-Bis(para-substituted phenyl)ethlyenediamine (L)		Complex formation constants with Ni(II) were determined by pH-titration in 50% aqueous dioxane and 70% aqueous ethanol.	[57]
Aminoethylaminoethanol (L)	$[NiL_2(NCS)_2]$	X-ray crystal structure determination. Octahedral coordination with NCS ligands occupying *trans*-axial positions.	[58]
2-(2'-Acetoxyethylamino)-ethylamine (L)	$NiLCl_2.0.25CH_3OH$	Spectroscopic and magnetic data indicate octahedral coordination for Ni(II).	[59]
	$NiLBr_2.0.25C_2H_5OH$		
$H_2NCH_2CH_2NHCH_2CH_2SPh$ (L)	NiL_2Cl_2	L is didentate, coordinating via 2N atoms.	[60]
(*R,R*)-1,2-Cycloheaxanediamine (L)	$[NiL_3]Br_2$	X-ray crystal structure determination. Octahedral coordination with a *lel* form resulting in the absolute configuration Λ.	[61]
dl- or *meso*-1,2-Cyclohexane-diamine (L)	$[NiL_2]X_2$	X = Cl, Br, NO_3. Thermal octahedral⇔square planar tranformation in the solid phase.	[62]
2,3-Diiminonaphthalene and 9,10-diiminophenanthrene (L)	NiL_2	NiL_2I_x (x = 0.13–3.30) were prepared by iodination of the original complexes.	[63]
1,5-Diazacyclooctane (L)	$[NiL_2](ClO_4)_2$	300 MHz proton NMR spectrum in D_2O.	[64]
Propane-1,3-diamine (L)	$[Ni(L)_2(NO_2)_2]$	Solid state thermal isomerisation $[Ni(L)_2(NO_2)_2] \rightarrow [Ni(L)_2(NO_2)](NO_2)$].	[65]

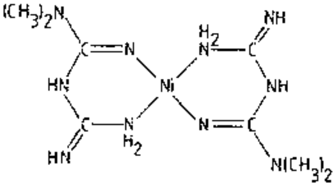
Table 1 (*continued*)

Ligand	Complex	Comments	Ref.
	$[Ni(L)_2(NO_3)](BPh_4)$	Crystal and molecular structure determination. Hexacoordinate with the nitrate ion functioning as a didentate, *cis*-coordinating, ligand.	[66]
Diethylenetriamine (L)		Stepwise stability constants determined for mixed ligand complexes of Ni(II) with en and thiosalicylic acid.	[54]
	$[NiL_2]WO_4$	Octahedral study. Spectroscopic and X-ray powder study.	[55]
2-Methyl-1,2-propanediamine (L)	$[NiL_2](ClO_4)_2$	Crystal and molecular structure. The Ni atom is essentially square planar coordinated by two didentate functioning L ligands.	[67]
1,2-Butanediamine (L)	$[Ni(L)_2(H_2O)_2]X_2$	X = Cl, Br, NO_3, ClO_4. Thermal octahedral<>square planar tranformation in the solid phase.	[68]
	$[Ni(L)_2]X_2$		
	$[Ni(L)_2X_2]$		
3,3-Dimethyl-1,2-butanediamine (L)	$[Ni(L)_2(H_2O)_2]X_2$	X = Cl, Br, NO_3, ClO_4. Thermal octahedral<>square planar transformation in the solid phase.	[68]
	$[Ni(L)_2]X_2$		
	$[Ni(L)_2X_2]$		

The compound $Ni(BiF_6)_2$ has been prepared, together with the ternary adducts $[Ni(CH_3CN)_6](BiF_6)_2$ and $[Ni(CH_3CN)_6](SbF_6)_2$. In addition, the crystal and molecular structure of $[Ni(CD_3CN)_6](SbF_6)_2$ has been determined. The Ni ion was found to be octahedrally coordinated by six acetonitrile ligand molecules via the nitrogen atoms [Ni–N = 2.07(1) Å] [70].

The 1:1 nickel(II) and copper(II) complexes of 3,7-dimethyl-1,5-diphenyl-3,7-diazabicyclo[3.3.1]nonan-9-one (L), $MLCl_2$, have been prepared and isolated. The crystal structure of the Cu(II) complex has been determined, revealing distorted tetrahedral coordination, in which L is coordinated in a didentate manner via the two N atoms [71].

Complexes of metal(II) ions with metformin have been synthesized and characterised by elemental analysis, IR, electronic, ^1H NMR and EPR spectra. Based on these data, the bonding of the nickel ion in the nickel(II) complex has been postulated as shown in (**8**). In addition, formation constants of the complexes have been evaluated by potentiometric techniques [72].

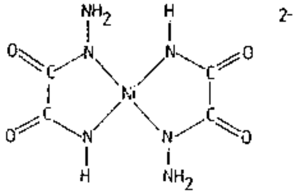


(8)

The overall formation constants of the complexes formed between Ni^{2+} and 2-amino-*N*-hydroxypropanamide have been measured at 25°C and $I = 0.5\ mol\ dm^{-3}$ (KCl). A square planar ligand field model (NiL_2) has been used to calculate ligand-field parameters. In addition, complexes with monoaminohydroxamic acids and Ni^{II} were shown to involve chelation via the hydroxamate moiety NHO⁻ and the amino group NH_2, which are pH sensitive [73].

The average structure of bis(oxamide oximato)nickel(II) × dimethyltetracyanoquinodi-methane × 2methanol has been reported. The complex is essentially planar in which the ligands coordinate in a didentate fashion via their nitrogen donor atoms, with Ni–N bond lengths of 1.853(4) and 1.841(4) Å. Mixed stacks of alternating, mainly neutral, nickel complex and dimethyltetracyanoquinodimethane molecules were formed [74]. Similarly, the related complex salt, [bis(oxamideoximato)nickel(II)][bis(oxalato)platinum(II)]dihydrate] × [bis-(oxamide oximato)nickel(II)], has been prepared and its crystal structure detemined. Segregated parallel stacks of $[Pt(C_2O_4)_2]^{2-}$ anions, $[Ni(C_2H_6N_4O_2)_2]^{2+}$ cations, and neutral $[Ni(C_2H_5N_4O_2)_2]$ complex molecules were found, interlinked by a network of strong intermolecular hydrogen bonding. Essentially square planar geometry was observed for both the nickel cation and neutral nickel complexes [75].

The vibrational spectra of the Ni(II) complex with oxamic hydrazide, as well as its thermal analysis, have been discussed. In this study, the spectra were consistent with the complex anion having the square planar structure as shown (**9**), with coordination occurring via the four amide nitrogen atoms [76].



(9)

The syntheses of 1-amidino-*O*-alkylurea sulphates (alkyl = *n*-propyl, *n*-amyl, *sec*-butyl) and their corresponding nickel(II) chloride and sulphate complexes have been described. Electronic spectral and magnetic data were found to be consistent with square planar stereochemistry, while bi-univalent electrolyte conductances were observed in aqueous solution [77].

Hydrazine and a number of its variously substituted analogues have been complexed with Ni(II). Complexes of nickel acetate with hydrazine that have been prepared and characterised include $Ni(CH_3COO)_2 \cdot 4N_2H_4$, $Ni(CH_3COO)_2 \cdot 2N_2H_4$ and $Ni(CH_3COO)_2 \cdot 2N_2H_4 \cdot 2H_2O$ [78]. Reaction of ethylhydrazine (EH) with nickel(II) salts yielded complexes of the type, $NiCl_2(EH)_2$ and $NiBr_2(EH)_2(H_2O)$, with spectroscopic evidence indicating that these complexes contain bridging hydrazine ligands. However, reaction of 2,2,2-trifluoroethylhydrazine (TFEH) with nickel salts produced complexes of the type $NiX_2(TFEH)_4$ (X = NCS, Cl), for which spectroscopic evidence indicated unidentate coordination by the hydrazine ligands. A crystal structure determination of $NiCl_2(TFEH)_4$ confirmed that the hydrazine ligand bonds to nickel through the NH_2 nitrogen only, in a tetragonal structure with axial chlorine atoms [79].

The synthesis and crystal structure determination of the complex (1,4-diphenyltetrazinido)bis(diphenylmethylphosphine)nickel, have been reported. Coordination about nickel was described as a tetrahedral, with distortion towards square planar. The 1,4-diphenyltetrazinido ligand functions in a didentate fashion with very short Ni–N bond lengths of 1.876(5) Å [80].

The interaction of thiocyanate ion with nickel(II) has been investigated in dmso. Visible absorption spectra and molar conductance curve data indicated the formation of mono- and dithiocyanate complexes in the Ni^{2+}–NCS^-–dmso system. Stability constants for these complexes were also determined [81]. In addition, the crystal structure of the complex $M[Ni(NCS)_4]$ [M = *p*-xylene-bis(tetraphenylphosphonium)$^{2+}$] has been determined. $[Ni(NCS)_4]^{2-}$ was found exist as pseudo-tetrahedral polyhedra which are distorted by packing forces and vibronic coupling effects of the Jahn–Teller type [82].

Turning to heterocyclic base ligands, pyridine and its variously substituted analogues are ubiquitous within this class of ligand. Table 2 lists some of these ligands and their corresponding nickel(II) complexes [83–100]. Extensive work has been published relating to their use as Werner Clathrates [87–90].

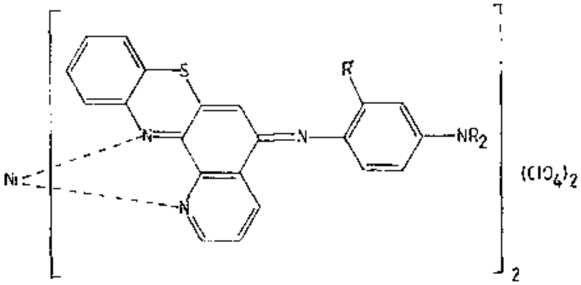
Table 2
Complexes of pyridine and its variously substituted analogues with nickel(II)

Ligand	Complex	Comments	Ref.
Pyridine (py)	[Ni(py)$_4$]Cl$_2$	Stepwise thermal decomposition. X-ray powder diffraction used to study the intermediates Ni(PY)$_2$Cl$_2$, Ni(PY)Cl$_2$ and Ni(PY)$_{2.3}$Cl$_2$.	[83]
	[Ni(L)$_2$Cl$_2$]	L py and quinoline. Single crystal electronic spectra of the tetragonal complexes measured with polarised light at liquid N$_2$ temperatures.	[84]
Pyridine; 3-methylpyridine; 3,4-dimethylpyridine; 3,5-dimethylpyridine;	Ni(L)$_5$ (NO$_3$)$_2$	ESR spectral study indicates octahedral distortion of these complexes to a seven coordinate structure.	[85]
Pyridine; 2-, 3-chloropyridine; 2,4-, 3,4-, 3,5-, 2,6-lutidine		Spectroscopic study of the interaction of these bases with nickel(II) acetate in acetic acid, with special emphasis given to the ionization of the solutes.	[86]
4-Ethylpyridine	[Ni(L)$_4$(NCS)$_2$]	X-ray crystal structure of the host complex and its Clathrates with *p*-, *m*-, and *o*-Xylene, carbon disulphide and carbon tetrachloride.	[87]
4-Vinylpyridine	[Ni(L)$_4$(NCS)$_2$].2CCl$_4$ [Ni(L)$_4$(NCS)$_2$].CHI$_3$ [Ni(L)$_4$(NCS)$_2$]-[Ni(L)$_3$(thf)(NCS)$_2$].2CHI$_3$	Studies in Werner Clathrates. Crystal structures of the complexes have been elucidated. Carbon tetrachloride clathrate has a similar packing to the previously described chloroform analogue. There is significant secondary bonding between the S (donors) and I (acceptors) in the iodoform-containing clathrates.	[88]
4-Phenylpyridine	[Ni(L)$_4$(NCS)$_2$]	Studies in Werner Clathrates. The crystal structures of the host complex (L = 4-phenylpyridine) and mixed guests (4-phenylpyridine + dmso), (4-phenylpyridine + 2-methoxyethanol), and (phenylacetylene + dmso) have been determined.	[89]
	[Ni(L)$_4$(NCS)$_2$]	Studies in Werner Clathrates. The crystal structure and thermal analysis of the benzene clathrate have been elucidated.	[90]
2-Aminopyridine		Spectrophotometric study of the coordination sphere of Ni(II) 2-aminopyridine complexes in aqueous ethanol solution.	[91]
2-Amino-5-methylpyridine		Spectrophotometric study of Ni(II) and L in aqueous ethanol solution.	[92]
2-Cyanopyridine; pyridine-2-carboxamide; *O*-methylpyridine-2-carboximidate; *N*-methylpyridine-2-carboximidate	[Ni(H$_2$O)$_2$L$_2$]X$_2$ [NiX$_2$L$_2$] [NiL$_3$]X$_2$ (X = Cl, Br, I, NCS)	The coordination of 2-cyanopyridine to Ni(II) was found to promote a nucleophilic addition of solvent molecule. Addition of water leads to the formation of solid complexes containing pyridine-2-carboxamide as a chelate ligand. However, an analogous reaction of 2-cyanopyridine with NX$_2$ in methanolic solutions gives complexes containing two or three molecules of *O*-methylpyridine-2-carboximidate.	[93]

Table 2 (*continued*)

Ligand	Complex	Comments	Ref.
Pyridine-2-amidoxime	$[NiL_2(NO_3)_2]$	Synthesis and X-ray crystal structure determination of both complexes.	[94]
	$[NiL_3](NO_3)_2$	Both complexes have a slightly distorted octahedral structure. L coordinates via the heterocyclic and oxime N atoms in both complexes.	
Pyridine-2-aldoxime		Nickel(II) complex formation was studied by emf titration in aqueous solution.	[95]
Pyridine-2-azo-*p*-dimethylaniline		The kinetics of formation of the Ni(II) complexes were studied in aqueous ethyleneglycol, aqueous glycerol and moderate NaCl solutions.	[96]
2-Methyl-4-(pyridin-2-yl)thiazole; 4-methyl-2-(pyridin-2-yl)thiazole; 2-(6-methylpyridin-2-yl)thiazole	$[NiL_3](ClO_4)_2$	Magnetic, spectroscopic and structural characterisation. The crystal structure of the complex with L 4-methyl-2-(pyridin-2-yl)thiazole has been reported. L functions as a N,N didentate chelating ligand.	[97]
R-2,6-Di-iminopyridyl (R = Et, Ph, CH_2Ph, $(CH_2)_3Ph$)	[NiL2](BF4)2	The crystal structure of the complex with R · $(CH_2)_3Ph$ has been determined, revealing distorted octahedral coordination for Ni(II). Four imine *N* donors occupy the equatorial sites, while two pyridyl *N* donors occupy the axial sites.	[98]
2,2′:6′,2″-Terpyridine	$[NiL(NO_2)(ONO)(H_2O)]$	X-ray crystal structure determination. 2,2′:6′,2″-Terpyridine functions as a tridentate ligand. Distortion from the octahedron to a trigonal prism has been observed.	[99]
	$[NiL(NCO)_2(H_2O)]$	X-ray crystal structure determination. Distorted octahedral coordination with 2,2′:6′,2″-terpyridine functioning as a tridentate ligand.	[100]

New nickel(II) complex dyes containing *N,N*-didentate pyrido[2,3-*α*]phenothiazine-type ligands have been prepared. These ligands were found to form chelate complexes readily with nickel(II), with coordination occurring via the nitrogen of the pyridine moiety and N(10), as shown in (**10**) [101].



R = Me, Et; R′ = H, Me

(10)

The use of ligands with multiple pyridine rings has also attracted interest. Apart from the more common 2,2′:6′,2″-terpyridine ligand [99,100], the potentially pentadentate ligand 2,2′:6′,2″:6″,2‴:6‴,2⁗-quinquepyridine has been complexed with nickel(II). The X-ray crystal structure of the resultant double helical bis-nickel(II) complex, $[Ni_2L_2(OAc)][PF_6]_3 \cdot 3MeCN$, has been reported, together with its electrochemical properties [102].

In a continuing study of the metal amide bond, a comparison of molecular distortions in the crystal structures of [*N,N*′-bis(2′-pyridinecarboxamido)-1,2-benzene]nickel(II) with its 6′-methylsubstituted analogue has been reported. Both complexes were found to be diamagnetic with essentially square planar stereochemistry for the Ni(II) ions [103].

The linear, pyridine-containing, pentadentate ligand, 1,9-bis-(2-pyridyl)-2,5,8-triazanonane (L), has been reacted with nickel(II) and copper(II) salts. The X-ray crystal structure of the copper complex cation, $[Cu(L)]^{2+}$, revealed a distorted square-based pyramidal structure for the metal ion, while spectroscopic and magnetic data led the authors to propose a trigonal bipyramidal structure for the nickel cation, $[Ni(L)]^{2+}$ [104].

Numerous studies involving the complexation of nickel(II) with 2,2′-bipyridine [105–111,113], 4,4′-bipyridine [112] and 1,10-phenanthrolene [111,113–116] have been reported. Details of these studies and the complexes formed are listed in Table 3.

The influence of ligand properties on the stoichiometry and stereochemistry of solid thiocyanate nickel(II) complexes with variously substituted piperidine derivatives has been investigated. The complexes prepared have been arranged into three groups by their composition:

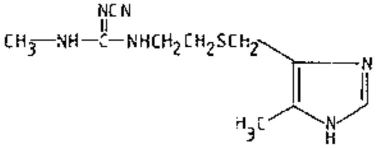
- $Ni(NCS)_2(pip)_4$ (pip = piperidine) with monomeric pseudo-octahedral coordination;
- $Ni(NCS)_2(L)_3$ (L = 4-methylpiperidine, 3,5-dimethylpiperidine) with trigonal bipyramidal coordination;

- $Ni(NCS)_2(L)_2$ with polymeric pseudo-octahedral coordination (L = piperidine, 4-methylpiperidine and 3,5-dimethylpiperidine) or square planar coordination (L = 2-methylpiperidine and 2,6-dimethylpiperidine).

These results were discussed in relation to the analogous complexes with pyridine ligands [117].

Turning to imidazole and related ligands, the crystal and molecular structure of tetrakis(1,2dimethylimidazole)nickel(II) diperchlorate and its corresponding Cu(II) complex have been determined. The Ni^{II} ion was found to be tetra-coordinated in a distorted square planar coordination environment to four N atoms of the dimethylimidazole ligands. Relevant crystal data are Ni–N = 1.888(5), 1.898(4), 1.903(4) and 1.911(4) Å [118].

The thermal behaviour of $NiL_2Cl_2 \cdot 2H_2O$ [L = cimetidine (**11**)] has been studied using TGA and DSC. The complex decomposed in two steps, namely dehydration and decomposition. Decomposition products were characterised by X-ray powder diffraction, and activation energies and heats of dehydration were determined [119].



(**11**)

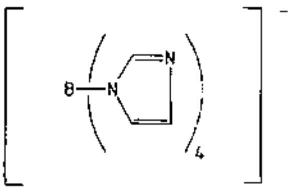
A number of 2-R-substituted-benzimidazole (R = Et, Pr, *iso*-Pr, *o*-aminophenyl, furyl) ligands have been reacted with Ni(II) halides. The resultant complexes, NiL_2X_2 (X = Cl, Br), varied in structure, depending on the R-substituent. Complexes with R = Et, Pr, *iso*-Pr were found to be tetrahedral, while those with R = *o*-aminophenyl and R = furyl, were found to be octahedral and square pyramidal, respectively. Complexes were characterised via spectroscopic and magnetic susceptibility methods [120].

Tetrakis(imidazolyl)borate anion, L = (**12**), has been synthesized and reacted with nickel(II). The resultant complex, NiL_2, has been characterised by chemical analysis, magnetic susceptibility, and IR and ligand field spectra. The authors have tentatively assigned an octahedral geometry to this complex, in which the ligand functions in a tridentate fashion [121]. In addition, the related ligand, dihydrobis(1-pyrazolyl)borate anion, L = (**13**), has also been reacted with nickel(II). The resultant complex cation, $[NiL_3]^-$, was isolated as its tetraethylammonium salt. This complex was assigned octahedral coordination geometry in which the ligand functions as a didentate N_2 donor [122].

The intermolecular hydrogen bonding in dichlorotetrakis(pyrazole-N^2)nickel(II) has been studied using low-temperature neutron diffraction and X-ray diffraction. Good agreement was observed between the X-ray and neutron studies, with the Ni–N and Ni–Cl bond lengths of 2.09 and 2.50 Å, respectively, in agreement with the tetragonal ligand-field spectra. The long Ni–Cl distances are indicative of the strong N–H···Cl interactions [123].

Table 3
Nickel(II) complexes with 2,2′-bipyridine, 4,4′-bipyridine and 1,10-phenanthroline

Ligand	Complex	Comments	Ref.
2,2′-Bipyridine	$[Ni(L)]^{2+}$, $[Ni(L)_2]^{2+}$, $[Ni(L)_3]^{2+}$, $[NiCl(L)]^{+}$, $[NiCl(L)_2]^{+}$, $[Ni(L)_2]^{2+}$, $[NiCl_2(L)]$, $[NiCl_2(L)_2]$	Spectrophotometric and calorimetric study of the formation of complexes in *N,N*-dimethylformamide. Electronic spectra of the indivdual complexes suggest that all ternary complexes have an octahedral six-coordinate structure, as do the binary complexes in solution.	[105]
		Determination of the stability constants of complexes with nickel(II) in aqueous dmso solutions.	[106]
		Thermodynamics of complex formation with nickel(II) in aqueous methanol solutions.	[107]
	$[Ni(L)(Q)CO]$.0.5 tol.	Q = η-3,4-diphenylcyclobutene-1,2-dione; tol = toluene. X-ray crystal structure determination. The cyclobutenedione ligand is coordinated to the Ni atom via its olefinic bond, while 2,2′-bipyridine functions as a didentate *N*-donor ligand.	[108]
		Coordination of nickel(II) with 2,2′-bipyridine as the primary ligand and dithiodiglycolic acid as the secondary ligand. Stability constants of the 1:1:1 *n*-fixed ligand complexes were determined using pH methods.	[109]
	$[Ni(L)_3]Br_2.2Br_2$	Prepared by the reaction of 2,2′-bipyridine with a series of nickel α-dioxime complexes.	[110]
	$[Ni(L)(H_2O)_3(NO_3)]NO_3$	Synthesis and X-ray crystal structure determination. Nitrate functions as a monodentate ligand.	[111]
4,4′-Bipyridine	$[Ni(Q)(L)](ClO_4)_2.2H_2O$	Q = tetrakis-anhydro-aminobenzaldehyde.	[112]
1,10-Phenanthroline	$[Ni(L)(H_2O)_4](NO_3)_2$	Synthesis and X-ray crystal structure determination. Nitrate not coordinated.	[111]
	$[Ni(L)(Q)_2]$	2,2′-Bipyridine and 1,10-Phenanthrolene adducts of the nickel(II) complexes of *S*-methyl hydrazine carbodithioate. Results obtained indicate the formation of the *cis*-octahedral monoadduct.	[113]
	$[Ni(L)_3]SO_4$, $[Ni(L)_3]X_2$	X = Cl, Br, I. The kinetics of the sulphate substitution by X have been studied in the solid state using TGA and DSC.	[114]
	$[Ni(L)_3]I_2.3H_2O$	X-ray crystal structure of the racemic complex with space group $P2_1/c$.	[115]
	$[Ni(L)_3]Br_2.2Br_2$	Prepared by the reaction of 1,10-phenanthroline with $Ni(dmg)_2$ (Hdmg = dimethylglyoxime).	[116]



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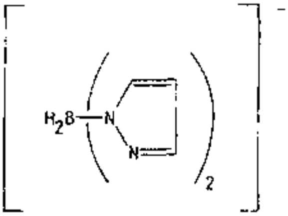


(13)

Four pairs of isomeric compounds of the type NiL_2X_2 and $Ni(L.X)_2$, where L = pyrazole and benzopyrazole, have been isolated and characterised using indirect methods. IR spectra of the two types of compound indicated that they are very dissimilar. On the basis of these data, it was suggested that in the NiL_2X_2 complexes, the dicyanamide or tricyanmethanide ligands are involved in didentate bridging functions, using nitrogen atoms of the two cyanide groups. With the $Ni(L.X)_2$ complexes, the authors have concluded that they are coligand isomers of the NiL_2X_2 complexes, arising from nucleophilic addition of one cyanide group with the imine nitrogen atom of the pyrazole ring [124].

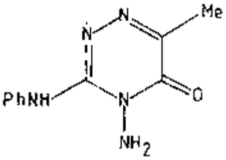
The crystal and molecular structure of bis[*N*,*N*-bis(1-pyrazolylmethyl)-amine]nickel(II) bis(tetrafluoroborate) have been reported. The Ni^{II} ion was found to be coordinated in an almost octahedral geometry, surrounded by four azole nitrogens at 2.02(1)–2.07(1) Å and two amine nitrogens at 2.17(1) and 2.182(9) Å. The two ligands, which function in a tridentate fashion, are in a *fac* arrangement [125].

Tetraaquabis(5-nitrotetrazolato-N^2)nickel(II) has been prepared and its crystal and molecular structure determined. The Ni atom was found to have octahedral coordination site symmetry, being bonded to two N atoms of different 5-nitrotetrazole rings in *trans* positions [Ni–N = 2.105(6) Å] (the nitro substituents are not coordinated), with the coordination sphere being completed by four water molecules in the equatorial plane [Ni–O = 2.125(5) Å] [126].

Several new complexes of $Ni(RCOO)_2$ ($R = C_6H_5$, 2-, 3-, 4-$O_2NC_6H_4$) with saturated diheterocyclic bases (L-L) of the type $Ni(RCOO)_2(L\text{-}L)_n$, where L-L = piperazine, 1-methylpiperazine, 2-methylpiperazine, 1-phenylpiperazine, 2,6-dimethylpiperazine, 2,5-dimethylpiperazine, 1,4-dimethylpiperazine and 4-methylmorpholine, and $n = 2$, 1 or 0.5, have been prepared and characterised [127]. In similar studies, the synthesis and thermal behaviour of some adducts of morpholine with nickel(II) nitrate, sulphate and perchlorate have been described [128], the mixed ligand complexes of nickel(II) pyrrolidonates with various nitrogen donor ligands have been prepared and characterised [129], and the complexing of nickel(II) acetate and nitrate with N-heteroaromatic ligands, piperidines and amines in dmf has been investigated [130].

Methyl and ethyl quinaldate (L) have been reacted with a variety of nickel(II) salts. Complexes of the type $NiL_2Cl_2 \cdot nH_2O$ (X = Cl, Br, NCS, NO_3; $n = 0$, 1) were isolated and characterised by IR, electronic and ESR spectra, and magnetic moment data. L was found to function as a monodentate, didentate, or both monodentate and didentate ligand in the same complex [131].

4-Amino-6-methyl-5-oxo-3-phenylamino-1,2,4-triazine (**14**) and the related ligand, cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine) (**15**), have been complexed with nickel(II). Nickel complexes with L=(**14**) that have been isolated include $[NiL_2X_2]\cdot 2H_2O$, where X=Cl, Br, I, or NCS. Complexes with X=Cl, Br were assigned pseudo-octahedral structures, while those with X=I, NCS were assigned pseudo-tetrahedral structures. Coordination via the amino nitrogen atom was postulated on the basis of spectral data [132]. Anionic complexes of the type $X_2[Ni(H_2L)_4]\cdot nH_2O$ ($X = Na, K, NH_4$; H_2L = anion of cyanuric acid; $n = 0, 4, 6$) were formed by complexation of (**15**) with nickel(II). These complexes were characterised via spectral and magnetic methods, with a slightly distorted octahedral structure proposed, with coordination occurring through the nitrogen atoms of the ligand [133].



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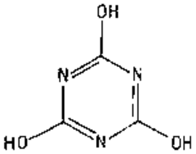
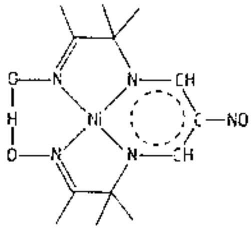


(15)

A number of Schiff-base and related ligands have been complexed with Ni(II) and function as nitrogen donor ligands. These include the Schiff bases derived from 2-aminobenzimidazole and 4-methylbenzaldehyde [134], and from 2-aminopyridine and 2-furylglyoxal [135], the oximes, salicylaldoxime [136] and benzimidazole-2-carboxaldoxime [137], the imine oximes, $HON{:}C(CH_3)C(CH_3) = NCH_2CH_2NR_2$ (R = Me, Et, Bu) and $HON{:}C(CH_3)C(CH_3) = NCH_2CH_2NHR$ (R = Me, Et, Pr, Ph) [138]. In addition, the crystal and molecular structures of dichlorobis(diacetylmonoxime-*S*-methyliosthiosemi-carbazone)nickel(II) [139] and *trans*-[bis(nitrito)-bis-*S*-methylthiosemicarbazide)nickel(II) [140] have been reported. In the former complex, the coordination geometry about Ni(II) was found to be octahedral with coordination to two Cl atoms and the hydrazine and oxime N atoms of the semicarbazones. The S atoms of the semicarbazone ligands were not coordinated to the Ni ion. The latter complex was also found to be octahedral, with coordination occurring via the four N atoms of the two semicarbazide ligands, and two O atoms from the NO_2 ligands which are positioned in a *trans* configuration.

Turning to polydentate ligand complexes, the crystal and molecular structure of [*N,N'*-propylenebis(2-pyrrolylmethyleneaminato)]nickel(II) have been determined. Two crystallographically independent complexes of the title compound were observed, both coordinated in a square planar fashion about the nickel atom. In one complex (*A*), the four Ni–N bond distances of the tetradentate ligand were found to be identical [1.900(2) Å] within the e.s.d.'s, whereas in the other (*B*), the Ni–N(pyrrole) distances [1.883(4) and 1.,884(4) Å] were found to be significantly shorter than the Ni–N(imine) distances [1.897(4) and 1.894(5) Å] [141].

Neutron and X-ray diffraction methods have been used to determine the structure of [3,3′-dimethyl3,3′-(2-nitrosopropanediylidenediamino)bis(2-butanone oximato)-*N*,*N*′,*N*″,*N*‴] nickel(II). The coordination geometry about the nickel(II) atom was found to be square planar, with the average Ni–N(amine) distance exceeding the Ni–N(oxime) distance by about 0.03–0.07 Å. The H atoms were located precisely from the neutron data, while the planarity of the six-membered chelate ring indicates a high degree of aromaticity (**16**) [142].



(**16**)

The crystal and molecular structure of [*N*,*N*′-bis(2-aminoethyl)-1,4-diazacycloheptane-*N*,*N*′,*N*″,*N*‴]nickel(II) diperchlorate have been determined, revealing essentially planar coordination about nickel(II), with the Ni atom 0.03 Å above the four N atoms. Ni–N distances are 1.892(5) and 1.902(4) Å, while in the solid state, the 1,4-diazacycloheptane ring adopts a boat conformation so that the apical C atom does not lie directly above the Ni atom [143].

A new Ni(II) tris{[(aminoisopropyl)amino]methyl}amine dichloride complex has been prepared by the template condensation reaction of $NiCl_2 \cdot 6H_2O$ with ammonia, formaldehyde and 1,2-propylenediamine. The complex was characterised via an X-ray crystal structure determination, as well as elemental analysis, magnetic and spectral measurements. A semisepulchrate structure was observed, with the ligand functioning in a hexadentate fashion [144]. Similarly, the crystal and molecular structure of the related Ni(II) perchlorate complex of tris{[(aminoethyl)amino]-methyl}amine have been reported. The perchlorate ions were discrete from the nickel cationic complex, Ni(II) tris{[(aminoethyl)-amino]methyl}amine, of which two enantiomeric forms were found to exist [145].

[Bis(1-amino-13-methyl-3,6,9,12-tetraazapentadec-12-en-14-one oximato-*N*,*N*′,*N*″,*N*‴,*N*⁗)-hydrogen(1)]dinickel(II) triperchlorate has been prepared and its crystal and molecular structure elucidated. The structure was found to consist of perchlorate anions and dinuclear complex cations, with the ligands functioning as hexadentate N donors. The two halves of the dimer are bridged by an O···H···O hydrogen bond between the oxime O atoms. Ni–N distances were found to range from 2.077(4) to 2.181(4) Å [146].

The preparation and properties of the nickel(II) complexes of *N,N,N′,N′*-tetrakis-(2-benzimidazolylmethyl)-1,2-diaminoethane (L) have been described, and the X-ray crystal structure of $Ni_2LCl_4(H_2O)_3(C_2H_5OH)_2$ reported. The crystal structure showed that the two nickel atoms are not bridged, but exist as two distinct octahedral species. Hexacoordination about one of the nickel atoms is produced exclusively by L, functioning as a hexadentate N donor, to give the cationic species $[NiL]^{2+}$. The second nickel ion achieves hexacoordination via an unusual combination of ligands to produce the novel complex, $[NiCl_2(H_2O)_3(C_2H_5OH)]$. Since the two remaining chloride ions are hydrogen bonded to two of the water molecules and the ethanol molecule of $[NiCl_2(H_2O)_3(C_2H_5OH)]$, the authors suggest that the entire complex can be considered to be formed by the cocrystallisation of the large cation, $[NiL]^{2+}$, by the "large anion" $\{[NiCl_2(H_2O)_3(C_2H_5OH)]Cl_2\}^{2-}$ [147].

3.2. Complexes with phosphorus donor ligands

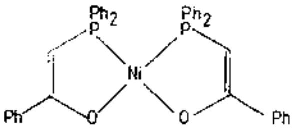
The crystal structures of dichlorobis(triphenylphosphine)nickel(II) [148] and diiodobis(triphenylphosphine)nickel(II) [149] have been reported. Both complexes were found to have distorted tetrahedral coordination geometry. In the chloride complex, a long Ni–P separation of 2.1380(2) Å was observed [Ni–Cl = 2.2075(2) Å], while in the iodo complex the average Ni–P and Ni–I distances were found to be 2.382(4) and 2.5307(25) Å, respectively. In addition, bromine and phosphorus ligand K-absorption edge EXAFS have been used to determine the coordination geometries at a number of nickel centres, including $NiCl_2(PPh_3)_2$, $NiBr_2(PPh_3)_2$, $NiBr_2(PEt_3)_2$, $NiCl_2(dppe)$, $NiCl_2$, $(NEt_4)_2[NiCl_4]$, and $NiBr_2$ [150]. Substitution reactions of the sterically hindered complexes, *trans*-$[NiBr(R)(PPh_3)_2]$ ($R = C_6Cl_5$, C_6F_5, $C_6H_2Me_3$-2,4,6, C_6HCl_4-2,3,5,6, C_6HCl_4-2,3,4,6, C_6HCl_4-2,3,4,5, $C_6H_2Cl_3$-2,3,4, $C_6H_3Cl_2$-2,4, or C_6H_4Cl-2) and *trans*-$[NiBr(R)(PR'_3)_2]$ ($PR'_3 = PEtph_2$ or $PMePh_2$; $R = C_6Cl_5$, C_6F_5, $C_6H_2Me_3$-2,4,6 or $C_6H_2Cl_3$-2,3,4) have been studied in acetone solution. The reaction rates were found to obey the well established two-term rate, law, $k_{obs} = k_s + k_{an}[\text{anion}]$, and seem to be controlled solely by steric factors [151].

Trifluorosilyl radicals, generated in a radio frequency glow discharge of hexafluorodisilane, have been reacted with metal atoms to give the first homoleptic trifluorosilyl metal compounds. $(SiF_3)_2Ni(PMe_3)_3$ was prepared in this fashion and its crystal and molecular structure determined. The complex was found to have D_{3h} symmetry, with the trifluorosilyl groups occupying axial positions [average Ni–S = 2.182 Å], while the trimethylphosphine ligands are positioned in the equatorial plane, with an average Ni–P bond length of 2.204 Å [152].

The compound $(Cy_3P)_2Ni(H)(CH_3)$ has been reacted with carbon dioxide to form a hydridonickel formate complex, $HNi(O_2CH)(Cy_3P)_2$. Interestingly, the analogous species, $(Cy_3P)_2Ni(H)(Ph)$, undergoes a simple CO_2 insertion into the Ni–H bond to quantitatively yield $HCO_2Ni(Ph)(Cy_3P)_2$ [153]. Related work has been carried out in which the *trans* influence of the ligands, X, on the spectroscopic properties of the Ni–H bond for the series of square planar nickel hydride complexes, *trans*-HNi(X)(Cy_3P)$_2$ (X = Me, Ph, CN, SCN, I, Br, Cl, SPh, S(*p*-tolyl), SH, OAc, O_2CH, O_2CPh, O_2CCF_3, OPh), has been investigated [154].

Turning to didentate ligands, the crystal and molecular structure of the complexes, bis(1,2-diphenylphosphinoethane)nickel(II) dinitrate and bis(*cis*-1,2-diphenylphosphinoethene)nickel(II) diperchlorate, have been determined. Both complexes reveal nearly ideal square planar coordination geometry for the nickel ion, with the ligands functioning as didentate P,P-donors. The Ni–P bond lengths are nearly identical within experimental error [Ni–P = 2.261(3) and 2.256(3) Å] [155]. In addition, the thermolysis of dibromobis(diphenylvinylphosphine)-nickel(II) has been investigated in butan-1-ol at 135 °C. Dibromo[1,2-bis-(diphenylphosphino)ethane]nickel(II), Ni(dppe)Br_2, was produced by sequential Michael reversion and addition reactions. The crystal structure of Ni(dppe)Br_2.CH_2Cl_2 was determined, revealing inequivalent Ni–Br [2.3205(7) and 2.3360(7) Å] and Ni–P [2.141(1) and 2.156(1) Å] bond lengths. The coordination geometry about Ni was found to be square planar with a slight tetrahedral distortion [156].

In an ongoing study of the complexes with functional phosphines, the reactivity of coordinated phosphino enolates and metallacycles toward chlorophosphines with diastereoselective formation of P–O and P–C bonds has been investigated, as well as the alkaline hydrolysis of the coordinated phosphinites, which leads to the formation of oxodiarylphosphoranido ligands. Thus, the nickel complex (**17**) reacted with chlorodiphenylphosphine producing the complex (**18**) [157].



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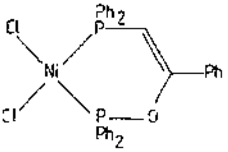


(18)

Divinylphenylphosphine has been reacted with 1-phenyl-3,4-dimethylphosphole in the presence of anhydrous nickel(II) bromide. The resultant complex, a single diastereomer of bromo[phenylbis(5,6-dimethyl-7-phenyl-7-phosphabicyclo[2.2.1]-hept-5-en-2-yl)phosphine]nickel(II) bromide, was formed as the result of two sequential stereoselective intramolecular [4+2] Diels–Alder cycloadditions. Similarly, the reaction of vinyldiphenylphosphine, 1-phenyl-3,4-dimethylphosphole and nickel(II) bromide resulted in the formation of both mono- and bis(2-(diphenylphosphino)-7-phenylphosphanorbornene)nickel(II) complexes. All of the complexes were characterised via a range of spectroscopic techniques and cyclic voltammetry [158].

In an ongoing study of complexes with functional phosphines, the crystal and molecular structures of *trans*-[Ni(HL)$_2$$X_2$], [HL = $Ph_2PCH_2C(O)Ph$, X = Cl, I] have been reported. Both complexes are essentially identical with the nickel(II) ion in a *trans*-square planar environment. Although the ketone group is bent towards the nickel atom, no significant Ni–O bonding interaction was found, as evident from the from the Ni–O distances of 3.230(4) Å in the chloride complex and 3.231(1) Å in the iodide complex. Other structural data of interest for the chloride complex are Ni–Cl = 2.162(1) Å and Ni–P = 2.245(1) Å, while for the iodide complex, Ni–I = 2.510(1) Å and Ni–P = 2.234(1) Å [159].

Arsenic(III) iodide has been reacted with $[Ni(H_2O)_6](ClO_4)_2$ and $CH_3C(CH_2PPh_2)_3$ (triphos). The resultant compound consists of the two complex cations, $[(triphos)NiI]^+$, and the arsenic-rich polyanion, $[As_6I_8]^{2-}$. The crystal structures of the cation and the anion have been determined. In the complex cation, the nickel coordination geometry was found to be distorted tetrahedral, with the triphos ligand functioning in a tridentate, tripodal fashion [Ni–P(average) = 2.244(4) Å], and the remaining coordination site being occupied by the iodine ligand [Ni–I = 2.414(4) Å]. The distortion has been mainly attributed to the steric constraints of the triphos ligand, which prevents attainment of the ideal values [160].

3.3. Complexes with oxygen donor ligands

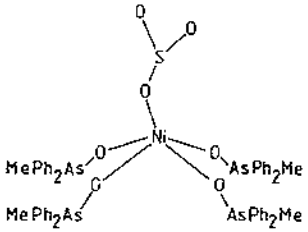
The coordination of water with Ni(II) continues to attract attention, with a number of crystal structures having been reported. These include the crystal and molecular structures of monoclinic nickel(II) sulphate hexahydrate [octahedral structure, with Ni–O ranging from 2.039(2) to 2.066(2) Å] [161], nickel(II) perbromate hexahydrate, determined at 169 K [slightly distorted octahedral structure, with Ni–O = 2.047(2) Å] [162], and diammonium hexaaquanickel(II) sulphate [determined using X-ray and neutron diffraction, the bond lengths of the essentially octahedral complex cation vary from 2.037(1) to 2.068(1) Å] [163].

Pyridine *N*-oxide and its substituted analogues, 2-, 3-, and 4-methylpyridine *N*-oxide (L) have been complexed with nickel(II). The thermal properties of the resultant complexes, $NiL_nX_2 \cdot xH_2O(EtOH)$ ($n = 3$ or 2; $x = 1$; X = NCS, Cl) were investigated, including the stoichiometry of thermal decomposition and the stereochemical changes associated with thermal decomposition [164].

A series of complexes of dimethyl phthalimidomethylphosphine oxide (L) have been synthesized and characterised using elemental analysis, electric conductivity and infrared and electronic spectra. Nickel complexes that were isolated include $[NiL_2(H_2O)_2Cl_2] \cdot 4H_2O$, $[NiL_3(CH_3OH)Cl_2] \cdot CH_3OH$ and NiL_2Cl_2. Coordination of L to the metal ion was found to occur via the phosphoryl oxygen atom [165].

The relative intensities of the polarised "d–d" transitions of tetrakis(diphenylmethylarsine oxide)nickel(II) nitrate have been reproduced quantitatively within a new ligand field scheme. The coordination geometry of $[Ni(OAsPh_2Me)_4NO_3]^+$ is shown below (**19**). The nitrates were found to be disordered in the tetragonal lattice [166].

Turning to sulphoxide ligands, a series of metal nitrate complexes of dibenzylsulphoxide (DBSO) have been isolated and characterised. Infrared spectra indicated that in all cases, including the nickel complex, $[Ni(DBSO)_3](NO_3)_2$, coordination of the DBSO ligand occurred through the oxygen atom in a monodentate fashion.



(19)

In addition, both chemical analyses and spectral studies suggest that a coordination number of six is manifested [167].

Similarly, nickel(II) perchlorate and nitrate complexes containing dimethyl, di-*n*-propyl, di-*n*-butyl, di-*i*-butyl and di-*t*-butyl sulfoxides have been synthesized and characterised. In the perchlorate complexes, the Ni:sulfoxide ratio was found to be 1:6, with the perchlorate groups being ionic. In the nitrate complexes, the molar ratio was found to decrease from 1:6 to 1:2 in accordance with the increase in steric bulk of the alkyl group. The nitrate group was found to be non-coordinating, or functioning as a monodentate or didentate ligand. All of the complexes were characterised as high-spin octahedral or distorted octahedral complexes with O-bonded sulphoxide ligands [168].

Acetylurea (L) has been complexed with a variety of nickel salts. Complexes isolated include $NiL_2Cl_2 \cdot H_2O$, $NiL_2(NO_3)_2 \cdot 2H_2O$, $NiL_4Cl_2 \cdot 4H_2O$, $NiL_4(NO_3)_2$, and $NiL_2SO_4 \cdot 7H_2O$. The complexes were characterised via IR spectra, X-ray diffraction and thermal analysis. L functions as a monodentate O donor ligand bonding through the carbamide O atom. Nitrate and sulphate are coordinated in the 1:2 metal:L complexes, while nitrate is outer sphere in the $NiL_4(NO_3)_2$ complex. In $NiL_4Cl_2 \cdot 4H_2O$, one water ligand is coordinated, while in $NiL_2SO_4 \cdot 7H_2O$, two water ligands are coordinated [169].

The protonation constants of methyliminobis(methylenephosphonic) acid (BL) and the stability constants of its complexes with nine cations have been determined potentiometrically at 25 °C and ionic strength $(NaClO_4) = 0.1$ mol dm^{-3}. Transition metal cations, including Ni^{2+}, were found to form complexes of the type $[ML]^{2-}$, $[ML_2]^{6-}$, and their protonated forms $[MHL]^-$ and $[M(HL)_2]^{4-}$. On the basis of these results, coordination of the ligand to Ni(II) was assumed to occur via the oxygen atoms only and not through the N atom [170].

Formation of the mixed-ligand complexes of nickel(II) with EDTA and *p*-methylaminophenol (HX) has been studied in aqueous solution. Spectral shifts indicated that HX coordinates to nickel(II) via the phenolic O atom, but that ligand deprotonation can lead to coordination via the amino N atom as well [171].

Numerous *β*-diketone ligands, including the ubiquitous acetylacetone (acac), have been completed with nickel(II). Table 4 lists a number of these ligands and the complexes that have been synthesized [172–184].

The synthesis and structure of (nitroacetato)((7*RS*, 14*RS*)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) have been reported.

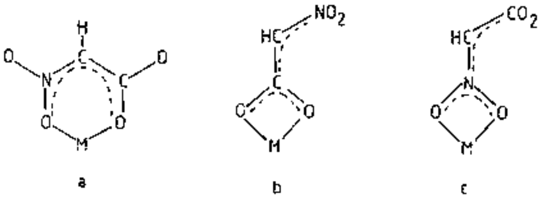
Table 4
Nickel(II) complexes with β-diketone and related ligands

Ligand	Complex	Comments	Ref.
Acetylacetone (or 2,4-pentanedione) (Hacac)	*trans*-[Ni(acac)$_2$(H$_2$O)$_2$]	IR and ^{1}H and ^{13}C NMR spectroscopic study. A comparative study of the Ni(II) complexes of 2,4-pentanedione, 4-imino-2-pentanone, 4-thioxo-2-pentanone and 2,4-pentane dithione.	[172]
	[Ni(acac)(dppe)]$^+$	dppe – 1,2-bis(diphenylphosphino)ethane. Electroanalytical and spectro-photo-metric investigation of the metal(II)-dppe-acetylacetonate system.	[173]
	Ni(acac)L$_2$	L = *N*,*N*-substituted thioureas. 12 complexes were prepared and characterised. A *trans* configuration with S-coordinated thioureas was proposed.	[174]
	Ni(acac)L	HL = pyrrole-2-carboxaldehyde. Ni(acac)L reacted with NH$_3$ or RNH$_2$ (R = alkyl) to give Ni(acac)Q (HQ = 2-pyrrolyhnethylideneamine), which reacted with HOCH$_2$CH$_2$NH$_2$ to give NiB(H$_2$O) (H$_2$B – 2-pyrrolylmethylidenetethanolamine).	[175]
	[Ni(HL)$_2$] [Ni(acac)$_2$X$_2$] [Ni(HL)$_2$][Co(acac)$_2$X$_2$]	HL – biguanide, 1-methylbiguanide, 1-ethylbiguanide: X = Cl, Br, I. Cations have been assigned square planar coordination, while [Ni(acac)$_2$X$_2$] and [Co(acac)$_2$X$_2$] have been assigned octahedral and square pyramidal geometry, respectively.	[176]
	Ni(acac)$_2$L$_2$	L = pyridine, picoline, 2,6-lutidine. Prepared from Ni(acac)$_2$(H$_2$O)$_2$, and characterised by IR spectra, electrical conductance and magnetic moment measurements.	[177]
Hexafluoroacetylacetonate (hfac)	Ni(hfac)$_2$(proxyl)$_2$	proxyl = 2,2,5,5-tetramethylpyrrolidinyl-1-oxy. Crystal and molecular structure determination reveals *trans* octahedral configuration with N O(hfac) = 1.998(4) and 2.024(4) Å and Ni–O(proxyl) = 2.100(4) Å.	[178]
	Ni(hfac)$_2$(NITR)$_2$	NITR = 2-R-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazole-1-oxyl-3- oxide (R = Me, Ph). Crystal structure determination of R – Ph complex. *Trans* octahedral configuration with N O(hfac) ranging from 1.998(5) to 2.035(6) Å and Ni–O(NITPH) = 2.090(5) and 2.087(5) Å.	[179]
Various β-diketones		Study of the energetics of metal–oxygen bonds, including Ni O, in metal complexes of β-diketones. Thermochemical data available for the standard enthalpies of formation, both in the crystalline and gaseous phases, have been discussed, and calculations of the enthalpies of gas phase decomposition of the complexes have been presented.	[180]
Substituted aryl furyl β-diketones		The coordination of transition metals, including Ni^{2+}, with a number of aryl furyl β-diketone ligands has been studied at 30 and ionic strength 0.1 M (NaClO$_4$) using the Calvin–Bjerrum technique. Stability constants of metal ligand complexes were evaluated by the Irving–Rosotti procedure.	[181]

Table 4 (*continued*)

Ligand	Complex	Comments	Ref.
o-, *m*-, *p*- and 4-Me-*o*-sulphobenzenehydrazopentane-2,4-dione (HL)	Ni $L_2.2H_2O$	1:1 and 1:2 metal:ligand complexes were observed by spectrophotometric and conductiometric methods. The stability constants of these complexes were determined, while the complex where HL − *p*-sulphobenzenehydrazopentane-2,4-dione was isolated and its IR spectrum compared with that of the free ligand.	[182]
4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dione (Htftbd)		Study of the kinetics and mechanisms of reaction of nickel(II) with Htftbd in aqueous solution at 25 . The kinetic data were found to be consistent with a mechanism in which the metal ion reacts with the enol tautomer of the ligand by acid-independent and inverse-acid paths. The equilibrium constants for reaction of Htftbd with proton and Ni^{2+} have also been reported.	[183]
1,3-Bis-(2-hydroxyphenyl)-1,3-propanedione (HL)	Ni L_2.2 solvent	This complex can be desolvated by controlled heating to form the square planar compound which is tetracoordinated by the β-ketonic oxygen atoms of the ligand. This complex has been reacted with pyridine and substituted-pyridine derivatives, yielding octahedral complexes in which the pyridine ligands occupy *trans* axial coordination sites. The structures were determined by spectroscopic methods and by comparison with the Cd analogue, the crystal structure of which has been determined.	[184]

Nitroacetate ion has the capability of coordinating in a variety of ways (**20a–c**). X-ray analysis has shown that the complex has a *cis*-NiO_2N_4 conformation, with the tetraazamacrocycle folded, and that the dianionic nitroacetate ligand coordinates to the nickel(II) ion via one oxygen atom of the CO_2^- moiety and one oxygen of the NO_2^- moiety, to form a six-membered chelate ring (**20a**) [185].



a b c

(20)

Similarly, the biuret molecule can adopt the *cis* or *trans* configuration. ESR spectra have been measured at X- and Q-band of manganese(II) ions doped at a nominal 1% in the lattices of $M(biuret)_2Cl_2$ (M = Ni, Cd, Co, Zn) and $M(biuret)_2Br_2$ (M = Ni, Co, Zn). It was found that the cobalt and nickel complexes closely resemble the zinc complexes, with coordination occurring via the oxygen atoms of the biuret ligand which adopts the *cis* configuration [186].

In principle, the squarate dianion is able to act both as a four-fold monodentate or as a chelating ligand and can also give rise to complicated structural formations. The isotypic compounds, $(MC_4O_4 \cdot 2H_2O)_3 \cdot CH_3COOH \cdot H_2O$ ($M = Ni^{2+}$, Zn^{2+}), have been prepared and characterised. The crystal structure of the Zn analogue showed that the metal ions are essentially octahedrally coordinated by two water molecules and four oxygen atoms of four squarate dianion ligands. Thus, in this case, the squarate ligands function as four-fold monodentate ligands, while the authors also assume the existence of strong hydrogen bonding between the water molecules and squarate ligands [187]. Similarly, the crystal and molecular structure of *catena*-diaqua(2,2′-bipyridyl)-*μ*-(squarato-O^1,O^2)-nickel(II) dihydrate have been determined. In this case, the crystal structure contains chains of squarato-O^1,O^2-bridged Ni^{II} metal atoms. These chains are held together by strong hydrogen bonds between the non-coordinating oxygen atoms of the squarate anions and the water molecules. The coordination sphere about the nickel ions is basically octahedral, with the squarate anions occupying *trans* positions [Ni–O = 2.105(3) and 2.124(3) Å], while the water molecules occupy *cis* equatorial positions [Ni–O = 2.030(3) and 2.054(3) Å] with the bipyridine ligand [Ni–N = 2.069(3) and 2.063(3) Å], which completes the coordination sphere [188].

A number of potentiometric studies examining the complexation of variously substituted hydroxamic acid ligands with nickel(II) have been reported. Hydroxamic acid ligands investigated include mandelohydroxamic acid [189] and the *p*-substituted *N*-*o*-chlorophenylbezohydroxamic acids, *o*-$ClC_6H_4N(OH)COC_6H_4X$-*p* (X = H, Me, OMe, F, Cl, Br, I or NO_2) [190].

Salicylic acid and its variously substituted analogues constitute a good source of O–O didentate ligands. Solution studies have been undertaken in which the equilibria and kinetics of complex formation of Ni^{2+} with 2-mercaptobenzoic acid, 2,6-dihydroxobenzoic acid and 3,5-dinitrosalicylic acid have been investigated at 25 °C [191]. In addition, the complexation behaviour of Ni(II) with 2-hydroxy-3-methoxybenzaldehyde has been investigated at 288, 298 and 308 K in aqueous solution using Crow's mean diffusion coefficient method [192,193], while a potentiometric study of the complexation of 3-hydroxy-2-naphthalene carboxylic acid with Ni(II) has also been undertaken in a 50% (v/v) dioxane–water solution at 25 °C [194]. Turning to the solid state, nickel complexes of the type $Ni(HL)_2 \cdot 4H_2O$, $NiCl_2 \cdot (H_2L)$ (H_2L = salicylic acid, *p*-aminosalicylic acid) and $Ni(L^1)_2 \cdot 2H_2O$ (HL^1 = salicylamide) have been prepared and characterised [195].

A range of carboxylic acid ligands ranging from benzoic acid to tetracarboxylic acid have been completed with nickel(II). Direct electrochemical synthesis has been employed in the preparation of the transition metal carboxylates, $M(O_2CR)n$ (M = Ni, Mn, Fe; R = CH_3, C_2H_5, C_6H_5, n-C_7H_{15}; $n = 2$, not all combinations), using suitable metal anodes in solutions of RCOOH in acetonitlile [196]. Complexes containing variously substituted benzoic acid ligands have also been isolated. These include $Ni(p\text{-}XC_6H_4COO)_2 \cdot 3H_2O$ (X = H, F, Cl, Br) [197], Ni^{2+} salts of 2-(2-, 4-dihydroxybenzoyl)benzoic acid [198], and $L_2Ni \cdot H_2O$ [HL = 2-(4-ethoxytelluro)benzoic acid] [199].

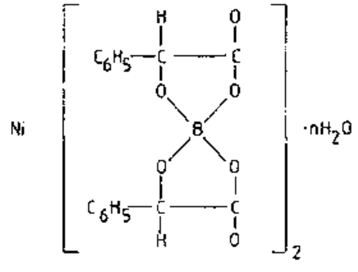
A number of γ-phenoxybutanoic acids have been completed with Ni(II). The crystal structures of the complexes diaquabis[4-(phenoxy)butanoato]nickel(II) and diaquabis[4-(4-chlorophenoxy)butanoato]nickel(II) have been determined. Both complexes are isomorphous and isostructural and have distorted octahedral NiO_6 stereochemistry, with two slightly asymmetric didentate carboxylate groups [Ni–O = 2.062(2), 2.181(2) Å and 2.068(2), 2.175(2) Å for each complex, respectively], and two water ligands [Ni–O = 2.021(1) Å and 2.016(2) Å for each complex, respectively] [200].

The complexation of nickel(II) with *cis*- 1,2,3,4-cyclopentanetetracarboxylic acid as primary ligand and pyrogallol as secondary ligand has been investigated in aqueous solution at 30, 40 and 50 °C [201]. An analogous study has been carried out using tannic acid as the secondary ligand, also at 30, 40 and 50 °C [202]. In addition, the tetracarboxylate ligand, 1,2,4,5-benzenetetracarboxylic acid, has been completed with Ni(II). IR spectra of the resultant complex, $Ni(C_{10}H_5O_8)_2 \cdot 12H_2O$, indicate the presence of very strong hydrogen bonding [203].

Novel nickel and manganese bis(mandelato)borates have been synthesised and characterised. The infrared spectra and chemical analysis data have led the authors to propose the structure formula (**21**) for the bis(mandelato)borates [204].

The complexation of nitrilotriacetic acid with nickel(II) has been investigated in aqueous solution. The heats of reaction of aqueous solutions of $Ni(NO_3)_2$ and nitrilotriacetic acid were measured at various pH values and metal:ligand ratios in the temperature range 288–308 K. Enthalpy changes and other thermodynamic functions for the formation of the nitrilotriacetate complexes have been calculated using these data [205].

A number of articles investigating the reaction of hydroxyethylidenediphosphonic acid with Ni(II) have been published. These include complexation in aqueous



n = 0-4
(21)

solution [206], as well as the isolation of distorted octahedral complexes in the solid state [207,208]. In addition, the extraction of Ni(II) from nitrate media by di-*n*-octylphosphonic acid dissolved in toluene has been studied over a range of pH and ligand concentrations [209], while complexes of the type $Mg_3[Ni(HL)]_2$, Ni_2H_2L and $Mg[Ni_2(HL)]_2$, where H_6L = nitrilotrimethylphosphonic acid, have been prepared and characterised. In these latter complexes, the coordination sphere about Ni(II) was found to be a highly distorted octahedron of ligand oxygen atoms [210].

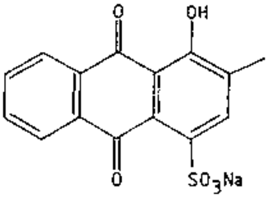
Quinone and related ligands have attracted significant interest. An article containing 68 references has reviewed *p*-quinone and *p*-quinone fragments as "non-innocent" ligands in electron rich complexes of the late *d* elements [211]. The complexation of catechol and pyrogallol with nickel(II) has been studied in aqueous solution. Thermodynamic stability constants and parameters for complexation were calculated from pH-titration data obtained at 30 and 40 °C [212]. A similar study has been undertaken with the Ni(II)/3,5-dinitrocatechol system. Results obtained in this latter study have been compared with those for 4- and 3-nitrocatechol [213].

Continuing with complexes containing catechol-type ligands, the complex NiL(TCCat)TCQ (L = 2,4,4-trimethyl-1,5,9-triazacyclododec- 1-ene, TCQ = tetrachloro-1,2-benzoquinone, TCCat = tetrachlorocatecholate) has been prepared via the reaction of NiL(TCCat) with tetrachloro-1,2-benzoquinone. A crystal structure of the complex was determined revealing that both dioxolene ligands are coordinated to the nickel ion in a highly distorted pseudo-octahedral coordination geometry. One of the dioxolene ligands functions as a didentate ligand [Ni–O = 2.12(1) and 2.10(1) Å], while the other functions as a monodentate ligand [Ni–O = 2.21(1) Å]. The three Ni–N distances were found to be 2.06(2), 2.11(1) and 2.08(2) Å, respectively [214]. In addition, the same group have reported the synthesis, electrochemical properties, and electronic and CD spectra of dioxolene adducts of the nickel(II) complex with the racemic and the (-)-*S*,*S*-isomer of the macrocyclic ligand 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L). Complexes that have been isolated include Ni(*S*,*S*-L)(DTBSQ)ClO_4 (DTBSQ = anion of 3,5-di-*tert*-butylbenzo-*o*-semiquinone), Ni(*S*,*S*-L)(TCCat)·H_2O and Ni(*S*,*S*-L)(TCSQ)ClO_4 (TCSQ = tetrachlorosemiquinonate) [215].

Nickel(II) ions have been used to promote the reaction of sodium 1,2-naphthoquinone-4-sulphonate with a variety of arylamines and 1, 1-bis[*p*-

(dimethylamino)phenylethylene to give 4-aminated, 4-arylated and 4-vinylated 1,2-naphthaquinones. Complex formation was found to be accompanied by absorption bands with absorption maxima in the near IR region occurring at larger wavelengths and with increased intensities [216].

The solution equilibria of Alizarin Red S (9,10-dihydro-3,4-dihydroxy-9,10-dioxo-2-anthracene sulphonic acid monosodium salt) (**22**) with Ni(II) have been investigated. A general procedure for speciation, developed from the work of Coleman et al. and Gampp et al., was used to determine the species in aqueous solution. Both 1:1 and 1:2 (metal:ligand) complexes were observed [217].



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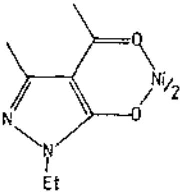
In an ongoing series looking at the reactions of metal ions with triketones in solution, the kinetics and mechanisms of the reaction of nickel(II) with 2-aceto-1,8-dihydroxynaphthalene, 2,2′dihydroxybenzophenone and 1,5-diphenylpentane-1,3,5-trione, respectively, have been studied in methanol–water (70:30 v/v) solution. The formation reactions of both the 1:1 and 2:2 dimerisation products were investigated and detailed mechanisms were proposed, which account satisfactorily for the kinetic data obtained [218].

Equilibrium studies of the interaction of Ni(II) with *o*-hydroxyphenone, 4-methyl-5-hydroxy-6acetylcoumarin and 1-(2′-furyl)-3-(4′-methyl-5′-hydroxycoumarin-6′-yl)propane-1,3-dione have been undertaken. Complexation was studied potentiometrically in 50 vol.% aqueous dioxane. Proton and metal ligand (1:1 and 1:2) stability constants were calculated [219]. In addition, structural and physiological studies have been undertaken on the complexes of nickel(II) with 4-hydroxy-3-aminocoumarin (HL) and 4-hydroxy-3-nitrocoumarin (HL^1). Complexes isolated include $[NiL_2(H_2O)_2]$ and $[NiL^1(H_2O)_2]Cl_2$. L was found to coordinate via the amino N and the deprotonated phenolic O atoms, whereas L^1 was found to coordinate through the nitro O and lactone carbonyl O atoms [220].

The nickel complex of 2′,4′-dihydroxy-5′-(4-methoxy)cinnamoyl-4-methoxychalcone (H_2L), $NiL(H_2O)_2$, has been isolated and characterised by IR, electronic spectra, magnetic susceptibility and molar conductance measurements. The ligand was found to coordinate in a didentate fashion through two O atoms [221].

The stability constants of the chelate species formed by the interaction of γ-benzoyl-2-hydroxy4-methoxy-3-methylacetophenone with Ni(II) have been determined potentiometrically at 20, 30, 40 and 50 C, respectively, in 75% (v/v) aqueous ethanol [222]. In addition, the chelating properties of 4-phenyl-3-hydroxy-2-quinolone with Ni(II) have been examined in mixed aqueous solutions of dioxane and acetonitrile at 25 °C. It was found that increasing the electron density on the O–O coordination sites of the ligands resulted in increased complex stability [223].

Bis(4-acetyl-1-ethyl-3-methyl-5-pyrazolonato)nickel(II) (**23**) has been prepared and characterised. Direct photolysis of the complex was carried out in a variety of solvents at different irradiation wavelengths [224].



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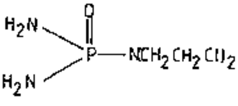
Transition metal(II) complexes with the monoprotic dehydroacetic acid ligand, 3-acetyl-4-hydroxy-6-methyl-2-pyrone (HL), have been prepared and characterised. Based on magnetic measurements at room temperature, the dihydrated nickel complex, $NiL_2 \cdot 2H_2O$, has been assigned an octahedral structure, similar to its Co(II) analogue, the crystal structure of which has been determined. IR spectra was used to confirm coordination of the ligand via its hydroxylic and carbonylic groups [225].

In a continuing study of metal complexes of alkylating agents, a number of complexes of phosphoramide mustard derivatives have been prepared. These include the nickel(II) complexes of the ligands $L^1 = $(**24**) and $L^2 = $(**25**), $[Ni(L^1)_5](ClO_4)_2$ and $[Ni(L^2)_2](ClO_4)_2 \cdot 4H_2O$, respectively. IR spectra show a P=O shift to lower frequency in all of the complexes, supporting the coordination of the metal to the phosphoryl oxygen atoms [226]. In addition, the structurally related ligand (**26**) has been completed with nickel(II). The resultant complex, bis{bis[(diphenylphosphinyl)methyl]ethylphosphinate}bis(ethanol)nickel(II) diperchlorate, was isolated and characterised. Magnetic data indicated a spin-free octahedral structure for this complex, while IR spectra confirmed that the central, as well as one of the exterior P=O groups, are coordinated to the metal ion [227].

An X-ray structure determination of the complex, $NiL_2(ClO_4)_2$ [L = (**27**)] has been



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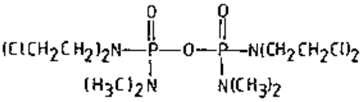

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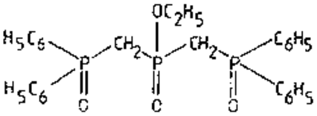
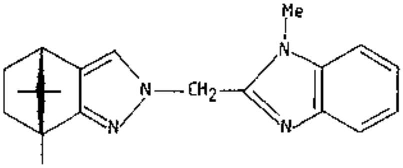


(26)

undertaken. The structure was found to consist of two different stereoisomers of $[NiL_2(ClO_4)]^+$, each of which contains a strongly coordinating didentate perchlorate ligand [228].



(27)

3.4. Complexes with sulphur donor ligands

A number of thiourea and related ligands have been completed with nickel(II). These include thiourea, *m*- and *p*-tolylthiourea, *o*- and *m*-methoxyphenylthiourea, *o*- and *p*-ethoxyphenylthiourea, *m*- and *p*-chlorophenylthiourea [229], and *N*,*N*′-dimethylthiourea [230]. IR spectral data generally indicated S-bonding of the thiourea ligand.

Thiolate and dithiolate complexation with Ni(II) continues to dominate this area of research. Table 5 lists nickel(II) complexes with dithiolate and related ligands [231–249]. In particular, maleonitriledithiolate [231–235] and 5,6-dihydro-1,4-dithiin-2,3-dithiolate [243–246] have been the subjects of a number of studies.

Xanthates constitute another class of ligand that has attracted considerable interest. The crystal and molecular structures of nickel(II) butylxanthate [250] and bis(trifluoroethylxantho-genato)nickel(II) [251] have been reported. Both complexes were found to be square planar with coordination occurring via four S atoms. In addition, the complex, $NiL_2(H_2O)_2$ ($HL = HOCH_2CH_2OCS_2H$), has been prepared and studied by different physicochemical methods. IR spectra confirmed Ni–S bonding and coordinated water, and the complex was assigned high-spin octahedral stereochemistry [252].

Mixed-ligand xanthate complexes have been studied, both in solution and in the solid state. ^1H and ^{13}C NMR spectroscopic studies of electron spin delocalisation in nickel(II) bis(alkyl xanthate) complexes of nitrogenous bases have been reported. Nickel(II) bis(alkyl xanthate) complexes studied include $Ni(R\text{-}xan)_2$, where R = Et, Pr, Bu, pentyl, hexyl and cyclohexyl, while nitrogenous bases complexed to them include 2-(iminomethyl)pyridine, 2-(iminoethyl)pyridine, 2-(imino-*n*-propyl)pyridine, 2-(imino-*iso*-propyl)pyridine, 2-(imino-*n*-butyl)pyridine and 2-(imino-*tert*-butyl)pyridine [253]. In addition, the structures of bis(*O*-benzylxanthato)nickel(II) and the benzene clathrate of its 1,10-phenanthroline adduct have been reported. The former complex is essentially square planar with Ni–S bond lengths of 2.2035(5) Å, while the latter complex is essentially octahedral with Ni–S = 2.452(3) and 2.437(3) Å, and Ni–N = 2.085(8) Å [254]. Similarly, a number of nickel(II) xanthates have been reacted with amines and carbon monoxide. In this case nickel(II)

Table 5
Nickel(II) complexes with dithiolate and related ligands

Ligand	Complex	Comments	Ref.
Maleonitriledithiolate	$[Ni(S_2C_2(CN)_2)_2]$	A number of monoanion salts of small cations were prepared and their electrical conductance and magnetic properties investigated.	[231]
	$[R_4N]_n[M(S_2C_2(CN)_2)_2]$	A spectroscopic study of the complexes where $n = 1$ or 2, M = Ni(II) or Ni(III), R = CH_3 or n-C_4H_9 has been reported	[232]
	$[Ni(S_2C_2(CN)_2)(L)]$	Spectroscopic and theoretical study of the mixed ligand complexes where L = diacetyldihydrazone or phenanthrequinone diimine.	[233]
	$[Fe(C_5Me_5)_2][Ni(S_2C_2(CN)_2)_2]$ $[Fe(C_5Me_5)_2][Ni(S_2C_2(CF_3)_2]$	Preparation and study of structural and magnetic properties of these complexes. Crystal and molecular structure of $[Fe(C_5Me_5)_2][Ni(S_2C_2(CF_3)_2]$ has been determined.	[234]
	$NH_4[Ni(S_2C_2(CN)_2)_2].H_2O$	X-ray crystal structure determination has revealed that the planar $[Ni(S_2C_2(CN)_2)_2]$ anions form an eclipsed equidistant stack structure with a repeat distance of 3.918(8) Å.	[235]
Ethane-1,2-dithiolate	$[Ni(S_2C_2H_4)_2]^2$ $[Ni_2(S_2C_2H_4)_3]^2$	Complex anions were isolated as their tetraphenylphosphonium salts. The crystal and molecular structure of $(Ph_4P)_2[Ni_2(S_2C_2H_4)_3]$ have been determined.	[236]
Cis-1,2-bis(trifluoromethyl)-1,2-ethylene dithiolate	$[NEt_4]_2[Ni\{S_2C_2(CF_3)_2\}_2]$ $[NEt_4]_2[Ni\{Se_2C_2(CF_3)_2\}_2]$	Synthesis, electrical conductivities, magnetic and spectroscopic properties of $[Ni\{S_2C_2(CF_3)_2\}_2]^2$ and $[Ni\{Se_2C_2(CF_3)_2]_2]^{2-}$ salts with small counter ions	[237]
3-R, 4-R′-Benzene-1,2-di-thiolate (L)	$[n\text{-}Bu_4N][NiL_2]$	R = NMe_2, R′ = H, Me, NMe_2. Complexes were characterised using electronic and near infrared spectroscopy.	[238]
5-Cyano-3,4-di-mercapto-iso-thiazole	$[Bu_4N]_2[Ni(C_4N_2S_3)_2]$	X-ray crystal structure determination.	[239]
2-Thioxo-1,3-dithiole-4,5-di-thiolate	$[Bu_4N]_2[Ni(C_3S_5)_2]$	X-ray crystal structure determination. Anion was found to form stacks, but the planes of the adjacent molecules within the stack are at angles of 78.9° to each other. Thus no metal metal interaction.	[240]
	$[R_4N]_2[Ni(C_3S_5)_2]$ (R = Me,*n*-propyl)	X-ray crystal structure determinations. The non-planar $[Ni(C_3S_5)_2]$ anions are stacked two by two with the pairs rotated 90° to each other resulting in no significant intermolecular Ni Ni or Ni–S distances.	[250]

Table 5 (*continued*)

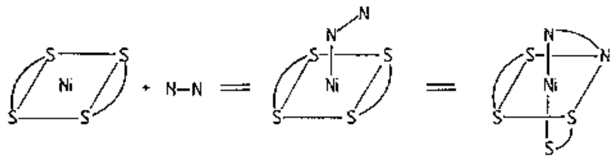
Ligand	Complex	Comments	Ref.
1,2-Bis(3′,4′-di-*n*-decyl-oxyphenyl) ethane-1,2-di-thiolate (L)	$[NiL_2]$	Complex synthesis and characterisation. Phase transformation behaviour of $[NiL_2]$ was studied by microscopy and DSC.	[242]
5,6-dihydro-1,4-dithiin-2,3-di-thiolate (DDDT)	$[n\text{-}Bu_4N]_2[Ni(DDDT)_2]$	X-ray crystal structure determination. Triclinic space group. In this structure $[Ni(DDDT)_2]$ molecules were found to form stacks, in contrast to those in $[Et_4N]_2[Ni(DDDT)_2]$.	[243]
	$[n\text{-}Bu_4N]_2[Ni(DDDT)_2]$	Independent X-ray crystal structure to the previous one. The bond lengths were found to be essentially the same, but the unit cell packing in this monoclinic form reveals association of the anions into pairs. The major difference between the pairs of the $[Ni(DDDT)_2]$ anions of the two neutral complexes is the separation distance.	[244]
		The bis Ni complexes have been prepared in different oxidation states, as anions and in a fully oxidised neutral form.	[245]
$ROCS_2H$ (R = Me, Et, Pr, Bu) (HL)	$[NiL_2L'_2]$	L′ = benzoxazole, benzothiazole, morpholine. Complexes were characterised from their elemental analysis, IR and UV-visible spectra, magnetic measurements and thermal analyses.	[246]
3-Thiolato-2(1H)-pyrazinethione	$[Ni(C_4N_2(1H)S_2)_2]$	Novel synthetic method using sodium 2-methyl-2-propylthiolate as a precursor.	[247]
3-Thiolato-2(1H)-quinoxalenethione	$[Ni(C_8N_2(1H)S_2)_2]$	Novel synthetic method using sodium 2-methyl-2-propylthiolate as a precursor.	[247]
2,3-Dithiolatepyrazine	$[Bu_4N]_2[Ni(C_4N_2S_2)_2]$	Novel synthetic method using sodium 2-methyl-2-propylthiolate as a precursor.	[247]
$R_2C_2S_2H$ (R = COPH, COOME)	$(PPh_4)[Ni(S_2C_2R_2)_2]$	Complexes have been characterised by various physicochemical methods.	[248]
Ethylenetetrathiolate Tetrathiafulvalenetetrathiolate Tetrathiosquarate		Large angle X-ray scattering and EXAFS investigation of the conductive amorphous nickel tetrathiolato polymers formed by reaction of nickel(II) with these ligands.	[249]

dithiocarbamate complexes and thiourethanes were formed, both products of nucleophilic substitution at the sp^2 carbon atom [255].

Continuing with nickel(II) dithiocarbamate complexes, the reactivity of ethylenebis(dithiocarbamate) and diethyldithiocarbamate ligands towards phosphine complexes of nickel(II) has been investigated. Depending on the nature of the phosphine and dithiocarabamate used, different complexes were obtained including square planar $[(Ph_3P)ClNi(\mu\text{-ebdtc})NiCl(PPh_3)]$, (ebdtc = ethylenebisdithiocarbamate), five coordinate [Ni(ebdtc)(dppe)], and the unusual six coordinate $[Ni(dedtc)_2(dppe)]$ (dedtc = diethyldithiocarbamate) [256]. In addition, a comparative study of the electronic structures of *N*,*N*′-diethyldithiocarbamate and pyrrole-*N*-carbodithioate and their nickel(II) complexes has been undertaken [257], while the crystal and molecular structure of bis(piperidine-1-dithiocarbamato)nickel(II) has been determined. The complex was found to have a pseudo square planar structure with Ni–S = 2.207(1) and 2.196(1) Å [258].

A convenient synthetic route to the preparation of carbodithioato derivatives of weak nitrogenous nucleophiles has been reported. *N*-Alkyldithiocarbamate ligands, when didentately coordinated to nickel(II), were found to undergo facile electrophilic substitution reactions with a diversity of electrophiles, yielding novel carbodithioato derivatives of weak nitrogenous bases, not available by other synthetic methods [259]. The same group have isolated nickel(II) complexes of the $Ni[S_2CN(E)R]_2$ (E = electrophile, i.e. CONPh, COOEt, $PhSO_2$, *p*-$MePhSO_2$; R = Me, *n*-butyl, phenyl, benzyl, *p*-phenyl). These complexes were characterised by chemical analysis as well as magnetic and spectral studies [260].

The 1,10-phenanthroline (phen) adduct complex of bis(*N*,*N*′-diethyldithiocarbamato)nickel(II), $Ni(dtc)_2$, has been reported. Evidently, this is the first example of the addition of a chelating diamine to square-planar bis(dithiocarbamato)nickel(II) to form the octahedral complex $Ni(dtc)_2(phen)$. The reaction scheme suggested proceeds via the pathway shown (**28**) [261].



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Continuing with adduct complexes, the crystal and molecular structure of (diisopropyldithiocarbamato) (1,1,1-trifluoro-2,4-pentanedithionate)nickel(II) have been reported. The Ni atom is coordinated by the plane of four S atoms, but these were found to be markedly distorted from square planarity, due to the differing bites of the ligands which form the four- and six-membered chelate rings, respectively. Ni–S distances were found to vary from 2.111(4) to 2.2224(4) Å [262].

The behaviour of *O*-alkyl dithiocarbonato complexes, $[Ni(S_2COR)_2]$, towards several phosphine ligands has been studied. Depending on the S_2COR derivative and phosphine (L) used, octahedral complexes, $[Ni(S_2COR)_2L_2]$ (R = cyclohexyl,

L_2 = dppe; R = Et, L = $PMePh_2$), paramagnetic five coordinate complexes, $[Ni(S_2COR)_2(dppe)]$, and square planar complexes, $[Ni(S_2COR)_2(PMe_2Ph_2)]$ (R = Et or cyclohexyl) and $[Ni(S_2COC_6H_{11})_2(PMe_2Ph_2)]$, have been obtained. In addition, the reaction of $[Ni(S_2COR)_2]$ (R = Me, Et, or cyclohexyl) with an excess of dppe produced $[Ni(S_2CO)(dppe)]$, possibly the first Ni^{II}-dithiocarbonate complex reported [263].

Nickel(II) ions have been extracted into chloroform as *N,N'*-diphenyldithiomalonamide complexes from aqueous solutions having pH values of 6.5–7.0 and 7.0–8.0. IR and NMR spectroscopy. were used to establish the type of coordination between *N,N'*-diphenyldithiomalonamide and the Ni(II) ions. It was concluded from the NMR spectra that two isomeric forms in the ratio 8:2 existed [264].

In a study of transition metal complexes of dithiooxamide ligands, the vibrational fine structure in the electronic spectra of symmetrically *N,N'*-disubstituted dithiooxamide ligands and their nickel(II) complexes has been investigated. *N,N'*-Disubstituted dithiooxamide ligands used in this study include HRNC(=S)C(=S)NRH, where R = H, Me, Et, *n*-Bu, *sec*-Bu, benzyl, *p*-chlorobenzyl, *o*-chlorobenzyl, triphenylmethyl and trimethylsilyl, respectively. These ligands function in a didentate S,S coordination mode, yielding complexes with square planar coordination geometry [265].

The complexes, $Ni(S_2C_2O_2)L_2$ {L = $P(Me)_3$ or $L_2 = [P(C_6H_5)_2CH_2]_2$ (dppe), $[P(C_2H_5)_2CH_2]_2$ (depe)}, were synthesized via reaction of $K_2S_2C_2O_2$ and $NiCl_2L_2$, with the exception of $Ni(S_2C_2O_2)(P(Me)_3)_2$, which was prepared from $NiCl_2$(1,2-dimethoxyethane), $K_2S_2C_2O_2$ and $P(Me)_3$. In all the complexes, coordination of the dithiooxalate ligand was found to occur through both S atoms, as evidenced by IR spectroscopy [266].

A number of nickel(II) *O,O*-alkylene dithiophosphates and their adducts with nitrogen bases have been prepared and their structures elucidated via a variety of physicochemical methods. Complexes investigated include NiL_2 (L = 2-mercapto-2-thiono-4,5-dimethyl-1,3,2-dioxa-phospholane, 2-mercapto-2-thiono-4,4,6-trimethyl-1,3,2-dioxaphosphorinane, 2-mercapto-2-thiono-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane and 2-mercapto-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane), $NiL_2 \cdot 2Q$ (Q = pyridine, γ-picoline, β-picoline) and $Ni[S_2]P(OC_2H_5)_2] \cdot 2pY$ [267]. In a continuation of this work, the X-ray crystal and molecular structure of (2,9-dimethyl-1, 10-phenanthroline)bis(4,4,5,5-tetramethyl-1,3,2-dioxaphospholane-2-thione-2-thiolato)nickel(II) have been determined. The structure has been interpreted as involving a pentacoordinated nickel atom with a distorted trigonal bipyramidal geometry, with both chelating and monodentate dithiophosphate moieties. Two equatorial positions are occupied by N atoms of the 2,9-dimethyl-1,10-phenanthroline ligand [Ni–N(average) = 2.01 Å], while the S atoms of the didentate dithiophosphate occupy one equatorial position [Ni–S = 2.499(3) Å] and one axial position [Ni–S = 2.344(3) Å]. The remaining axial position is occupied by the S atom of the monodentate dithiophosphate ligand [Ni–S = 2.398(3) Å] [268]. Similarly, the crystal structure of the adduct of bis(*O,O'*-dibutyldithiophosphato)nickel(II) with bipyridyl has been reported. In this case, distorted octahedral coordination geometry was found, with Ni bound to four S

Table 6
Nickel(II) complexes with Schiff-base ligands containing nitrogen and oxygen donor atoms

Ligand	Complex	Comments	Ref.
Didentate			
N-alkylsalicylaldimine (HL)	[NiL_2]	Alkyl = $(CH_2)_2$Ph, $(CH_2)_3$Ph, $(CH_2)_4$Ph, $(CH_2)_2$(4-hydroxy-Ph); Kinetics of ligand substitution.	[276]
N-2-phenyl-ethylsalicylaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.84(1) Å, Ni–N = 1.93(1) Å].	[277]
N-methyl-5-chlorosalicylaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.818 Å, Ni–N = 1.924 Å].	[278]
N-ethyl-5-chlorosalicylaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.830 Å, Ni–N = 1.916 Å].	[278]
5-Chlorosalicylaldimine (HL)		Formation constants of nickel(II) complexes with Schiff bases derived from **HL** and six sulpha drugs.	[279]
N-*n*-propylsalicylaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.826(2) Å, Ni–N = 1.920(2) Å].	[280]
N-*l*-menthylsalicylaldimine (HL)	[NiL_2]	Pseudotetrahedral stereochemistry.	[281]
2-(Salicylideneamino)fluorene (HL)	[NiL_2]	Ni(II) complex appears to be a mixture of two forms with planar and tetrahedral geometries.	[282]
Salicylideneethylenediamine (HL)	NiLQ.py	HQ = benzoylacetone, dibenzoylmethane. Hexacoordinate complexes.	[283]
N-(2,2-diethoxyethyl)salicylaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.840(4) Å, Ni–N = 1.926(6) Å].	[284]
N-(2,2-diethoxyethyl)-2-oxo-1-naphthylmethylideneimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.827(3) Å, Ni–N = 1.904(4) Å].	[284]
N-(2,2-diethoxyethyl)-3-oxo-1-naphthylmethylideneimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.834(3) Å, Ni–N = 1.937(5) Å].	[284]
N-[(1,3-dioxolan-2-yl)methyl]salicylaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.829(2) Å, Ni–N = 1.913(4) Å].	[285]
N-[(1,3-dioxolan-2-yl)methyl]-2- hydroxy-1-naphthaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.832(2) Å, Ni–N = 1.912(3) Å].	[285]
N-[(1,3-dioxolan-2-yl)methyl]-3- hydroxy-1-naphthaldimine (HL)	[NiL_2]	X-ray crystal structure. Square planar coordination [Ni–O = 1.828(3) Å, Ni–N = 1.941(3) Å].	[285]
(α-Benzoylmethylbenzylideneimino) benzenesulphonic acid (H_2L)		Potentiometric determination of Ni(II) complex stability constants at various temperatures.	[286]

Table 6 (*continued*)

Ligand	Complex	Comments	Ref.
N-(2-hydroxy-3-methoxybenzylidene)-cyclohexylamine		Stability constants of Ni(II) complexes determined in 75 vol.% aqueous dioxane.	[287]
N-(2-hydroxyethyl)-*β*-resorcylaldimine (HL)	NiL_2	Preparation and characterisation via IR spectra.	[288]
Tridentate			
2-(α-Methylsalicylideneamino)phenol (H_2L)	$NiL(H_2O)_3$	Potentiometric study carried out at 25, 35 and 45 .	[290]
Bis(*N*-alkylsalicylaldimine)	$Ni(R\text{-}sal)_2$	R = $-CH(CH_2OH)CH(OH)Ph$, $-CH(CH_3)(CH(OH)Ph$, $(CH_2)_2Ph$; A study on the reactivity of square planar versus octahedral coordination.	[291]
2-(Salicylideneamino)ethanol (HL)	NiL_2	Prepared and characterised via elemental analysis and IR spectra.	[292]
2-(Salicylideneamino)-2-benzothiazole- carbohydrazide (H_2L)	$NiL(H_2O)_3$	L functions as a tridentate dibasic O,N,O donor in the octahedral structure.	[293]
2-(Salicylideneamino)-2-hydroxy-1-naphthaldehyde (H_2L)	$NiL(H_2O)_3$	L functions as a tridentate dibasic O,N,O donor in the octahedral structure.	[293]
N-(4-antipyrino)salicylaldimine (HL)	NiLX	X = Cl, Br, I, SCN, OAc. Square planar or distorted tetrahedral structures.	[294]
N-(5-antipyrino)salicylaldimine (HL)	$[Ni(HL)(H_2O)_2Cl]Cl.H_2O$	Schiff bases coordinate via the carbonyl O of the pyrazolelone ring, the quininoid O and the secondary N atoms.	[295]
N-(5-antipyrino)-2-hydroxynaphthaldimine (HL)	$[Ni(HL)(H_2O)_3]Cl_2.4H_2O$	Schiff bases coordinate via the carbonyl O of the pyrazolelone ring, the quininoid O and the secondary N atoms.	[295]
N-(5-antipyrino)-2,4-dihydroxybenzaldimine (HL)	$[Ni(HL)(H_2O)Cl_2].3H_2O$	Schiff bases coordinate via the carbonyl O of the pyrazolelone ring, the quininoid O and the secondary N atoms.	[295]
4-(2-Pyridylmethylene)amino-1-phenyl -2,3-dimethyl-5-pyrazolone (HL)	$[NiL_2](ClO_4)_2$	L coordinates via pyridyl N, azomethine N and carbonyl O atoms.	[296]
$MeC(O)CH_2C(Me){:}NC_6H_4OH\text{-}o$ (H_2L)	NiL.ROH	R = Pr, iso-Pr. Tetrameric pseudooctahedral structure.	[297]
$MeC(O)CH_2C(Me){:}NCH_2CH_2OH$ (H_2L)	NiL.iso- PrOH	Tetrameric pseudooctahedral structure.	[297]
3-(*N*-α-methyl-2-hydroxybenzylideneimino)-propanoic acid (H_2L)	$NiL.nH_2O$	Octahedral coordination geometry.	[298]
7-Hydroxy-8-[(2-mercaptomethyl)iminomethyl]-4-methyl-2*H*-1-benzopyran-2-one		Tridentate Schiff base was prepared and its complexation with Ni(II) studied pH-metrically in aqueous dioxane (70%v/v).	[299]
Vanillideneanthranilic acid (H_2L)	$[NiL(H_2O)]_2$	Ligand is tridentate coordinating via azomethine N, phenolate O and carboxylate O atoms.	[300]
N-(8-acetyl-7-hydroxy-4- methylcoumarin)-2-imino-ethanamine (HL)	NiL_2	Octahedral complex with ligand coordinating via azomethine and amino N atoms, and phenolic OH group.	[301]
N-(8-acetyl-7-hydroxy-4- methylcoumarin)-2-imino-1- methylethanamine (HL)	NiL_2	Octahedral complex with ligand coordinating via azomethine and amino N atoms, and phenolic OH group.	[301]

Table 6 (*continued*)

Ligand	Complex	Comments	Ref.
Tridentate			
N-(2-hydroxy-l-naphthylidene)amino acid (H_2L)	$[Ni(L)].H_2O$	Amino acid = glycine, L-alanine, L-valine, L-leucine, DL-isoleucine, DL-norleucine, L-serine and L-aspartic acid.	[302]
N,*N*-bis(3,5-di-*tert*-butylsemiquinone) amine (HL)	$[NiL_2]$	X-ray crystal and molecular structure determination. Octahedral coordination with ligand functioning as a O,N,O donor.	[303]
Tetradendate			
N-substituted salicyaldimines		A new synthetic route for the preparation of transition metal complexes with Schiff bases.	[305]
Bis(salicylidene)ethylenediamine (H_2L)	$Ni(L).0.5NH_4X$	The square planar structure of Ni(L) is retained in these adducts.	[306]
	$2Ni(L).NH_4X$-$EtOH$ $3Ni(L).2NH_4I_3.EtOH$	A novel type of interaction via hydrogen bonding between phenolic oxygen atoms of Ni(L) and NH_4^+ is observed.	
N-[2-(2-aminoethylamino)ethyl] salicylidene-amine (HL)	$[NiL](ClO_4)$	X-ray crystal structure determination. Approximate square planar coordination via three N and one O atoms.	[307]
N-[2-(2-aminoethylamino)ethyl] salicylidene-amine (HL)	$[NiL]NCS$	X-ray crystal structure determination. Distorted square planar coordination via one O atom and three N atoms.	[308]
N-{2-[2-(2-aminoethylanino)ethyl amino]ethyl}-salicylideneamine (HL)	$[Ni(HL)](ClO_4)_2$	X-ray crystal structure determination. Irregular square pyramidal coordination sphere about Ni with HL coordinating in a tetradentate fashion via one O atom and three N atoms.	[309]
4′,5′-Bis(salicylideneamino)benzo[15- crown-5] (H_2L)	$NaNi(L)(NO_3).xH_2O$	L functions as a N_2O_2 donor. ^1H NMR, IR, UV-visible and conductance data were reported.	[310]
Bis(salicylideneamino)semi carbazide (H_3L)	M[NiL] (M = Li, Na, K, Rb, Cs)	Analogous complexes were prepared using 5-Cl, 3-OMe, 5,6-dibenzo and 3,5-dichloro-substituted salicylaldehydes.	[311]
5-(2-hydroxyphenyldiazo) salicylaldehyde (H_2L)	[NiL]	Octahedral geometry assigned on the basis of elemental analysis, conductance, magnetic, and IR and electronic spectral data.	[312]
N,*N*′-bis(4-hydroxysalicylidene) ethylene-diamine (H_2L)	NiL-$[O(CH_2)_n Br]_2$ NiL-$[O(CH_2)_6 MV]_2$-$Br_2I_2.12H_2O$	Bromoalkyl derivatives of the Schiff-base complex [NiL] with $n = 2.5$ were prepared, as well as the complex NiL-$[O(CH_2)_6MV]_2$-$Br_2I_2.12H_2O$ in which [NiL] is linked to two Viologen molecules via number six of the methylene groups.	[313]
N,*N*′-*o*-phenylenediiminebis(3- formylsalicylicacid) (H_4L)	$Ni(H_2L)(H_2O)_2$ $Ni(H_2L)(H_2O)Q.nH_2O$ $Ni_2L(H_2O)_2Q_2.nH_2O$	Complexes were found to be nonelectrolytes with pseudooctahedral structures on the basis of IR and electronic spectra, thermal analysis, magnetic moment and electrical conductivity measurements.	[314]

Table 6 (*continued*)

Ligand	Complex	Comments	Ref.
Tetradentate			
N,N′-propylenediiminebis(8-acetyl-7- hydroxy-4-methyl-coumarin) (H_2L)	NiL	Square planar configuration was assigned on the basis of elemental analysis, electrical conductivity, magnetic, electronic and IR measurements.	[315]
N,N′-*o*-phenylenebis(2- furylglyoxaliniine) (L)	Ni(L)Cl_2	A hexa-coordinate structure was proposed on the basis of elemental analysis, molar conductance, magnetic moment data, electronic and IR spectral studies.	[316]
4-[2-(2-Aminoethylamino) ethylimino]pentan-2-one (HL)	[NiL]I.H_2O	X-ray crystal structure determination. Almost square planar coordination sphere about Ni, with L coordinating in a tetradentate fashion via one O atom and three N atoms.	[317]
Diethyl *N,N″*-ethylenebis(2-hydroxyimino-3-iminobutanoic acid) (H_2L)	[NiL]	Preparation and characterisation via electronic absorption, ^{13}C NMR, infrared, and CD spectra.	[318]
Diethyl *N,N″*-[(*R*)-1-methylethylene] bis(2-hydroxyimino-3-iminobutanoic acid) (H_2L)	[NiL]	Preparation and characterisation via electronic absorption, ^{13}C NMR, infrared, and CD spectra.	[318]
N,N″-R-diiminebis(1-phenyl-3-methyl- 4-benzoylpyrazol-5-one) (H_2L)	NiL.2H_2O	R = ethylene, propylene and *o*-phenylene. All complexes were found to be octahedral.	[319]
3,3′-(1,2-Phenylenediimino)diacrolein (H_2L)	[NiL]	Square planar coordination geometry assigned on the basis of mass, electronic, vibrational, NMR and ESR spectroscopy and magnetic susceptibility measurements.	[320]
N,N″-bis(salicylidene)-3,4- diaminofurazan (H_2L)	[NiL]	Template condensation yielded 82% of the nickel complex.	[321]
Glyoxal-bis(*o*-hydroxyanil) (H_2L)	[NiL]	Spectroscopic and theoretical investigation.	[322]

atoms of the *O,O'*-dibutyldithiophosphato ligands and two N atoms of the bipyridyl ligand [269]. In addition, the interaction of NiL_2, where L = bis(2,4-dimethylphenyl)dithiophosphinate, with several pyridine-type base adducts was investigated via relative isotropic ^1H NMR spectroscopic shift studies. Pyridine-type ligands investigated include pyridine, α-picoline, β-picoline, γ-picoline, 3,5-lutidine and 4-phenylpyridine [270].

3.5. Complexes with selenium donor ligands

The preparation of $(Bu_4N)_2NiL_2$ (H_2L = 2-thio-1,3-dithiole-4,5-diselenol) has been reported. This complex can be used as a precursor for mixed sulphur/selenium heterocycles. In addition, a general reaction scheme for the preparation of 4,5-alkylseleno-1,3-dithiole-2-thione has been described [271].

A series of quasi-two-dimensional molecular conductors with formula $[TMTSF]_2[M(tds)_2]$ (TMTSF = tetramethyltetraselenafulvalene; tds = [bis(trifluoromethy)ethylene]diselenato; M = Ni, Pt, Cu) has been reported. In the nickel complex, a novel first-order structural transition in which the low-temperature state exhibits enhanced conductivity, was observed. The crystal and molecular structure of this complex was also reported. The centrosymmetric $[Ni(tds)_2]^-$ anions were found to be essentially planar, with an average Ni–Se bond length of 2.259 Å [272]. The structurally related complex, $[Ph_4P][Ni(Se_2C_2(CF_3)_2)_2]$, has been prepared and compared with its Pt and Au analogues [273].

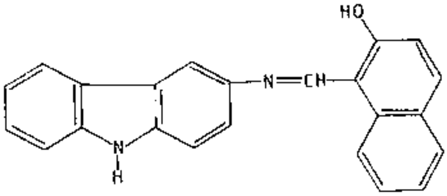
3.6. Complexes with nitrogen–oxygen donor ligands

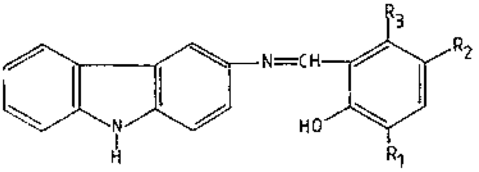
By way of introduction, two articles of general interest have been published. One reports a crystallographic and thermodynamic study of metal ion size selectivity in ligands with groups containing a neutral oxygen donor atom. A number of N,O-donor ligands are included in this study [274]. The second article involves a reappraisal of the amide coordination mode. In this study, the solution properties of nickel(II) complexes of ligands involving simultaneous enamine and amide groups have been discussed [275].

Schiff-base and related ligands continue to dominate this class of ligand. Table 6 lists Schiff-base ligands with nitrogen and oxygen donor atoms that have been complexed with nickel(II). Apart from the didentate ligands listed in Table 6 [276–288], the coordination compounds of Ni(II) with the didentate Schiff-base ligands (**29**) have been prepared and their stereochemistry investigated by magnetic susceptibility studies [289].

Table 6 also lists tridentate ligands that have been prepared and reacted with nickel(II) [290–303]. In addition, tetraphenylborate salts of nickel(II) complexes have been prepared where the nickel(II) is bound to the tridentate Schiff-base adducts of unsymmetrical *N,N*-dimethyl or *N,N*-diethylethylenediamine and the β-dicarbonyl compound, MECOCHRC(O)H (R = MECO or EtOCO or 2-acetyl-5,5-dimethyl-1,3-cyclohexanedione) [304].

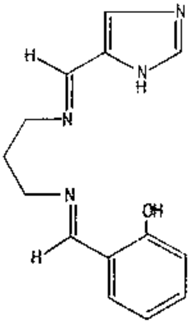
Some tetradentate ligands and their Ni(II) complexes are also listed in Table 6





$R_1 = R_2 = H, R_3 = NO_2$
$R_2 = R_3 = H; R_1 = NO_2$
$R_3 = R_1 = H; R_2 = NO_2$
(29)

[305–322]. Further Schiff-base ligands that have been complexed with Ni(II) include the unsymmetrical Schiff-base ligands (**30**) and (**31**), which have been prepared via the reaction of *N*-(3-aminopropyl)salicylaldimine with imidazole-4(5)-carbaldehyde and imidazole-2-carbaldehyde, respectively [323]. In addition, the nucleophilic replacement of the halogen on the methine carbon of the unsymmetrical tetradentate Schiff-base nickel(II) complex (**32**) by mercaptoacetate has been investigated in dichloromethane [324].



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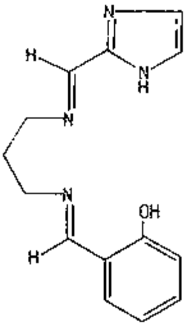
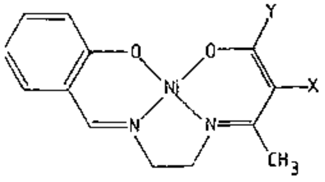


(31)

In a synthetic strategy to prepare a new family of Lacunar Schiff-base complexes, Busch and co-workers have investigated the steric control of electronic effects in diacetylated nickel(II) complexes of the well-known Schiff-base ligand, bis-(acetylacetone)ethylenediamine. In this work, X-ray crystal structures of [3,3′-diacetyl-4,4′-(1,2-ethanediyldinitrilo-κ^2N)bis(2-pentanonato-κ^2O)nickel(II) and [3,3′-diacetyl-4,4′-(1,2-ethanediyldinitrilo-κ^2N)bis(2-butanonato-κ^2O)nickel(II) were reported [325]. The synthetic strategy was successfully completed by this group



(32)

and the lacunar ligands were prepared by adding a long bridging group spanning the plane of the bis(acetylacetone)ethylenediamine Schiff-base ligand. X-ray crystal structures of two of the nickel(II)-lacunar Schiff-base complexes were reported, confirming the bridging lacunar structures. The coordination geometry of the Ni(II) ion in both complexes was found to be essentially square planar (Ni–N varying between 1.802 and 1.848 Å; Ni–O varying between 1.837 and 1.865 Å) [326].

An ongoing study of compartmental Schiff bases is been undertaken by Vigato and co-workers. Work published by this group includes the synthesis, characterisation and catalytic properties of mononuclear and dinuclear complexes of nickel(II) with compartmental Schiff bases derived from 2,6-diformyl-4-chlorophenol and polyamines [327], the preparation, properties and crystal structures of nickel(II) complexes with the acyclic Schiff bases derived from 2,6-diformyl-4-chlorophenol and 1,5-diamino-3-thiapentane or 3,3′-diamino-*N*-methyl-dipropylamine [328], and the metal complexes of dinucleating ligands derived from 2,6-diformyl- and 2,6-diacetyl-4-methylphenol and the facultative diamine 1,5-diamino-3-oxapentane and the functionalised diamine 1,3-diamino-2-hydroxypropane [329].

Nickel(II) complexes of the hexadentate Schiff-base ligands obtained by the condensation of salicylaldehyde-5-sulphonate with polyamines in the presence of nickel ions, have been characterised in aqueous solution using ^{1}H NMR spectroscopy. Polyamines used in the preparation of these complexes include $H_2NC_2H_4NRC_2H_4NRC_2H_4NH_2$ (R = H, CH_3), $CH_3C(CH_2NH_2)_3$, and $N[CH_2)_2NH_2]_3$ [330].

The complexation of hydrazone and hydrazide ligands has been investigated extensively. Complexes containing hydrazone ligands that have been isolated in the solid state include $Ni(HL)_2Cl_2 \cdot 4H_2O$ and $NiL_2 \cdot nH_2O$ (HL = 2-acetylpyridine 2-furoylhydrazone [331], diamagnetic NiL_2 (HL = 2-hydroxy-3-methoxybenzaldehyde phenylhydrazone and 2-hydroxy-1-naphthaldehyde phenylhydrazone) [332], $Ni(HL)_2Cl_2 \cdot 2H_2O$ (HL = monoisonicotinoylhydrazone of diacetyl), $Ni(HL^1)_2Cl_2 \cdot H_2O$ (HL^1 = monoisonicotinoylhydrazone of acetylacetone), NiL^2_2 (HL^2 = bis(isonicotinoylhydrazone) of diacetyl) [333], and $[Ni(H_2L)(H_2O)_2](NO_3)_2 \cdot 3/2H_2O$ (H_2L = 2,6-diacetylpyridine bis(2-hydroxybenzoylhydrazone) [334]. The crystal structure of the latter complex, revealed pentagonal-bipyramidal coordination for the $[Ni(H_2L)(H_2O)_2]^{2+}$ ions, held together with the nitrate ions and uncoordinated water molecules via a three-dimensional network of hydrogen bonds. Hydrazone ligands that have been studied in solution include acetoacetanlidehydrazone [335], benzilmono(lepidyl)hydrazone [336], 5,5-dimethylcyclohexane-2-(2′-hydroxyphenyl)hydrazono-1,3-dione [337] and 2,4-dihydroxybenzylidene phenylhydrazone [338]. This last study also included an investigation of 2,4-dihydroxybenzylidene thiosemicarbazone.

A study of nickel complexation with acid hydrazides has resulted in the isolation and characterisation of NiL_2 ($HL=NH_2NHC(O)R$ {R = 4-pyridyl, *o*-, *m*-, *p*-ClC_6H_4, Ph, *p*-$NO_2C_6H_4$, *p*-$MeOC_6H_4$} and $NH_2NHC(S)NH_2$). Coplanar orientation of the ligands relative to the metal ion was observed in all cases, with NiL_2 ($HL=NH_2NHC(S)NH_2$ and *o*-$ClC_6H_4C(O)NHNH_2$) having a *cis* configuration, with the other complexes having a *trans* structure [339]. Other hydrazide complexes that have been isolated include octahedral $NiL\cdot nH_2O$ (H_2L = *N,N*-diacetyloxaldihydrazide and *N,N*-diacetylmalondihydrazide) [340], octahedral NiL_2 (HL = 3(*p*-dimethylaminoanilino)methylsalicylic acid hydrazide) [341], and $[NiL_2Cl_2]\cdot H_2O$, $[NiL_3]Cl_2\cdot H_2O$, $[NiL_3]Br_2\cdot H_2O$, $[NiL_3]I_2\cdot H_2O$, $[NiL_2SO_4]\cdot 4H_2O$, $[NiL_2(NCS)_2]$ and $[NiL_2(OAc)_2]$, where L is the hydrazide of 1-naphthylacetic acid [342].

Turning to semicarbazone ligands, complexes that have been isolated in the solid state include $NiL_2(H_2O)_2$ (HL = 4-benzoylsemicarbazone-1-phenyl-3-methyl-2-pyrazolin-5-one) [343], $[Ni(HL)_2](ClO_4)_2$, $[Ni(HL)_2(NO_3)_2]$, $[Ni(HL)_2Cl_2]$, $[Ni(HL)_2Br_2]$, $[Ni(L)_2](ClO_4)_2$, $[Ni(L)_2(NO_3)_2]$, $[Ni(L)_2Cl_2]$, and $[Ni(L)_2Br_2]$, where HL is *N*-methyl-2-[1-(2-pyridinyl-1-oxide)ethylidene]-hydrazinecarbothoamide [344]. In this last study, the deprotonated ligand was found to function in a didentate N,O donor fashion, while the protonated ligand functioned in a tridentate N,O,S donor fashion. In addition, a variety of solution studies have been reported. Ligands investigated include 2-hydroxy-1-naphthaldehyde monosemicarbazone [345,346], *o*-vanillinsemicarbazone [347,348], and 3-semicarbazono-1-butanecarboxylic acid [349]. Solid chelates of the last ligand were also isolated and spectral evidence suggests that the resultant complexes are octahedral, with the ligand functioning as a monobasic tridentate donor, coordinating via the azomethine N and carbonyl O atoms.

In a study of transition metal complexes with thiosemicarbazide ligands, the synthesis, crystal and molecular structure and spectra of *S*-methyl-*N*(1)-salicylidene-*N*(4)-α-methoxypicolylisothiuosemicarbazidonickel(II) have been reported. The Ni^{II} coordination environment was found to be slightly distorted square planar with the ligand functioning as a N,N,N,O donor. The Ni–O bond length was 1.831(4) Å, while the Ni–N bond lengths were 1.835(5), 1.803(5) and 1.908(5) Å, respectively [350]. The same group have published the crystal and molecular structure of ammine(benzoylacetone-*S*-methylisothiosemicarbazonato)nickel(II) iodide. Again the complex was found to be slightly distorted from square planar, with the coordination sphere consisting of the O,N,N atoms from the tridentate thiosemicarbazide ligand [Ni–O = 1.817(5) Å and Ni–N = 1.824(6) and 1.847(6) Å] and completed by the ammine N atom [Ni–N = 1.918(5) Å] [351]. Other semicarbazide ligands that have been complexed with Ni(II) include 1-isonicotinoyl-4-phenyl-3-semicarbazide [352], *N*1,*N*4-di(salicylidene)isochalcogenosemicarbazide ligands [353], and a series of polythiosemicarbazide ligands [354].

Oximes, structurally related to Schiff base, hydrazone and semicarbazone ligands, have also attracted some interest as N,O donor ligands. A number of complexes have been isolated in the solid state including the new species K[Ni(cbqo)(cbsqo)], where cbqo = 4-chloro-1,2-benzoquinone 2-oximate and cbsqo = 4-chloro-1,2-benzosemiquinone 2-oximate [355], Ni(β-ketox)$_2$(H_2O)$_2$, where Hβ-ketox = benzoylacetaldehyde mono-oxime and acetylacetonate mono-oxime) [356], Ni(HL)$_2$ where H_2L = 1,2-hydroxylaminooximes [357], NiL where H_2L = bis(1,2-diphenyl-1-hydroxyimino-2-ethylidene)-1,2-diaminobenzene and Ni(H_2L)X_2 (X = Cl, Br, I, ClO_4, NO_3) [358], and complexes of 2-hydroxy-1-acetonaphthone oxime and its isomer 1-hydroxy-2-acetonaphthone oxime [359]. Solution studies have also been undertaken to examine the complex-formation equilibria occurring in aqueous solutions of 2-amino-*N*-hydroxyhexanamide and α-amino-1*H*-indole-3-*N*-hydroxypropanamide and nickel(II). These ligands were found to be bound to the metal ion through the N atom of the α-amino group and the deprotonated NHO^- group [360]. In addition, the solvent extraction of *N*-ethylglyoxylanilide oxime and its nickel(II) complexes into chloroform has been investigated. It was found that Ni(II) is extracted as NiL_2 or NiL_2(HL), depending on the ligand concentration [361].

$NiLCl_2$ (L = cyanobenzphenacylidene *p*-*N*,*N*-diethylaniline) has been prepared as part of an ongoing physicochemical study of α-cyano-3:4-benzphenacylidene *p*-*N*,*N*-diethylaniline with some transition metal ions. The complex was characterised via elemental analysis, magnetic susceptibility and IR spectral methods. L was found to chelate via its carbonyl O and azomethine N atoms [362].

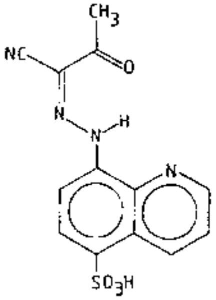
The crystal and molecular structure of chloro(3,7-diazanonanediamide)nickel(II) perchlorate have been elucidated. This compound was found to be a penta-coordinate nickel(II) complex in which the metal ion is in a slightly distorted square pyramidal coordination geometry. The diaminodiamide ligand occupies the equatorial positions [Ni–N = 1.996(3) and 2.004(3) Å; Ni–O = 1.959(2) and 1.966(3) Å], while the chloride ligand occupies the axial position [Ni–Cl = 2.558(1) Å] [363].

In a study of the complexation of 2-(3-phthalhydrazidylazo)-1,3-ketone ligands with transition metal ions, H_2L = phthalhydrazidylazoacetylacetone, phthalhydrazidylazobenzoylacetone and phthalhydrazidylazodibenzoylmethane have been reacted with Ni(II). The resultant complexes, NiL(H_2O), were characterised on the basis of their analytical, magnetic moment, molar conductance, IR and ^{1}H NMR spectral data. The ligands were found to function in a dibasic, tridentate fashion [364].

The salicylaldazine ligand, H_2L = *o*-HOC_6H_4CH:NN:CHC_6H_4OH-*o*, has been complexed with nickel(II). IR spectral studies indicate that the ligand functions in a tetradentate fashion in the octahedral complex, NiL · $2H_2O$. Coordination was suggested to occur via two azomethine N atoms and both the phenolic O atoms [365].

A number of coordination complexes with diphenylacetylhydrazine and its chlorinated derivative (L) have been prepared. The nickel complexes, [NiL_3](NO_3)$_2$ · H_2O, were found to have octahedral coordination, with the ligand functioning in a didentate N,O donor fashion [366].

The kinetics of ternary complex formation between nickel(II) 2,2′:6′,2″-terpyridine and the tridentate quinolylazo dye, α-(8-quinolylazo)-α-acetoacetonitrile (**33**), have been investigated by stopped-flow and conventional spectrophotometry at pH 6–8. Both a short-lived and long-lived intermediate were observed. The dye (**33**) was found to be able to form either of two tridentate chelates with a five- and six-membered ring, and the slow relaxation observed was attributed to the isomerisation of the rapidly formed, metastable tridentate chelate to a more stable form. The conversion of the shortlived to the long-lived species was attributed to a slow ring closure from a didentate intermediate [367].



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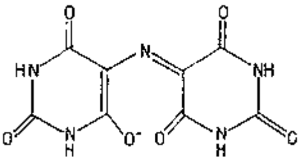
Spectral studies on the magnetically anomalous Ni(II) complexes of variously substituted phenylazo-2,4-dinitrosoresorcinol compounds have been undertaken. Complexes of the type [Ni(L)(H_2O)] (H_2L = *o*-carboxyphenylazo-2,4-dinitrosoresorcinol) and [NiCl(L)(H_2O)] (HL = *o*-chlorophenylazo-2,4-dinitrosoresorcinol, *o*-tolylazo-2,4-dinitrosoresorcinol, *m*-chlorophenylazo-2,4-dinitrosoresorcinol, *m*-tolylazo-2,4-dinitrosoresorcinol, *m*-nitrophenylazo-2,4-dinitrosoresorcinol) were prepared and characterised. IR spectra showed that all of the ligands, except *o*-carboxyphenylazo-2,4-dinitrosoresorcinol, function in a monobasic didentate fashion coordinating to nickel(II) via the enolised phenolic oxygen and azo-nitrogen atoms. *o*-Carboxyphenylazo-2,4-dinitrosoresorcinol was found to function as a dibasic, tridentate *O,N,O*-donor ligand. Planar⇔tetrahedral equilibrium for these complexes was also observed [368].

Continuing with azo-containing ligands, 1-(2-fluoronylazo)-2-naphthol (HL), has been complexed with nickel. The resultant complex, NiL_2, was assigned a square planar configuration on the basis of magnetic susceptibility measurements [369]. Similarly, the nickel(II) complexes of a number of 1-[2-hydroxy-4(5)-nitrophenyl]-3-alkyl-5-(2-benzazolyl)formazan ligands have been isolated. These complexes varied in coordination geometry depending on the ligand and solvent employed [370].

Turning to solution studies, the complexation of murexide (**34**) with nickel(II) has been studied spectrophotometrically in aqueous ethanol mixtures. Stability constants were determined and the effect of solvent was also investigated [371]. In addition, pH-metric titration has been used to determine the stepwise stability constants of the nickel(II) complexes with 3-[α-(*o*-hydroxyphenyl)ethylidenehydrazino]-6-phenylpyridazine in aqueous solution [372], and the nickel(II) complexes with *N*-hydroxy-*N*-phenyl-*N'*-*p*-anisoylbenzamidine in aqueous dioxane (50%) [373], while complex formation of 1,15-diaza-3,4:12,13-dibenzo-5-8,11-trioxacycloheptadecane with Ni(II) has been investigated potentiometrically in 95% aqueous methanol solution [374].



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The X-ray crystal and molecular structure of the nickel(II) complex formed with 3,3′,4,4′-tetrachloro-5,5′-dicarbethoxy-2,2′-dipyrromethene (HL) have been reported. [NiL_2] was found to be six-coordinate with a distorted octahedral configuration consisting of the four pyrrole nitrogen atoms [Ni–N = 1.968(4), 1.983(4), 2.082(4) and 2.107(4) Å] and two oxygen atoms [Ni–O = 2.285(4) and 2.326(4) Å] of the ligand [375]. Similarly, the X-ray crystal and molecular structure of bis(isothiocyanato) (2,2′,2″-trihydroxytriethylamine-*N,O,O′,O″*)nickel(II) have been elucidated. In this complex, the nickel(II) ion was found to be octahedrally coordinated by the N atoms of the NCS^- ions [in mutually *cis* positions; Ni–N = 2.000(2) and 2.023(2) Å] and the N and O atoms of the tetradentate 2,2′,2″-trihydroxytriethylamine ligand [Ni–N = 2.079(2) Å, Ni–O = 2.072(2), 2.115(2) and 2.140(2) Å] [376].

A number of variously substituted amino-sulphonic acid and related ligands have been complexed with nickel(II). Solution studies include the complexation of *N*-(tris(hydroxymethyl)-methyl)-2-amino-ethanesulphonic acid [377], 2-[α-phenyl-2-hydroxybenzylidene)amino]ethane-sulphonic acid [378], several 1-nitroso- and 2-nitrosonaphtholsulphonate ligands [379], and 1-(4′-phenoxy-3′sulphophenyl)-3-stearolamino-δ-2-pyrazolin-5-one [380]. Complexes of nickel(II) with sulphaguanidine (L), $NiLCl_2 \cdot 2H_2O$, and sulphadimidine (HL^1), [$NiL^1(OH)]_2$, were isolated in the solid state. Both ligands were found to function in a didentate fashion, coordinating via the sulphonyl O atom and an N atom, forming a six-member chelate [381].

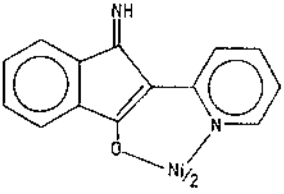
The complex formation of 2-hydroxypropylene-1,3-diamine-*N,N,N′,N′*-tetramethylenephosphonic acid with Ni(II) has been studied by potentiometric titration in aqueous solution. Complex formation constants for a variety of complexes have been determined and modelled mathematically [382].

Variously substituted pyridine ligands provide an ideal source of N,O-donor ligands, a number of which have been complexed with nickel(II). 3-Acetylpyridine (L) has been reacted with a variety of nickel(II) salts, yielding complexes of the type [NiX_2Ln] (X = Cl, Br, or NCS; n = 2 or 4). Polymeric and monomeric octahedral coordination geometries were obtained, depending on the nickel salt and reaction conditions employed [383].

Picolinic acids have also been used to great effect. Pyridine-2,6-dicarboxylic acid (H_2pdc) has been complexed with Ni(II). The resultant complex, $Na_2[Ni(pdc)_2] \cdot 3H_2O$, was characterised as high-spin octahedral, based on molar conductance, magnetic susceptibility, IR and electronic spectra, and thermogravimetric measurements [384]. Similarly, the tetradentate bis(picolinic acid) ligand, 1,1-bis(6-carboxy-2-pyridyl)-1-methoxypropane, has been reacted with Ni(II). Spectroscopic data indicate the presence of a 1:1 complex in which the dibasic ligand functions as a N_2O_2 donor [385]. In addition, the formation constants of the ternary chelates of nickel(II) with a series of picolinic acids and some N,O and O,O donor ligands have been determined in aqueous media [386].

A variety of pyridine carboxamide ligands have been prepared and reacted with Ni(II). These include *N*-(2-pyridyl)pyridine-2′-carboxamide (HL), which yielded complexes of the type $Ni(HL)Cl_2 \cdot H_2O$, $Ni(HL)_2X_2$ (X = Cl, Br, NCS, ONO_2) and $NiLCl.nH_2O$ [387], and *N,N,N′,N′*-tetramethylpyridine-2,6-dicarboxamide (tdpa), *N,N′*-dimethyl-*N,N′*-diphenylpyridine-2,6-dicarboxamide (dpda), and *N,N,N′,N′*-tetraisopropylpyridine-2,6-dicarboxamide (ppda), which produced the corresponding complexes, octahedral $Ni(tpda)_2(ClO_4)_2$, distorted octahedral $Ni(ppda)_2(ClO_4)_2$, tetrahedral $(NiCl_2)_3(tpda)_2$, pentacoordinate $\alpha NiBr_2(dpda)$, pentacoordinate NiBr(dpda)(2,2-dimethoxypropane), square pyramidal $\beta NiBr_2$-(dpda), and square pyramidal NiBr(dpda)(acetone), respectively [388].

The complex formation of Ni(II) with aminopyrophthalone has been studied by means of electronic, IR, EPR and ^{1}H NMR spectroscopy. It was found that with Ni(II), two isomeric complexes were formed. On the basis of spectral data obtained, these complexes were assigned structures (**35**) and (**36**), respectively [389].



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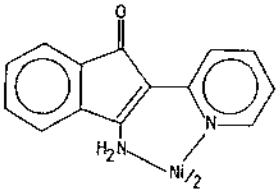

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Other substituted pyridine ligands that have been studied include 2,3-hydroxypyridine [390], cinchomerate (3,4-diamidopyridine) [391], 2-(2′-pyridyl)-4,4-di(hydroxymethyl)oxazoline) [392] and 1,2-diphenyl-2-(2′-pyridylimino)ethanol [393].

As usual, 8-hydroxyquinoline and related ligands have attracted considerable interest. A general article has appeared in which the vibrational spectra of some solid 8-hydroxyquinoline metal complexes have been reported together with a correlation of coordination bond length and type of metal ion [394]. In addition, the crystal and molecular structures of bis(5,7-dibromo-8-quinolato-*N,O*)bis(pyridine)nickel(II)-1.25pyridine [395] and bis(5,7-dichloro-8-quinolato-*N,O*)bis(pyridine)nickel(II) [396] have also been reported. Both complexes were found to exhibit pseudo-octahedral coordination for Ni(II), via the two quinolinol ligands and two pyridine ligands in *cis* positions.

Solvent extraction studies have also been undertaken. In one study, the effect of an alkyl chain substituent on the kinetics and thermodynamics of complexation of 8-hydroxyquinolines with Ni(II) was investigated in methanol [397]. In a second study, the equilibrium and structure of species formed in the extraction of divalent transition metal ions with 8-quinolinol (Hq) were investigated. Factors varied in this study included anions and organic solvents. Three species were found to be responsible for extraction *viz.* $Ni_2q_3(Hq)_3X$, $Niq_2(Hq)$ and $Ni_2q_4(Hq)_2$. The crystal structure of $Ni_2q_4(Hq)_2$ was also elucidated, revealing two nickel atoms surrounded by three didentate ligands with facial and meridional configurations about their oxygen atoms, and that these two isomers form a binuclear structure joined by two strong hydrogen bonds [398]. In addition, in a separate study, the effect of solvent composition on the completing of nickel(II) with 8-hydroxyquinoline has been investigated [399].

A number of mixed chelate and ternary complexes of nickel with 8-hydroxyquinoline have been isolated. These include $NiLL^1$, $NiLL^1L^2$ and $NiLL^1L^2L_2$, where $HL = HS_2CNEt_2$, HL^1 = 8-hydroxyquinoline, dimethylglyoxime, pyridinecarboxylic acid, $L^2 = H_2O$ or pyridine-*N*-oxide. Spectral and magnetic data were used to assign tetracoordination to $NiLL^1$, pentacoordination to $NiLL^1L^2$ and hexacoordination to $NiLL^1L^2L_2$, respectively [400].

The complexation of amine–acetic acid and related ligands with nickel(II) has been widely studied. Ligands that have been investigated in aqueous solutions containing Ni^{II} include ethylenediamine-*N,N'*-diacetate [401], iminodiacetate and nitrilotriacetate [402], hydroxyethyl-iminodiacetate [403], β-hydroxyethyliminodiacetate [404], 3,6-bis(methyleneiminodiacetic acid)catechol [405], *n*-octyliminodiacetate [406], ethylenediaminedisuccinic acid [407], 1,3-phenylenediamine-*N,N'*-disuccinic acid [408], the ubiquitous *N,N,N',N'*-ethylenediaminetetracetic acid [409,410], (*N*-(2-hydroxyethyl)ethylenediaminetriacetic acid [411], and 4-chloro-1,2-phenylenediamine-*N,N,N',N'*-tetraacetic acid [412]. In addition, a ^{13}C NMR spectroscopic study of (*meso*-2,3-butanediaminetetracetato)nickelate(II) has been undertaken. Results of this study have shown that the ligand functions as a hexadentate coordinator at all temperatures accessible in deuterated water and over a pH range from 1 to 13. Less than 1% of the ligands were found to act as pentadentate coordinators [413].

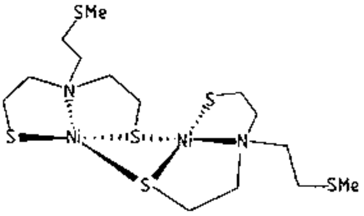
Computer-aided potentiometric studies have been carried out at 25 and 35 °C in 50% (v/v) dioxane–water media on systems of the type NiL'L'', where L' = *N*-phenyl-2-furrohydroxamic acid, *N*-phenyl-2-thenohydroxamic acid, or one of their *ortho*, *meta* or *para* derivatives, and L'' = 1,10-phenanthroline. The formation of mixed ligand complexes of high thermodynamic stability was observed [414].

3.7. *Complexes with nitrogen–sulphur donor ligands*

X-ray crystal methods have been used to determine the structures of a number of nickel(II) complexes with imidazolyl-thioether and related ligands [415–421]. Essential details about these complexes are listed in Table 7.

Reaction of $[NiCl_4]^{2-}$ with preformed or generated *in situ* thiolates from pyridine-2-thiol (py2SH) and pyrimidine-2-thiol (pm2SH), yielded the thiolato complex anions $[Ni(S2py)_3]^-$ and $[Ni(S2pm)_3]^-$, respectively. Isolated as their tetraethylammonium and tetraphenylphosphonium salts, respectively, the crystal and molecular structures of these two complex anions have been elucidated. Both were found to have a distorted octahedral structure containing three four-membered N,S chelate rings with exceptionally small N–Ni–S bite angles of about 67°. The average Ni–N and Ni–S distances were found to be 2.052(4) and 2.5289(1) Å in $[Ni(S2py)_3]^-$ and 2.043(4) and 2.495(2) Å in $[Ni(S2pm)_3]^-$ [422].

In a study investigating ligand oxidation in nickel thiolate complexes, the reaction of *N,N*-bis(2-mercaptoethyl)-2-(methylthio)ethylamine with anhydrous nickel(II) acetate yielded the dimeric product (**37**). Chemical oxidation of (**37**) with iodine resulted in the immediate formation of the distorted square pyramidal complex (**38**), the structure of which has been determined [Ni–S = 2.407(4) and 2.377(4) Å, Ni–N = 2.109(10) Å, and Ni–I = 2.627(2) and 2.620(2) Å] [423]. Oxidation of (**37**) with molecular oxygen resulted in the square planar sulphinato complex (**39**), the structure of which has also been elucidated [Ni–S = 2.175(3) and 2.146(3) Å, Ni–N = 1.973(7) Å, and Ni–CN = 1.875(10) Å] [424].



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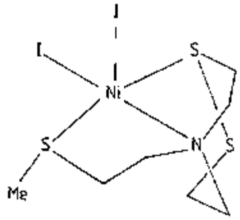

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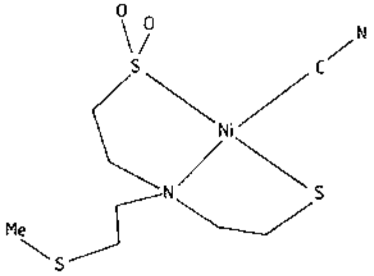

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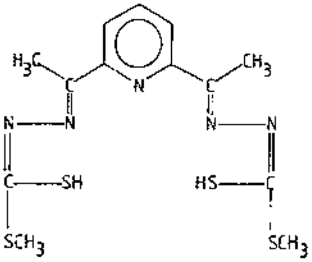
Thiosemicarbazone and thiosemicarbazide ligands constitute a good source of N,S donor ligands. Complexes that have been isolated and characterised in the solid state include $Ni(L)\cdot 2H_2O$ [L = acetylacetone bis(4-phenylthiosemicarbazone)] [425], [NILX] (HL = 3-azabicyclo[3.2.2]nonane-3-thiocarboxylic acid 2-{1-(2-pyridinyl)ethylidene]hydrazide; X = Cl, Br, NCS, N_3, NO_2, NCSe) [426], NiL_2 (HL = acetone thiosemicarbazone, 2-butanone thiosemicarbazone) [427], $NiL_2\cdot 2H_2O$ (HL = 5-R-substituted-isatin 3-thiosemicarbazone; R = H, Me, Cl, Br, NO_2) [428], NiL_2 (HL = thiophene-2-aldehyde 4-phenylthiosemicarbazone) [429], NiL_2 (HL = thiosemicarbazone or 4-Ph- or 4-methylthiosemicarbazone of 2-furfural or

2-thiophenecarbaldehyde or *o*-nitrobenzaldehyde) [430], NiL_2 (HL = thiophene-2-aldehyde thiosemicarbazone) [431], $[NiL(H_2O)_2]\cdot n(H_2O)$ (H_2L *p*-chlorophenyloxalylthiosemicarbazide) [432], and *trans*- and *cis*-NiL_2,(HL = thiosemicarbazide) [433]. In addition, thermodynamic studies of the complexation of Ni(II) with 2-mercaptophenyl-4-benzamidothiosemicarbazide were carried out using pH-titration methods [434].

Similarly, the following nickel(II) complexes have been prepared using thiohydrazone ligands; $NiL_2\cdot 2H_2O$ (HL = thiophene-2-aldehyde nicotinic acid hydrazone) [435], NILNCS (HL = pyridine-2-carboxaldehyde thioisonicotinoylhydrazone) [436], and $[Ni(HL)_2$ (H_2L = thioaroylhydrazones; R = H, NO_2) [437]. In addition, the Schiff base obtained by the reaction of *S*-methyldithiocarbazate with 2,6-diacetylpyridine, H_2L = (**40**), has been reacted with Ni(II). The resultant complex, [NiL], was assigned a low-spin five-coordinate structure with the ligand functioning as a dinegatively charged pentadentate N_3S_2 chelating agent [438].



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As part of an ongoing study of metal chelates of heterocyclic nitrogen containing ketones, some transition metal complexes of sulphur–nitrogen–nitrogen containing ligands have been prepared and isolated. These include trigonal bipyramidal $[NiLX]_2$ [HL = MeSC(S)NHN:CPhCH$_2$R; R = 2-pyridyl] and square planar $[NiL^1]_2X_2$ [HL^1 = MeSC(S)NHN:CPhCH$_2$R; R = 6-methyl-2-pyridyl; X = Cl, Br, I] [439].

The ligand NCC(:NOH)C(S)NH$_2$(HL) has been prepared and reacted with nickel(II). The resultant complex, NiL_2, is tetracoordinate, with the methanide ligand L^- functioning in a didentate fashion coordinating via the nitroso N and the S atoms. Adduct complexes, NiL_2.2py, NiL_2(en) and NiL_2Q (Q = tetramethylcyclam) were also prepared [440].

A number of 2-alkylthio-5-mercapto-1,3,4-thiadiazole ligands have been complexed with Ni(II). These include 2-methylthio-, isopropylthio, or butylthio-5-mercapto-1,4,4-thiadiazole. Complexation was investigated in dmso solution and complexes were also isolated in the solid state. IR spectral evidence indicates involvement of both N and S atoms in bonding with Ni(II) [441].

The properties of the complexes {Ni[NHNC(S)SMe]$_2$}, {Ni[NPhNC(S)SMe]$_2$}, and {Ni[N(CH$_2$Ph)NC(S)SMe]$_2$} have been investigated using electronic, IR, ESR and XPS spectral methods. In addition, the X-ray crystal

Table 7
X-ray crystallographic data for nickel(II) complexes with imidazolyl-thioether and related ligands

Ligand (L)	Complex	Structural data	Ref.
1,3-Bis(5-methyl-4-imidazolyl)-2-thiapropane	$[NiL_2]SiF_6 \cdot 5H_2O$	The Ni(II) ion is octahedrally coordinated by four imidazole N atoms and two S atoms of L in a *cis* configuration. Ni N = 2.040(6), 2.044(6), 2.041(5) and 2.068(6) Å; Ni–S = 2.513(2) and 2.496(2) Å.	[415]
1,6-Bis(4-imidazolyl)-2,5-dithiahexane	$[NiL_2(H_2O)_2](NO_3)_2$	The Ni(II) ion is octahedrally coordinated by two imidazole N atoms and two S atoms of L, and two O atoms of *cis* coordinated water ligands. Ni N = 2.027(3) and 2.050(3) Å; Ni S = 2.448(1) and 2.453(1) Å, and Ni 0 – 2.077(2) and 2.084(3) Å.	[416, 417]
1,7-Bis(5-methyl-4-imidazolyl)-2,6-dithiaheptane	$[NiLX_2]$	(X = Cl, Br, NCS). Distorted octahedral geometry with both anions and the tetradentate L coordinated. Cis coordination of X and the S atoms, and *trans* coordination of the imdiazolyl N atoms was proposed on the basis of the crystal structure of the Co analogue.	[418]
5-Methyl-4-(ethyl-mercaptomethyl)imidazole	$[NiL_2(H_2O)_2](NO_3)_2$ $[NiL_2(NCS)_2]$	Crystal structure of $[NiL_2(H_2O)_2](NO_3)_2$ reveals distorted octahedral coordination with Ni coordinated to two thioether S atoms and two imidazole N atoms of L, and two O atoms from coordinated water molecules, all in a *trans* configuration. Ni N = 2.012(2) Å; Ni S = 2.4929(7) Å, and Ni O – 2.116(2) Å.	[419]
1,12-Bis(3,5-dimethylpyrazol-1-yl)-2-diaza-5,8-dithiadodecane	$[NiL](X)_2$	$X = ClO_4$, BF_4; Crystal structure of $[NiL](BF_4)_2$ reveals that the Ni ion is octahedrally chelated by two S atoms, two amine N atoms and two pyrazolyl N atoms of the hexadentate ligand. Ni N(amine) 2.117(4) and 2.099(4) Å; Ni S – 2.435(2) and 2.434(2) Å, and NiN(pyrazol) · 2.111(5) and 2.125(5) Å.	[420]
1,1,10,10-Tetrakis(3,5-dimethylpyrazol-1-yl)-2-diaza-5,8-dithiadecane 2-Aminoethanethio)	$Ni_2L(X)_4(H_2O)_n$	$X = BF_4$, $n = 2$; $X = NCS$, $n = 0$: All complexes are hexacoordinate, as deduced from their spectroscopic properties.	[420]
	$[NiL_3]_2Hg_3Cl_4(H_2O)_4$	The compound consists of the anionic species, $[NiL_3]^-$, held together in a network with $(Hg_3C_4)^{2-}$ ions via bridging thiolato groups. The coordination of Ni(II) is octahedral with Ni N and Ni S distances ranging from 2.088(7) to 2.120(8) and 2.413(2) to 2.473(3) Å respectively.	[421]

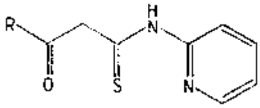
structure of $\{Ni[PhNC_6H_4NNC(S)SMe]\}(NCS)$ was determined. According to spectroscopic evidence, $\{Ni[NHNC(S)SMe]_2\}$ and $\{N[NPhNC(S)SMe]_2\}$, are both diamagnetic, while $\{Ni[N(CH_2Ph)NC(S)SMe]_2\}$ is paramagnetic at room temperature. The ligands function as a tridentate N,N,S donor in each of the complexes [442].

Some 3-*N*-(R-substituted)-4-oxoquinazoline-2-thione ligands (HL; R = Me, Et, Pr, iso-Pr, Bu, allyl, Ph, *p*-tolyl, *p*-methoxyphenyl, *p*-ethoxyphenyl, *p*-chlorophenyl, *p*-bromophenyl) have been complexed with nickel(II) and the resultant complexes isolated and characterised. Their adducts with pyridine were also prepared and characterised. Analytical evidence suggests that coordination occurs via the N atom at position 1 and the S atom [443]. In addition, the same group have prepared the mixed-ligand complexes of nickel(II) with 2-mercapto-3-phenyl-4-quinazolinone and various nitrogen-containing heterocyclic bases such as pyridine, β-picoline, imidazole, 2,2′-bipyridine and *o*-phenanthroline [444].

A number of variously substituted α-cyano-β-aminodithioacrylate ligands (HL) have been prepared and reacted with nickel(II). The resultant complexes, NiL_2, were characterised using ESCA spectroscopy. Coordination of the chelating ligand was found to occur via the dithioester sulphur atom and the amine nitrogen atom, as evidenced by the S2p and N1s electron binding energies in the ESCA spectra [445].

5(3)-Methylpyrazole-3(5)-thiocarboxamide (HL) has been complexed with a variety of nickel(II) salts. The resultant octahedral complexes, $Ni(HL)_3X_2 \cdot H_2O$ ($X = Cl, NO_3, 0.5SO_4, ClO_4$), and square planar complex, $Ni(L)_2 \cdot 2H_2O$, were isolated and characterised in the solid state by magnetic and electronic spectra. Both HL and L^- function in a didentate fashion, with coordination occurring via the pyrazolyl ring N and the thioamide S atoms [446].

N-(2-Pyridinyl)ketothioacetamides (**41**) have the capability to be potential N,S,O donor ligands. Complexes of the type, NiL_2 [HL = (**41**)] have been prepared and characterised. Spectral and magnetic properties of these complexes have been determined, suggesting tetracoordinate structures in which coordination of the ligands occurs via the S,N donor sets with the O donor atom remaining uncoordinated [447].

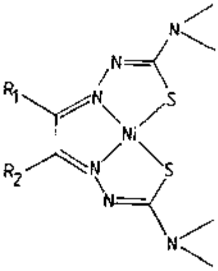


R = Me, Ph

(**41**)

In an ongoing study of sulphur–nitrogen-bonded metal chelates, the reactions of nitriles, alkenes, alkynes, PHNCS and CS_2 with coordinated azide in nickel(II) chelates of the type $[NiL(N_3)]$ ($L = L^1$-L^3), $[L^1Ni(N_3)NiL^1](ClO_4)$, and $[L^1Ni(N_3)NiL^3](ClO_4)$, where HL^1 = methyl 2-[(2-aminomethyl)amino]cyclopent-1-enedithiocarboxylate, HL^2 = methyl 2-{[2-(dimethylamino)ethyl]amino}-cyclopent-1-enedithio-carboxylate, and HL^3 = methyl 2-{[2-(diethylamino)-ethyl]amino}cyclopent-1-enedithiocarboxylate, have been investigated [448]. Similarly, the same group have investigated the reactions of the structurally related nitrile complexes, $[NiL(NCR)](ClO_4)$ (HL^1 = methyl 2-[(2′-aminomethyl)-amino-lcyclopent-1-enedithiocarboxylate, HL^2 = methyl 2-[(2′(dimethylaminoethyl)-aminolcyclo-pent-1-enedithio-carboxylate, and HL^3 = methyl 2-[(2′-(diethyl-amino)ethylamino]cyclopent-1 -enedithiocarboxylate; R = H, Me, Et or Ph), with methanol and ethanol under different experimental conditions. Complexes isolated include $[Ni_2L_2(\mu\text{-OMe})](ClO_4)$, $[Ni_2L_2(\mu\text{-OH})](ClO_4)$, and $[NiL\{NH{=}C(OMe)R\}](ClO_4)$ [449].

In a similar study on the reactivity of some coordinated ligands containing sulphur towards nucleophilic substitution reactions, the kinetics and mechanism of the reaction of [1,2-diphenylethanediylidene bis(*S*-methylhydrazinecarbodithioate)-*N*,*N*′,*S*,*S*′(-2)]nickel(II) with the alicyclic secondary amines, piperidine and morpholine, have been investigated. Two successive steps were observed, the substitution of the first SMe group deactivating the second SMe group, yielding the final complex (**42**) [450].



R_1 = Ph, R_2 = H
(**42**)

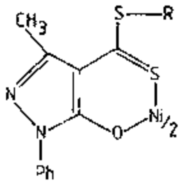
A novel synthetic approach has been used to prepare metalla-sulphur–nitrogen compounds. Metal atom vapour synthesis has been used to generate nickel atoms which, when reacted with disulfurdinitride, yielded the complex $[Ni(S_2N_2H)_2]$ in about 15% yield [451]. In addition, the crystal and molecular structure of the related complex, $(NH_4)[Ni(S_2N_2)(S_2N_2H)]$ has been elucidated. Two planar $[Ni(S_2N_2)(S_2N_2H)]^-$ anions [Ni–S = 2.137(2) and 2.138(2) Å; Ni–N = 1.849(5) and 1.867(5) Å], related by an inversion centre, were found to be linked by hydrogen bonding to form a dimer [452].

3.8. *Complexes with oxygen–sulphur donor ligands*

In a structural study of metal complexes with thiosemicarbazide derivatives, the nickel(II) complex, NiL_2, where HL = 1-cyanoacetyl-4-cinnamoylthiosemicarbazide, has been synthesized and characterised. An octahedral structure has been suggested with coordination occurring via the thiocarbonyl S and two carbonyl O atoms [453].

Nickel(II) when reacted with 2-thio-6-picoline *N*-oxide (HL) yielded the *trans*-square planar complex, NiL_2, as verified by the single IR absorption bands assignable to both ν(Ni–O) and ν(NiS). This complex was reduced to its Ni(I) analogue upon exposure to ^{60}Co γ-rays, while reaction with 3,4-lutidine yielded the mono adduct, NiL_2.3,4-lutidine [454].

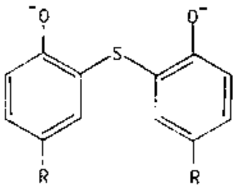
A number of 4-alkyldithioate-5-hydroxy-3-methyl-1-phenylpyrazoles (alkyl = n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$) have been prepared and complexed with nickel(II). All complexes were found to have a metal:ligand ratio of 1:2 and were assigned square planar structures on the basis of analytical and spectroscopic data. Although a number of coordination sites are available, the ligands were found to coordinate through the S and O atoms, as shown in (**43**) [455].



R = n-C_6H_{13}, n-C_8H_{17}, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$
(**43**)

The synthesis and structure of bis(1,1 -diethyl-3-(2-chlorobenzoyl)-thioureido)nickel(II) have been reported. Ni(II) was found to be coordinated in a planar fashion by two S and two O atoms of the two didentate uninegative ligands, in a *cis* arrangement. The Ni–S and Ni–O bond lengths are approximately 2.14 and 1.84 Å, respectively, with the two bonds of each type differing only slightly [456].

The reactions of 2,2′-thiodiphenolato(2-) ligands (**44**) (R = H, Me, Br), with nickel(II), cobalt(II) and copper(II) chlorides have been described. Nickel(II) complexes of the type $Li_2NiL_2 \cdot x$MeOH$\cdot y H_2O$ were isolated. An X-ray structure of the analogous copper(II) complex was carried out revealing octahedral coordination, in which the ligand functions as a O,S,O tridentate donor [457].



R = H, Me, Br
(**44**)

Potentiometric studies have been undertaken by the same group, which investigate the complex formation of nickel(II) ions with 3-(2-naphthyl)-2-mercaptopropenoic acid [458] and 2-mercapto-3-phenylpropenoic acid [459]. Both studies were carried out in aqueous ethanol solutions at 25 °C. Formation constants for the 1:1 and 1:2 (Ni:ligand) complexes were reported.

3.9. Complexes with nitrogen–oxygen–sulfur donor ligands

In an ongoing study of the vibrational spectra of complexes with planar monothio-oxamides, the nickel(II) complex, $NiL \cdot H_2O$, where $H_2L = N,N'$-dimethyl-monothio-oxamide, has been prepared and characterised. The complex is square planar, with L^{2-} functioning as a bridging S,N/N,O tetradentate ligand, giving rise to a polymeric structure [460].

The Schiff-base disulfide ligands *N,N'*-[1,1'-dithiobis(phenylene)]bis(salicylideneimine), H_2salps, and *N,N'*[1,1'-dithiobis(ethylene)]bis(salicylideneimine), H_2sales, have been reacted with nickel(II) acetate tetrahydrate in methanol. The resultant complexes, [Ni(salps)(MeOH)] · MeOH and [Ni(sales)], have been characterised by spectroscopic, magnetic and electrochemical methods. In addition, the X-ray crystal structure of [Ni(salps)(MeOH)].MeOH has been elucidated. The salps ligand was found to function as a quinquedentate ligand in this complex, coordinating via two phenoxalate O atoms, two imine N atoms, and only one of the disulphide S atoms. The sixth coordination site is occupied by the O atom from a methanol ligand. The coordination sphere was found to be highly distorted octahedral as indicated by the range in bond lengths and angles. On the other hand, based on its spectral and magnetic properties, the complex [Ni(sales)] appears to be square pyramidal with a Ni–S bond [461].

A number of thiosemicarbazone ligands have been prepared and complexed with Ni(II). These include 28 thiosemicarbazones prepared from acetophenone, acetone, formic acid, pyruvic acid, *o*-aminobenzaldehyde and thiosemicarbazide [462], pyruvic acid anilide thiosemicarbazone [463] and salicylaldehyde thiosemicarbazone [464]. The crystal and molecular structures of the last two complexes were reported. Both ligands were found to function as tridentate, dinegative S,N,O donors.

The complex, NiL_2, where $HL = HS_2CN(CH_2CH_2OH)_2$, has been prepared and isolated from an aqueous solution of Ni(II), $HN(CH_2CH_2OH)_2$ and CS_2. Complex characterisation was carried out using elemental analysis, magnetic susceptibility, IR, UV and mass spectroscopy [465].

The stable free-radical complexing reagents, 4-xanthato-2,2,6,6-tetramethylpiperidine-1-oxyl (KL), 4-carboxy-4-amino-2,2,6,6-tetramethylpiperidine-1-oxyl (HQ) and their Ni(II) and Cu(II) complexes have been prepared and characterised. NiL_2 and CUQ_2 were characterised by their XPS, UV, IR and ESR spectra [466].

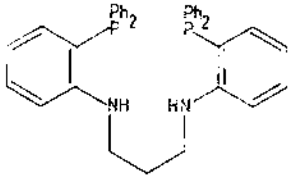
Turning to solution studies, the complexation of nickel(II) with 2-hydroxy-, 2-hydrazo-, and 2-phenylaminobenzothiazole has been investigated in aqueous ethanol solutions [467]. In addition, the absorption spectra of nickel(II) complexed with 2-(6-bromo-2-benzothiazolylazo)-5-diethylaminophenol have been investigated in aqueous solution [468], while the same group have studied the colour reaction of nickel(II) and 2-(6'-bromo-2'-benzothiazolylazo)-5-carboxyphenol in aqueous solution [469].

The reactions of octahedral bis[2(1-methyl-2-oxo-propylidenehydrazine-*S*-methylcarbo-dithioato)*NSO*(-1)]nickel(II) with aromatic heterocyclic amines (pyridine, 3- and 4-methylpyridine), secondary aliphatic amine (diethyl, di-*n*-propyl and di-*n*-butylamine) and alicyclic amines (piperidene and morpholine) have been studied in benzene. Spectroscopic studies have shown that these reactions proceed via nucleophilic displacement of the two coordinated carbonyl O atoms to give the corresponding bis(amine) adducts [470].

3.10. Complexes with nitrogen–phosphorus donor ligands

The preparation of the new phosphine–amine ligand, L = HN-$(CH_2CH_2CH_2PMe_2)_2$, and its complexation with Ni(II) have been reported. The resultant complex, $NiCl_2L$, has been characterised via elemental analysis, magnetic susceptibility, conductivity and NMR and IR spectral methods. On this basis, the complex has been assigned a five-coordinate structure in which the ligand functions as a tridentate *P,N,P*-donor [471].

The new multidentate P_2N_2hybrid ligand, *N,N'*-bis[2-(diphenylphosphino)phenyl]propane-1,3-diamine, H_2L = (**45**), has been prepared by demetallisation of its neutral deprotonated complex, [NiL], obtained by the metal-template-catalysed condensation of bis(2-phenylphosphinophenylamido)nickel(II) with 1,3-bis(toluene-*p*-sulfonyloxy)propane in the presence of base. The crystal and molecular structure of [NiL] have also been elucidated. The ligand, L^{2-}, was found to behave as a P_2N_2 tetradentate ligand giving a distorted square planar geometry about the Ni(II) ion. Bond distances were Ni–P = 2.160(3) and 2.148(3) Å, and Ni–N = 1.923(7) Å for both Ni–N bonds [472].



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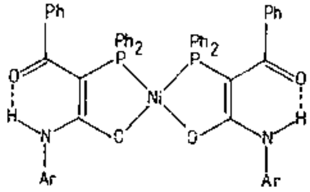
3.11. Complexes with phosphorus-oxygen donor ligands

In an ongoing study of complexes with functional phosphines, the carbon–carbon coupling reactions by isocyanate insertion into nickel-coordinated β-phosphino enolates have been investigated. Complexes of the type (**46**) (Ar = Ph, *p*-MeC_6H_4) were isolated and the crystal structure of the complex with Ar = p-MeC_6H_4 was determined. The nickel atom was found to be in a nearly planar environment with the phosphorus atoms occupying cis positions. Ni–P = 2.170(3) and 2.170(2) Å, while Ni–O = 1.876(4) and 1.878(4) Å [473]. In addition, the same group have examined carboncarbon coupling between nickel-coordinated β-phosphino enolate complexes and the alkyne $MeO_2CC\equiv CCO_2Me$. Similar coordination, with the ligand functioning in a didentate P,O donor fashion was observed [474].



Ar = Ph, p-MeC_6H_4
(46)

3.12. Complexes with halide ligands

The compound $(Xe_2F_{11}^+)_2NiF_6$ has been prepared via the reaction of nickel difluoride, krypton difluoride and xenon hexafluoride in anhydrous hydrogen fluoride. In addition, the crystal and molecular structure have been determined. NiF_6^{2-} was found to be essentially octahedral with Ni–F distances ranging from 1.77(1) to 1.79(1) Å [475].

In a study of protonated phosphorus ylide tetrachlorometallates, the crystal and molecular structure of $2[C_6H_5C(O)CH_2P(C_6H_5)_3]^- \cdot [NiCl_4]^{2-}$ have been elucidated. The coordination environment about nickel(II) was found to be tetrahedral surrounded by two protonated ylide cations. Ni–Cl bond lengths ranged from 2.251(2) to 2.270(2) Å [476].

Turning to solution studies, the complexation of Ni(II) with chloride ions has been studied by calorimetry and spectrophotometrically in *N,N*-dimethylformamide [477], while the interaction of $NiCl_2$ with LiCl, $CaCl_2$ and HCl has been investigated spectrophotometrically in aqueous solution [478]. In addition, the formation of the chloro complexes of Ni(II) in dmso have been studied potentiometrically at 25 °C [479].

Similarly, the bromo-nickel(II) species occurring in dmso solutions have been investigated. The bromo-nickel(II) species identified from their ligand field spectra consisted of the octahedral species $[NiBr(dmso)_5]^+$ and $[NiBr_2(dmso)_4]$, and the tetrahedral species $[NiBr_3(dmso)]^-$ and $[NiBr_4]^{2-}$ [480].

Calorimetry has been used to study the effect of 2,2′-bipyridine on nickel(II)-halide interactions within their ternary complexes in *N,N*-dimethylformamide. The data obtained in this study were well explained in terms of the presence of $[NiBr(bpy)]^+$ and $[NiBr(bpy)_2]^+$. Similar results were obtained for the chloride system [481].

4. Nickel(II) macrocyclic complexes

A number of articles of general interest have been published in this ever increasing area of research. A review with 68 references entitled "Heavy metal chemistry of mixed donor macrocyclic ligands. Strategies for obtaining metal ion recognition" has appeared. This work discusses the design and preparation of macrocycles which are specific for particular metal ions, and the kinetic, thermodynamic and theoretical aspects of these interactions [482]. A review containing 30 references has also appeared which describes the acid-hydrolysis of some Co(III) macrocyclic complexes of the type $[CoLCl_2]^+$ and the acid-catalysed dissociation of Cu(II) and Ni(II) complexes of the type $[CuL]^{2+}$ and $[NiL]^{2+}$ [483].

4.1. Macrocycles with nitrogen donor atoms

By way of introduction to this section, articles of general interest concerning nitrogen donor macrocyclic complexes that have appeared include a study of the kinetics of acid-promoted dissociation of diamine–diimine macrocyclic complex cations with nickel(II) and copper(II) [484], the determination of the equilibrium constant for binding hydroxide to tetraazamacrocyclic–nickel(II) complexes [485], the preparation of 14 new TCNQ (7,7,8,8-tetracyanoquinodimethane) simple salts of the type $ML(TCNQ)_3$, where M = Ni, Cu and L = tetraaza macrocyclic ligands [486], and a potentiometric study of the equilibria between Ni(II) and the large polyazacycloalkanes of the series $[3k]aneN_k$ ($k = 7$–12) carried out in aqueous medium at 25 °C [487].

1,4,8,11-Tetraazacyclotetradecane (cyclam) and its variously substituted analogues continue to attract considerable interest. Data relating to a number of these ligands and their nickel(II) complexes are listed in Table 8 [488–497]. In addition to the complexes in Table 8, the isolation and characterisation of a paramagnetic nickel(II)–peroxoacetimido derivative of $[NiL](ClO_4)_2$ (L = *dl*-hexamethyl-1,4,8,11-tetraazacyclotetradecane) (**47**) has been reported [498].

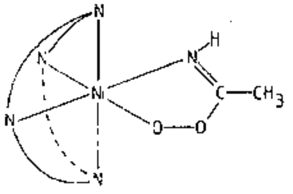
Another area of research that is gaining much popularity is the preparation of macrocyclic complexes with pendent arms that may or may not take part in coordination to the metal ion. Pendant groups containing acid, hydroxy, acetyl, amine, and heterocyclic base functional groups have been used to great effect in this regard.

In an ongoing study, the synthesis, properties and structures of the mononuclear complexes of Ni(II) with 12- and 14-membered tetraazamacrocycle-*N*,*N*′,*N*″,*N*‴-tetraacetic acids have been investigated. Structural data indicate that the complexes are octahedral, with coordination occurring via the four N atoms of the macrocycle and two O atoms of the carboxylate groups [499]. As part of the same study, the one-step synthesis of mono-*N*-substituted azamacrocycles with a carboxylic group in the side chain and their complexes with Ni(II) and Cu(II) has been reported. Macrocycles prepared in this study include 1,4,8,11-tetraazacyclotetradecane-1-acetic acid, 3-(1,4,8,11-tetraazactyclotetradec-1-yl)propionic acid, 4-(1,4,8,11-tetraazactyclotetradec-1-yl)methylbenzoic acid, 1,4,7-triazacyclononane-1-acetic acid, 4-(1,4,8,11-tetraazactyclotetradec-1-yl)butyric acid, and 2-(1,4,8,11-tetraazactyclotetradec-1-yl)methylbenzoic acid [500]. Other macrocycles containing pendant arms with acid functional groups that have been complexed with Ni(II) include 1,4,8,12-tetraazacyclopentadecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid [501], 1-oxa-4,7,10-triazacyclododecane-*N*,*N*′,*N*″-triacetic acid [502], and (7*R*,14*S*)5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid [503,504].

Synthetic and equilibrium studies have been carried out on the nickel(II) com-

Table 8
Nickel(II) complexes of cyclam (1,4,8,11-tetraazacyclotetradecane) and its variously substituted analogues

Ligand (L)	Complex	Comments	Ref.
1,4,8,11-Tetraazacyclotetradecane	$[NiL(ClO_4)](ClO_4)$	X-ray crsytal structure determination. Axially disposed anions are shared between octahedra, with Ni–N distances ranging from 1.93(2) to 2.00(2) Å.	[488]
		Formation constant for the Ni(II) complex has been measured by an out-of-cell technique to be 20.1 ± 0.5 in 0.5 M NaCl at 25°C.	[489]
	NiL^{2+}	The electrocatalytic properties of these complexes with respect to CO_2 and H_2O reduction have been investigated in water, dmf and CH_3CN.	[490]
	$Ni_2(biscyclam)^{4+}$	Used as a catalyst in the photochemical reduction of CO_2 to CO in water. Yields of both CO and H_2 were found to be pH dependent.	[491]
	$[NiL]Cl_2$	Variable temperature and pressure equilibrium study in the coordinating solvents CH_3CN, dmf, dmso, PHCN, H_2O and $ClCH_2CN$. Complex exists as an equilibrium mixture of *R,S,R,S*-$[NiL]^{2+}$ and *R,S,R,S*$[NiL(solvent)]^{2+}$.	[492]
1,4,8,11-Tetramethyl-1,4,8,11-tetraazacyclotetradecane	$[NiL](ClO_4)_2$	Study of axial coordination and ion-pair formation of *R,S,R,S*-$[NiL]^{2+}$ in *N,N*-dimethylacetamide, or CH_3CN, with nitrobenzene.	[493]
C-meso-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane	$[NiL](ClO_4)_2$	X-ray crystal and molecular structure determination as part of a study on Ni(II) complexes of *N*-substituted tetraaza macrocycles. The complex was found to have elongated octahedral geometry in which the perchlorates coordinate weakly to the apical sites.	[494]
C-meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane	$[NiL](ClO_4)_2$	X-ray crystal and molecular structure, determination. The Ni atom was found to sit in the plane of the four N atoms of the macrocycle [Ni–N 1.942(6) and 1.941(9) Å].	[495]
dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane	$[NiL](ClO_4)_2$	DTSBQ = 3,5-di-*tert*-butylsen-fiquinone; Y = ClO_4, $B(Ph)_4$, PF_6. X-ray crystal structure determination of [NiL(DTSBQ)] PF_6 reveals distorted *cis*-octahedral coordination sphere for Ni(II).	[496]
Rac-hexamethyl-1,4,8,11-tetraazacyclotetradecane	[NiL(DTSBQ)]Y	Equilibrium study in the coordinating solvents CH_3CN, methylformamide, dmso, dmf and Me_2NAc.	[497]



(47)

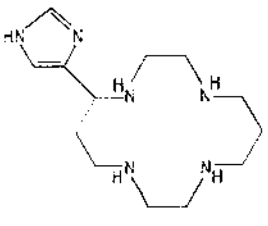
plexes of N,N',N'',N'''-tetrakis(2-hydroxyethyl)-1,4,8,11-tetraazacyclotetradecane. The synthesis of the ligand and the formation of the complexes, $[NiL]^{2+}$, $[NiLH_{-1}]^+$ and $[NiLH_{-2}]$ in solution, have been described. In addition, the crystal and molecular structure of the complex, $[NiL_{-1}](ClO_4)$, have been determined. The complex was found to contain two independent centrosymmetric subunits, with the coordination sphere about Ni(II) almost regular octahedral with four equatorial N atoms and two axial O atoms of two centrosymmetric hydroxyethyl side arms. The macrocyclic ligand was found to adopt the *trans* III stereochemistry [505]. Other hydroxy-containing pendant arin ligands that have been prepared and complexed with Ni(II) include the optically active C-functionalised cyclam, (*S*)-5-(hydroxymethyl)-1,4,8,11-tetraazacyclotetradecane [506], and 6,14-diacetyl-10-hydroxy-7,13-dimethyl-1,4,8,11-tetraazacyclopentadeca-4,6,12,14-tetraene [507].

Turning to macrocycles with amine-containing pendant arms, the hexamine ligand, 1,4,7-tris(3-aminopropyl)-1,4,7-triazacyclononane (L), has been prepared and reacted with Ni(II). The crystal structure of the complex $[Ni(L)]Br_2 \cdot H_2O$ has been elucidated, revealing an approximate three-fold symmetry. Ni–N bond lengths were found to range from 2.128(14) to 2.160(2) Å. In addition, oxidation of the complex cation with NO^+ gave rise to a Ni(III) species [508]. Other complexes involving tetrazaa macrocycles with amine-containing pendant arms that have been prepared include octahedral $[NiL](ClO_4)_2$ (L = 6,13-diamino-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane), the crystal structure of which has been elucidated [509], and octahedral $[NiL(H_2O)](ClO_4)_2$ and square planar $[Ni(HL)](ClO_4)_3$, where L = 5-aminomethyl-2,5,10,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane. A crystal structure of the Co analogue of $[NiL(H_2O)](ClO_4)_2$ indicates that the pendant N atom coordinates in a *trans* configuration to the water ligand [510].

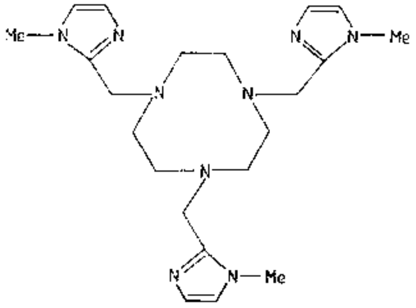
Heterocyclic base-pendant arms have been attached to a variety of macrocycles. The nickel(II) complexes of 5-oxo-7-phenyl-1,4,8,11-tetraazacyclotetradecane (L) and 5-oxo-7-(2-pyridyl)1,4,8,11-tetraazacyclotetradecane (L′) have been prepared and the crystal and molecular structures determined as their perchlorate salts. The complex $[Ni(H_{-1}L)](ClO_4)$ was found to be essentially square planar, while the complex $[Ni(H_{-1}L')(H_2O)](ClO_4)$ was found to be hexacoordinate with the pendant pyridine N atom *trans* to the coordinated water ligand [511].

In part five of an ongoing study of pendant-arm macrocyclic ligands, the two new pyridinecontaining penta aza macrocycle ligands, 7-[2′-(1″-pyrrolidinyl)ethyl]- and 7-[3′-(1″-pyrrolidinyl)propyl]-3,7,11,17-tetraazabicyclo[11.3.1] heptadeca-1(17),13, 15-triene (L^1 and L^2, respectively) have been prepared and reacted with nickel(II). The resultant complexes, octahedral $[Ni(L^1)(OClO_3)](ClO_4)$ and planar $[Ni(HL)](ClO_4)_2$ where $L = L^1$ or L^2, were isolated and characterised. Coordination of perchlorate and the pendant pyrrolidinyl N atom in $[Ni(L^1)(OClO_3)](ClO_4)$ was verified via a crystal structure determination [512].

Macrocycle ligands containing pendant arm-imidazole groups that have been complexed with Ni(II) comprise L=(**48**) [513], L′=(**49**) and L″=(**50**) [514]. Coordination by the pendant arm imidazole N atom was found to occur in all of the complexes. Of particular interest is the fact that (**48**), when reacted with Ni(II), yielded two isomeric complexes with the stoichiometry, $Ni(L)(ClO_4)_2$. X-ray crystal structure determinations of these two complexes revealed that one isomer contained the ligand in a folded conformation with the imidazole N and a perchlorate O atom occupying the remaining two cis sites, while the other, which was recrystallised in acetonitrile, revealed high-spin Ni(II) with planar cyclam in the chair form with the imidazole N and acetonitrile N atoms occupying *trans* axial positions. Conversion from the folded cyclam complex to the square planar cyclam complex was found to occur by heating the folded complex.



R = H, X = H_2 (5HCl salt)
(48)



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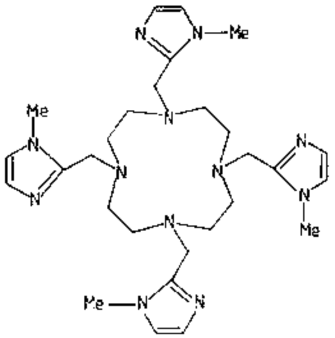
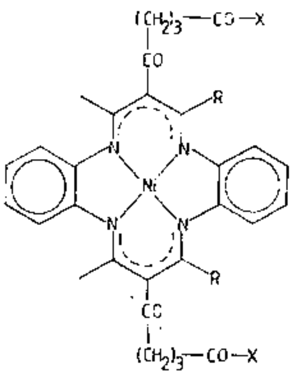


(50)

New penta- and hexaazamacrocycles based on tri- and tetraazamacrocycles have been prepared via a single pendant coordinating 2,2′-bipyridyl-6-ylmethyl-arm. The quinquedentate ligand, 2′,2″-bipyridyl-6′-ylmethyl-1,4,7-triazacyclononane (L), has been complexed with Ni(II) and the crystal structure of the resulting complex cation, $[Ni(L)(H_2O)]^{2+}$, isolated as its perchlorate salt, has been elucidated. The complex is essentially pseudo-octahedral with Ni–N ranging from 1.978(8) to 2.123(8) Å, and Ni–O = 2.152(7) Å [515].

Considerable attention has been paid to the synthesis and structural elucidation of lacunar Ni(II) macrocycle complexes. On the synthetic aspects, Cameron and Graham have reported the synthesis and characterisation of some new nickel(II) macrocyclic complexes of the "lacunar" type, in which the ligand has, as part of its superstructure, either 4-vinylphenyl or allyl groups capable of undergoing polymerisation reactions with selected co-monomers [516]. Eilmes has also concentrated on developing a synthetic approach to these complexes and has published work relating to the synthesis of new γ,γ'-disubstituted derivatives of macrocyclic Jäger-type Ni(II) complexes [517]. This has been extended by further work in which they, γ,δ-unsaturated-δ-lactonic substituents of these γ,γ'-disubstituted derivatives of macrocyclic Jäger-type Ni(II) complexes have been transformed into new open-chain peripheral substituents carrying carboxyl and ester functions [518]. In addition, an efficient synthetic route to peripherally substituted and lacunar nickel(II) complexes of dibenzotetraaza[14]annulenes has been reported. Aminolytic cleavage of γ,δ-unsaturated-δ-lactonic substituents of disubsdtuted nickel(II) complexes of dibenzotetraaza[14]-annulenes was accomplished by means of aliphatic amines and diamines, leading to amide containing derivatives having either pendent open-chain γ,γ'-substitutuents (**51**) or γ,γ'-bridging groups (**52**), respectively [519].



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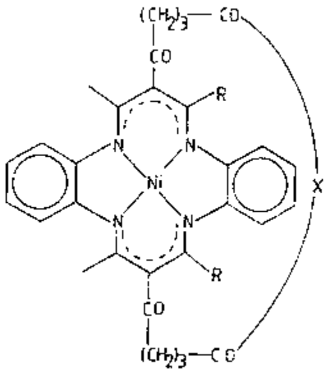


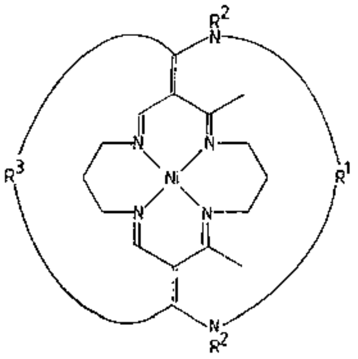
(52)

Busch and co-workers have published a number of articles relating to the structural elucidation of lacunar nickel(II) cyclidene macrocycle complexes. In chronological order of appearance, their work includes:

- The elucidation of structural relationships and assignment of the ^1H NMR spectra of five nickel cyclidene macrocycles using DEPT and two-dimensional NMR spectroscopic techniques [520].
- As the initial phase of a study on transition metal complexes of superstructured

cyclidene macrobicycles, the synthesis and X-ray crystal structures of seven unbridged complexes have been reported and analysed. In this study, it was shown that the saddle conformation is critical to the bridging reaction which produces the cavities in the lacunar and vaulted complexes [521].

- By combining a new retro-bridge with previously known bridging reaction, both lacunar (**53**) and vaulted (**54**) doubly bridged cyclidene complexes of nickel(II) have been prepared. In addition, the X-ray crystal structure determination of $\{Ni[(CH_2)_8(CH_2pipz)_2(3,6\text{-dur})[16]\text{-cyclidene}]\}(PF_6)_2.CH_3CN$ was also reported [522].



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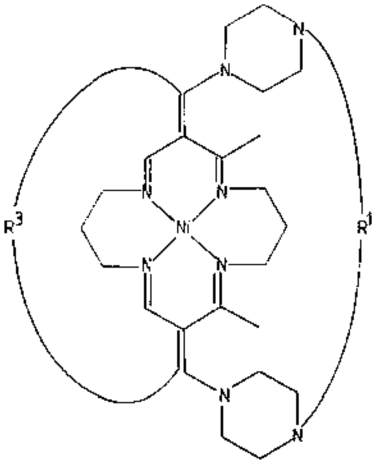


(54)

- The synthesis, via a template process, of lacunar nickel(II) complexes of 15-membered cyclidene ligands having $(CH_2)_n$ ($n = 5$–8, 12) or *m*-xylene bridging units. This study includes the crystal structure of (2,3,10,11,13,19-hexamethyl-3,10,14,18,21,24-hexaazabicyclo[10.7.6]pentacosa-1,11,13,18,20,24-hexaene-κ^4N)nickel(II) hexafluorophosphate [523].
- A detailed structural analysis on the cavities of lacunar cyclidene complexes having polymethylene chains as bridging groups, in which bridge lengths ranged from trimethylene to dodecamethylene [524].

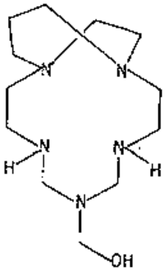
Template synthesis has been used to prepare the 13-membered tetraazamacrocycle, 12-methyl-12-nitro-1,4,7,10-tetraazacyclotridecane. Reaction of formaldehyde and nitroethane or nitropropane with nickel(II) complexes of 1,8-diamino-3,6-diazaoctane in methanol was used to prepare the complexed macrocycle [525].

The new macrocyclic ligand, 6,14-dimethyl-1,5,9,13-tetraazacyclohexadeca-5,13-diene ($Me_2[16]$diene), has been prepared by the non-template condensation of 1,3-propanediamine monohydroperchlorate and methyl vinyl ketone at −10 °C under anhydrous conditions. Reduction of $Me_2[16]$diene with sodium borohydride yielded *C-meso-* and *C-rac-*Me_2[16]diene. All three macrocycles were found to undergo facile complexation with nickel(II) [526].

A donor–acceptor molecular solid with the formula, [Ni(L)][TCNQ], where NiL = (hexamethyldibenzotetraazaannulenato)nickel(II) and TCNQ = tetracyanoquinodimethane, has been synthesised and its crystal and molecular structure determined. The coordination sphere about nickel was found to be pseudo-square planar with Ni–N distances of 1.859(2) and 1.871(3) Å [527].

The distorted octahedral complexes, [Ni(TML)X_2], where TML = the tetradentate macrocyclic ligand derived from *m*-phenylenediamine and 2,3-butanedione and X = Cl, Br, NO_3 and NCS, have been prepared and characterised. In these complexes, TML was found to coordinate via all of the azomethine N atoms, which are bridged by biacetal moieties [528].

A structural and molecular mechanics study has been undertaken on some novel, structurally reinforced, tetraaza macrocyclic ligands of high field strength. In this study, the synthesis of the complexes of low-spin Ni(II) with the three ligands (**55**), (**56**) and (**57**) has been described, together with the crystal structures of the cations, isolated as their perchlorate salts [529].



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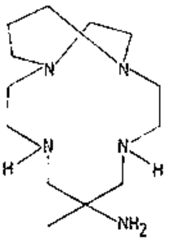

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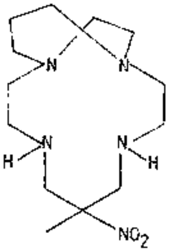


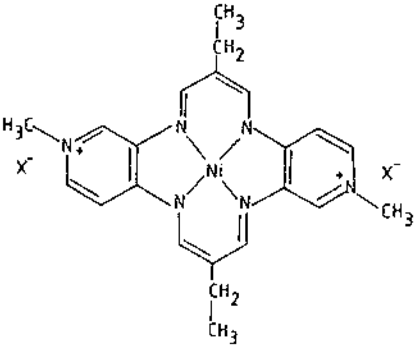
(57)

Suh and co-workers have investigated the nickel(II) complexes of new ligands containing a tetraazabicyclononane ring. In this work, they have reported the syntheses and crystal structures of [3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo-[3.3.1]nonane]nickel(II) perchlorate and (8-methyl1,3,6,8,10,13,15-heptaazatricyclo[13.1.1.$1^{13,15}$]octadecane)nickel(II) perchlorate [530], the syntheses and properties of the nickel(II) complexes of the 14-membered hexaaza macrocycles, 1,8-diethyl- and 1,8-diethyl-1,3,6,8,10,13-hexaazacyclotetradecane [531], and the template condensation synthesis and characterisation of the nickel(II) complexes of the hexaaza macrotricyclic ligands, 1,3,6,9,11,14-hexaazatricyclo[12.2.1.$1^{6,9}$]-octadecane and 1,3,6,10,12,15-hexaazatricyclo[13.3.1.$1^{6,10}$]eicosane [532].

A number of synthetic approaches have been used to prepare tetraaza macrocycle nickel(II) complexes with fused aromatic rings on the macrocycle. In an ongoing series, Black and co-workers have employed metal template reactions in the general synthesis of "dibenzocorromins" and related nickel(II) complexes including: (a) variously substituted 6,7,8,9-tetrahydro-5*H*-tribenzo[b,f,m][1,4,8,12]tetraazacyclopentadecinato(2-)nickel(II), variously substituted 6,7,8,9,9,16,17-hexahydro-5*H*-dibenzo[f,m][1,4,8,12]tetraazacyclopentadecinato(2-)nickel(II), variously substituted 5,6,7,8,9,16,17,18-octahydrodibenzo[b,k][1,5,9,13]tetraazacyclohexadecinato(2-)nickel(II), and complexes formed by their oxidative dehydrogenation [533]; (b) macrocyclic amide and ester complexes via 1,1′-oxalylbisisatin, including 13,20-disubstituted-5,6,7,8-tetrahydrotribenzo[b,f,l][1,4,8,11]tetraazacyclotetradecine-6,7-dionato(2-)nickel(II) complexes [534]; and (c) variously substituted di(pyrrolidin-1-ylcarbonyl)-5,6,7,8-tetrahydrotribenzo[b,f,l][1,4,8,11]-tetraazacyclotetradecine-6,7-dionato(2-)nickel(II) [535].

Balasubramanian has also employed template condensation to synthesise macrocyclic complexes of nickel(II) with highly unsaturated planar tetraaza type ligands. Complexes prepared in this fashion were 1,2,9,10-tetraphenyl-3,4,7,8-tetraazadeca-2,4,6,8-tetraene-1,10-dione and its 5-methyl-analogue, (4,9-dihydroxy-3,4,9,10-tetraphenyl-6-,7-benzo)-1,2,5,8,11,12-hexaazacyclo-tetradeca-2,6,10,12,14-pentaenato)nickel(II) and its 5-methyl-, 3,4-dimethylbenzo- and 3-methyl-benzoanalogues [536].

Sakata and co-workers have prepared 1,2,3,4,5,6,7,8,9,10,11,12,13,14,15,16,17,18,19,20,21,22-docosahydrodibenzo[b,i][1,4,8,11]tetraazacyclotetradecine by the hydrogenation of the benzo analogue. While five isomers are potentially possible, only two have been isolated. The nickel(II) complexes of these two isomers were found exhibit square planar and square planar-distorted octahedral coordination geometries, respectively [537]. The same group have prepared and characterised the nickel(II) complexes of the water-soluble macrocyclic ligands, 6,15-diethyl-4,13-dihydro-1,10-dimethyl-(*E*)-dipyridinio[b,i][1,4,8,11]tetraazacyclotetradecine iodide or methyl sulphate. These complexes (**58**) were found to be square planar via a number of analytical techniques [538].



$X = I, SO_4CH_3$

(58)

A detailed electrochemical characterisation of the Ni(II) complex of the new ligand, 5,7,12,14-tetraphenyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene, has been carried out in an effort to more fully understand the mechanism of electropolymerisation of the tetramethyl analogue of the macrocycle. Evidence from this study lends support to the radical mechanism proposed for the electropolymerisation of the

Ni(II) complex of the tetramethyl analogue [539]. In a continuation of this work, the same group have investigated in detail the mechanistic nature of the electropolymerisation of the Ni(II) complexes of dibenzo[b,i][1,4,8,11]tetraaza[14]annulene and 5,7,12,14-tetramethyldibenzo[b,i][1,4,8,11]tetraaza[14]annulene [540].

The macrocyclic complex, (2,3:9,10-dibenzo-5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclo-tetradeca-2,4,6,9,11,13-hexaenato(2-)-k^4N)nickel(II), has been reacted with cyanogen under mild conditions. Addition-insertion was found to occur at the methine C–H group. The two resulting complexes were characterised by one or two cyanoimino methyl, -C(=NH)CN, substituents, from which HCN can easily be released, yielding the corresponding cyano derivatives [541].

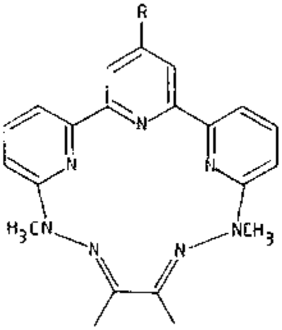
Moore and co-workers have contributed significantly to the synthesis and study of pyridine-containing tetraaza macrocycles. Work published by this group in chronological order includes:

- The synthesis of 3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene and its 3,11-dibenzyl and 3,7,11-tribenzyl derivatives, as well as their nickel(II) complexes [542].
- The preparation and complexation of 3,7,11-trimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene (L) with nickel(II). Crystal structures of the unsymmetric isomer of $[NiL](ClO_4)_2$ and the five coordinate complexes $[NiL(dmso)](ClO_4)_2$ and [NILCl] (ClO_4) [543].
- Preparation of the three related pentaaza macrocyclic ligands, 6,9-dimethyl-2,13-dioxo-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene, 6,9-dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene, 3,6,9,12-tetramethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-1(18),14,16-triene, and their complexation with Ni(II) [544].
- The synthesis and complexation of 6,12-dioxo-1,5,13,17,22-pentaazatricyclo[15.2.2.$1^{7,11}$]-docosa-7(22),8,10-triene and 1,5,13,17,22-pentaazatricyclo[15.2.2.$1^{7,11}$]-docosa-7(22),8,10-triene. This includes the crystal structure determinations of 6,12-dioxo-1,5,13,17,22-pentaazatricyclo[15.2.2.$1^{7,11}$]docosa-7(22),8,10-triene and 1,5,13,17,22-pentaazatricyclo[15.2.2.$1^{7,11}$]docosa-7(22),8,10-trienenickel(II) [545].
- Variable temperature and pressure proton NMR spectroscopic studies of the rates and mechanisms of *N,N*-dimethylformamide and acetonitrile exchange with the square-pyramidal complexes mono(solvento)-{3,7,11-tribenzyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene}-nickel(II) [546].

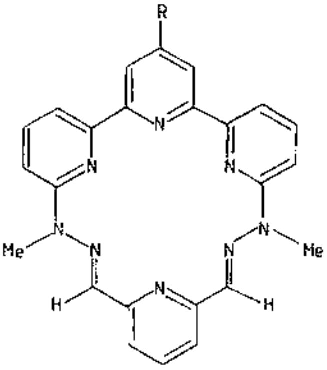
Similarly, the new complexes, $[NiLCl]ClO_4$ and $[NiL](ClO_4)_2$, where L = meso-2,3,7,11,12-pentamethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene, have been prepared and characterised. X-ray crystal and molecular structures have been reported for both complexes. The former complex cation has a distorted tetragonal pyramidal structure, while the latter has a square pyramidal structure with one of the perchlorate ligands coordinated [547].

The synthesis, characterisation and X-ray structure of the octahedral nickel(II) complex of the pentadentate ligand, chloro(9-(methoxymethyl)-1,4,6,9,11,14-hexaazabicyclo[12.2.1]heptadecane)nickel(II) perchlorate have been reported. The coordination geometry about Ni(II) was found to be essentially octahedral with Ni–N of the pentadentate macrocycle varying from 2.082(5) to 2.190(5) Å, with Ni–Cl = 2.398(1) Å [548].

Terpyridine macrocycles have also been prepared and coordinated with Ni(II). In an ongoing study, the preparation and coordination of the 2,2′:6′,6″-terpyridine macrocycles (**59**) [549] and (**60**) [550] with nickel(II) have been reported. Incorporation of the 2,2′:6′,6″-terpyridine moiety into the ligand structure was achieved via the use of a transient template reaction.



R = Ph, H
(59)



R = H, Ph
(60)

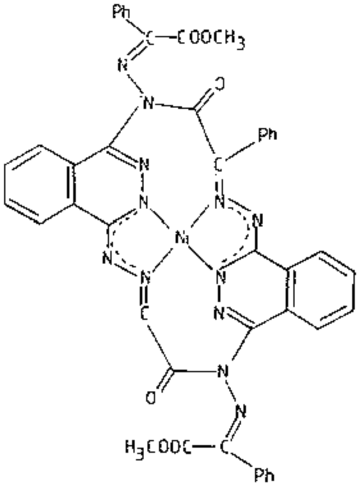
The syntheses of the pentaazamacrocyclic ligands, 1,4,7,10,13-pentaazacyclopentadecane, 1,4,7,10,13-pentaazacyclohexadecane, 1,4,7,10,14-pentaazacycloheptadecane, 1,4,7,11,14-pentaazacycloheptadecane, 1,4,7,11,15-pentaazacyclooctadecane, 1,4,8,11,15-pentaazacyclooctadecane, 1,4,8,12,16-pentaazacyclononadecane and 1,5,9,13,17-pentaazacycloeicosane, as well as the new linear pentaamine, *N*-(3-aminopropyl)-*N*′-[3-[(3-aminopropyl)amino]propyl]propane-1,3-diamine, have been described. In addition, the nickel(II) complexes have been prepared and characterised. The Ni(II) complexes of the smaller macrocycles and pentaamine were found to contain Ni(II) in a tetragonally distorted octahedral environment in the presence of coordinating anions or in aqueous solution, whereas the Ni(II) cations of the larger macrocycles were found to be penta-coordinate both in the solid state and in solution [551].

The pentadentate macrocycle, 1,4,7,10,13-pentaazacyclohexadecane (L), has been prepared and reacted with nickel(II). The resultant complex, $[NiL(H_2O)](ClO_4)_2$, was characterised and found to have an octahedral coordination geometry. The kinetics of dissociation of this complex in acidic solution has also been reported [552]. In a similar study, the acid catalysed dissociation of the nickel(II) complex of the macrocyclic ligand, 1,3,6,9,11,14-hexaazacyclohexadecane, has been investigated in aqueous solution, and the kinetics determined [553].

7,8,15,16,17,18-Hexahydro-3,12-dinitrobenzo[*e*,*m*][1,4,8,11]tetraazacyclotetradecane, 7,8,9,10,11,12,13,20,21,22,23-undecahydro-3,17-dinitrodibenzo[*e*,*r*][1,4,8,12, 16]pentaazacycloionadecane and 7,8,9,11,12,13,20,21,22,23-decahydro-*N*(10)-methyl-3,17-dinitrodibenzo[*e*,*r*][1,4,8,12,16]pentaazacyclononadecane have been prepared by the condensation of *N*,*N*′-bis(2-formyl-4-nitrophenyl)ethylenediamine with ethylenediamine, bis(3-aminopropyl)amine and *N*,*N*-bis(3-aminopropyl)methylamine, respectively. The complexation of these ligands with Ni(II) has also been investigated [554].

In the first of an ongoing series, the synthesis and characterisation of a variety of nickel(II) complexes of the macrocycle ligand, 2,7-dimethyl-3-6-[1,1′-(2,2′-biimidazolo)]-1,3,6,6,11,14-hexaazacyclohexadeca-1,7-diene (L), have been described. The complexes, $[NiL]X_2$ ($X=ClO_4$,I), were found to be diamagnetic, while the complexes, $[NiL]Br_2$ and $[NiL]Cl_2 \cdot H_2O$, were found to be paramagnetic [555].

1,4-Bis(a-carboxybenzylidenehydrazino)phthalazine has been prepared and reacted with nickel(II). The resultant template effect results in the formation of the macrocyclic complex (**61**), which was characterised via mass spectrometric, IR, NMR and UV–VIS spectroscopic data [556].



(61)

A paper has been published in which the electron transfer reactions of encapsulated metal ions, including nickel(II), have been studied. In this paper, the self-exchange rate for (3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane)nickel(III/II) couple has been reported and compared with those for the analogous Ru, Mn and Fe complexes [557].

A variety of octaaza macrocyclic ligands have been prepared via the template condensation of *S*-alkylisothiocarbohydrazides with a number of symmetrical α-diketones. The nickel(II) complexes of these ligands have been synthesised and studied by NMR, infrared spectroscope, magnetochemistry and mass spectrometry. The mode of coordination has been established using these methods [558].

Bis(difluoroboron-α-furilglyoximato)nickel(II) has been synthesised by cyclization of its hydrogenbonded precursor with $BF_3 \cdot OEt_2$. The crystal and molecular structures of the complex have also been determined, revealing a square planar coordination environment about the Ni(II) ion. It was also found that the 14-membered macrocycle is planar, with the exception of the boron atoms, and that no metal–metal interactions were present within the complex [559]. In addition, the crystal structure of tetraethynylborato(1,4,8,11-tetraazaundecane)nickel(II) tetraethynylborate has been elucidated. The coordination geometry of the Ni atom in this complex was found to be square planar as well [560].

Porphyrin and related ligands continue to attract considerable interest both in terms of solid-state structural studies and in terms of solution equilibria. Table 9 lists information relating to nickel(II) complexes of some substituted porphyrin ligands [561–570]. Other studies involving these complexes include one which examines the question of whether one-electron transfer to nickel(II) porphyrins involves the metal or the porphyrin ligand. In this study, UV–VIS and ESR spectroscopic data obtained in dmf and benzonitrile indicated the presence of a Ni(I) species rather than the anion radical of the nickel(II) porphyrin [571]. In addition, a molecular mechanics model of the metalloporphyrin complexes of Ni(II), Fe(II), Zn(II), Pb(II) and P(V) has been developed. This model was found to be capable of predicting, with considerable accuracy, the bond lengths and angles, and extent of S_4 ruffling of the porphyrincore as the metals are changed [572].

As part of a study of the structural relationships between the hemiporphyrazine macrocyclic ligand, $H_2L = (\mathbf{62})$, and its metal complexes, the crystal structure of the nickel(II) complex, [NiL], has been elucidated. The coordination geometry about Ni(II) was found to be essentially square planar, with Ni–N distances of 2.020(3) and 2.220(3) Å [573].

The preparation of pure metal(II) 4,9,16,23-phthalocyanine tetraamine 2-hydrates of nickel, copper, cobalt and zinc have been reported. The complexes were characterised on the basis of elemental analysis, electronic and FT-IR spectra, powder X-ray diffraction, magnetic susceptibility measurements, dynamic thermogravimetric MS and GC-MS spectral data [574]. In a separate, ongoing study, soluble metallophthalocyanine compounds of Ni(II) and Cu(II) with alkyloxycarbonyl groups (alkyl = 1- or 2-octyl, or 1-decyl), substituted at either the 2 or 3 position of the benzene ring, were synthesised [575].

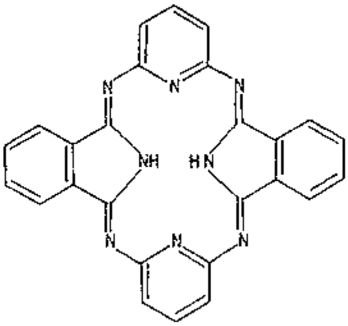
2,7,12,17-Tetramethyl-, tetraethyl- and tetrapropylporphycene have been prepared, together with the nickel(II) complex of tetrapropylporphycene. In addition, the crystal structures of both tetrapropylporphycene and its nickel(II) complex were determined [576]. In a separate study on the electrochemical, theoretical and ESR characterisation of porphycenes, the π anion radical of nickel(II) porphycene has been investigated [577].

4.2. Macrocycles with oxygen donor atoms

18-Crown-6 and its substituted analogues fall within this category of ligand. The crystal and molecular structure of the complex tris(ethanol-(1,4,7,10,13,16-hexaoxacyclooctadecane)-nickel(II) bis(hexafluorophosphate) have

Table 9
Nickel(II) complexes with porphyrin and variously substituted porphyrin ligands

Ligand (H_2L)	Complex	Comments	Ref.
5,10,15,20-Tetramethylporphyrin	$[NiL]_2[PF_6]$	X-ray crystal structure determination. Complex prepared by the electrochemical oxidation of [NiL] in the presence of hexafluorophosphate.	[561]
Octaethylporphyrin	[NiL]	Isolation and X-ray crystal structure determination of new crystalline phase. Essentially square planar coordination geometry with average Ni–N distance of 1.952(8) Å.	[562]
	[NiL]	Study of ruffling of [NiL] in methylene chloride solution. Presence of multiple forms coexisting in solution.	[563]
	[NiL]	Low-temperature (12 K) resonance Raman study for tetragonal and triclinic crystallises of [NiL] and its meso-d_4, $^{15}N_4$ and methylene-d_{16} isotopomers.	[564]
5,15-Dialkyl-5,15-dihydro-2,3,7,8,12,13,17,18-octaethylporhyrin	[NiL]	Alkyl = Me, Et, *i*-Pr, and *t*-Bu. Synthesis and spectral characterisation of stereoisomers in deuterated chloroform solution via ^1H NMR spectroscopy.	[565]
Tetra(*p*-vinylphenyl)porphyrin	[NiL]	Spectroscopic study involving concentration effects on the absorption and emission properties of the Ni(II) and Zn(II) complexes.	[566]
Tetrapyridylporphyrin	[NiL]	Electrochemical and spectroelectrochemical study of these complexes in dmf.	[567]
Tetrakis[*p*-(sodiosulphonato)phenyl]-porphyrin		All three compounds could be reduced by one electron to form π anion radicals or oxidised by one or two electrons to form π cation radicals and dications.	
Tetrakis(*p*-diethylaminophenyl)porphyrin (meso-Tetrakis(1-methylpyridinium-4-yl)-porphyrin	$[NiL](ClO_4)_4$	Electrochemical and spectral characterisation of the monomer–dimer equilibrium of [NiL] in dmf.	[568]
(*meso*-Tetrakis(3,5-di-*t*-butyl-4-hydroxyphenyl)-porphyrin	[NiL]	X-ray crystal structure has been determined. The geometry about Ni(II) was found to be square planar and the Ni–N bond lengths of 1.91 Å are among the shortest reported thus far for metalloporphyrin complexes.	[569]
meso-Substitutedporphyrin		Electronic and resonance Raman spectral study of the water soluble Ni(II)porphyrin complexes, with the following ligands: tetrakis(2-*N*), (3-*N*) and (4-*N*)-methylpyridylporphyrin, tris(4-*N*-methyl-pyridyl)monophenylporphyrin, two isomeric forms of bis(4-*N*-methylpyridyl)diphenylporphyrin, and tetrakis(4-*N*,*N*,*N*-trimethylanilinium)porphyrin.	[570]



(62)

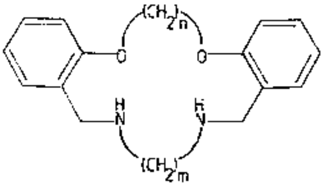
been reported. The Ni(II) ion was found to be coordinated to three adjacent O atoms of the crown (O1, O4, O7) and the O atoms of three ethanol solvate molecules, in a distorted octahedral coordination environment [578]. Similarly, $(NH_4L)_2[Ni(NCS)_4]$, in which L = dibenzo-18-crown-6, has been prepared [579].

4.3. Macrocycles with sulphur donor atoms

In a study of crown thioether chemistry, the Ni(II) complexes of 1,4,7,10,13,16-hexathiacyclooctadecane, 2,5,8-trithianonane, 1,5,9-trithiacyclododecane, and 1,5,9,13,17,21-hexathiacyclotetracosane have been prepared and characterised via single-crystal X-ray diffraction and electronic spectroscope. Each of these complexes was found to contain a high-spin $[Ni(thioether)_6]^{2+}$ cation with octahedral symmetry. Comparison of the complexes showed that, within a conserved coordination sphere, variation of the ring size could change the Ni–S distance by up to 0.05 Å [580].

4.4. Macrocycles with nitrogen–oxygen donor atoms

Lindoy et al. have published a number of articles which describe the synthesis and metal ion complexation involving mixed donor macrocyclic ligands. One article reports that minor changes in the substitution pattern of the backbone of a 17-membered macrocyclic ring incorporating O_2N_3 donor atoms had a significant influence on the ligand coordination modes in the corresponding nickel thiocyanate complexes. Comparative IR and FAB mass spectrometry were used in the characterisation of these complexes. In addition, the X-ray crystal structures of three of the complexes were determined [581]. A second paper examines the interaction of Ni(II), Co(II) and Cu(II) with a series of new oxygen–nitrogen donor macrocycles. In all, 10 new macrocycles were prepared by the tetrahydroborate reduction of a range of Schiff-base di-imine macrocycles. The stabilities of selected complexes were determined using the potentiometric titration technique, while structural effects were investigated via single crystal X-ray structure determinations [582]. The same group have published a third paper which investigates the effect of medium on the stabilities of the complexes of Ni(II), Co(II) and Cu(II) with the 14- to 16-membered O_2N_2-donor macrocycles (**63**). Parameters varied included the background electrolyte and solvent, from 95% methanol to 65% ethanol. It was found that the stability order was maintained regardless of the solvent and in the case of the Ni(II) complexes, the stability increases from the 14- to the 16-membered ring in accordance with a previous prediction that the fit of the latter ring is nearly ideal for high-spin Ni(II) [583].

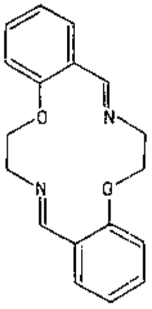


n = 2,3,4; m = 2,3
(**63**)

Speciation studies of the Ni(II) and Cu(II) complexes of the dibenzo-pyrido-macrocycle, 3,22-dioxa-11,14,28-triazatetracyclo-[22.3.1.$0^{4,9}$.$0^{16,21}$]octacosa-1(28), 4,6,8,16,18,20,24,26-nonaene (L), have been carried out in dmso. These studies reveal the presence of 1:1 and 1:2 metal: ligand ratios. In addition, the crystal structure of the nickel(II) nitrate complex, $[NiL_2(NO_3)](NO_3)$.2MeOH, has been elucidated. The complex cation was found to be hexacoordinate with the two macrocycle ligands coordinating in an exocyclic manner via their two N atoms. The coordination sphere is completed by the nitrate ion functioning in a didentate fashion [584].

Complexes of Ni(II) and Co(II) with the macrocycle..1,7,10,16-tetraoxa-4,13-diazacyclooctadecane (L), have been prepared and characterised. The resultant complexes were characterised by elemental analysis, IR spectra, DTA thermogravimetry, electrical conductance, visible and near IR solid reflectance spectra and magnetic moment data [585].

In paper entitled "Synthesis and Structural Studies of Nickel(II) Complexes of 14-membered *trans*-N_2O_2 and *trans*-N_2S_2 Quadridenate Macrocycles", the synthesis of the macrocycles (**64**), (**65**), (**66**) and (**67**) and the preparation and characterisation of their nickel(II) complexes have been reported. In addition, crystal structures of the complexes $[NiCl_2L]$ [L = (**65**)] and $[NiCl_2L].0\cdot 5H_2O$ [L = (**67**)] have been determined. In the former complex, the nickel ion was found to be in an octahedral coordination environment consisting of four donor atoms of the *trans*-N_2O_2 macrocycle in an approximately square planar array, with the two chloride ions in the *trans* axial sites. The latter complex was found to have a different configuration altogether, with the chloro ligands *cis* to one another and the four donor atoms of the *trans*-N_2S_2 macrocycle occupying the remaining coordination sites [586].



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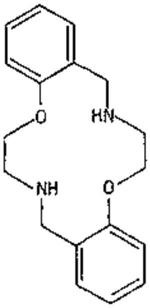

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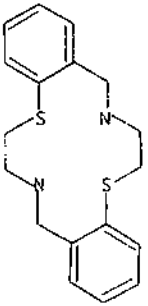

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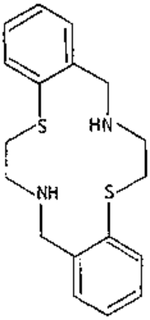


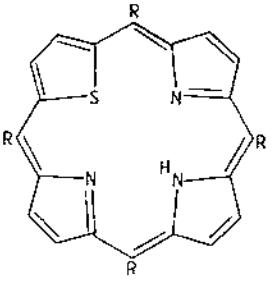
(67)

4.5. Macrocycles with nitrogen–sulphur donor atoms

Apart from the *trans*-N_2S_2 macrocycle complex described in the last paragraph of the previous section, a new tetradentate ligand, 10,10-dimethyl-9,11-dioxo-1,5-dithia-8,12-diazacyclo-tetradecane (H_2L), has been prepared and reacted with a number of metal(II) ions. This ligand was found to complex with Pt(II) and Pd(II), but not with Ni(II), Cu(II) or Co(II) under similar conditions. Reduction of the oxo-functions yielded the ordinary N_2S_2 tetradentate macrocycle ligand which complexed unselectively to Ni(II), Cu(II) and Co(II) ions as well [587].

The potential S_3O_3 macrocycle ligand, 4,7,10-trioxa-1,13-dithia[13](2,5)-1,3,4-thiadizolophane (L) has been reacted with nickel(II) nitrate. The complex, $L_2Ni(NO_3)_2$, was isolated together with its Cu and Co analogues. A crystal structure determination of the copper bromide analogue revealed that the ligand does not accommodate the metal ion inside the cavity of the macrocycle, but rather coordinates on the exterior via the ring nitrogen atom [588].

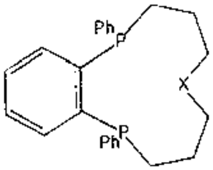
21-Thiaporphyrin, HL=(**68**), has been reacted with nickel(II) chloride. The crystal structure of the resultant complex, [NILCl], was determined, revealing a five coordinate structure with approximate square-pyramidal geometry and an apical chloride ligand. Relevant crystal data are Ni–N = 1.963(4), 2.084(3) and 2.094(3) Å, Ni–S = 2.296(1) Å, and Ni–Cl = 2.275(1) Å [589].



R = Ph
(68)

4.6. Macrocycles with phosphorus sulphur donor atoms

Nickel(II) complexes formed from the 14-membered macrocyclic ligands (**69**) were isolated and characterised. The coordinating ability of these ligands was determined by solution-phase competition experiments, and was found to depend on the metal species, the nature, number and disposition in the ring of the heteroatoms, and the relative stereochemistry of the substituents on the phosphine sites. X-ray crystal structures of three of the nickel(II) complexes were elucidated confirming the significant effects on stereochemistry caused by variations in the macrocycle [590].



X = PPh, S, NMe
(69)

4.7. Polynuclear complexes containing macrocyclic ligands

To conclude the section on nickel(II) macrocyclic complexes and to introduce the following section on polynuclear complexes, we review polynuclear complexes which contain macrocycle ligands. Essentially, the complexes can be divided into three broad categories: (a) large ring macrocycles and macrobicycles which can incorporate several metal ions; (b) bis(macrocycles), i.e. two macrocycles linked together via a bridging moiety; and (c) macrocycle complexes bridged via an external bridging group.

In an investigation of mono- and dimetallic complexes of tetraiminato macrocyclic complexes, the first dimetallic complex of the macrocyclic ligand derived from 1,3,5-triketones and diamines has been synthesized and characterised by single crystal X-ray diffraction and NMR spectroscopy. It was shown that the mono- and dimetallic complexes, NiH_2L and Ni_2L, where H_4L = 5,14-dimethyl-

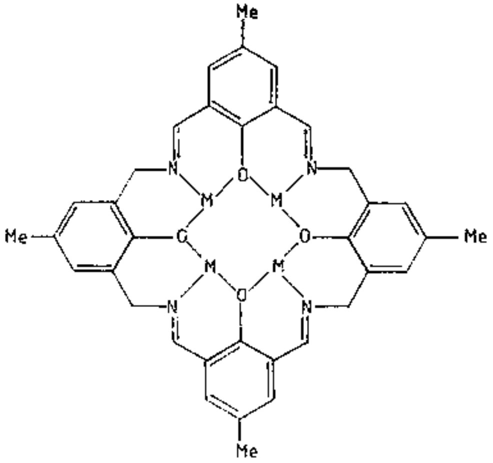
9,18-diisopropyl-1,4,10,13-tetraazacyclooctadeca-5,8,14,17-tetraene-7,16-dione, are isomorphous. The dimetallic complex was found to be highly planar with a Ni–Ni distance of 2.859(2) Å [591].

The macrocyclic ligand, 3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.1^{11,15}]-triaconta-1(28),11,13,15(30),25,26-hexaene (L), has been prepared and isolated as the hexachloride. Reaction with Ni(II) has been investigated and the stability constants of the mono- and binuclear complexes have been determined. The dinuclear complexes were found to show a strong tendency toward hydroxide ion bridging between the metal ions [592].

An interesting article has appeared which describes the synthesis of a macrocycle via the condensation of pentane-2,4-dione with pyridine-2,6-dicarbohydrazide. Originally thought to be the macrocycle, 4,6,19,21-tetramethyl-2,3,7,8,17,18,22,23-octaaza[9.9](2,6)pyridinophane3,6,18,22-tetraene-1,9,16,24-tetraone (L), it was found, via a crystal structure determination, to be the macrocycle 5,6,20,21-tetrahydro-4,6,19,21-tetramethyl-7,8,22,23-tetraaza[3](1,5)pyrazolo[1](2,6)pyridine[3](1,5)pyrazolo[1](2,6)pyridinophane-1,9,16,24-tetraone (L^1). Reaction of L^1 with nickel(II) acetate yielded a dinuclear complex with a metal to ligand ratio of 2:1. However, a crystal structure determination of this complex revealed a dinuclear complex, $[Ni_2L]\cdot 5H_2O$, in which L^1 had rearranged to L on reaction with Ni(II) [593].

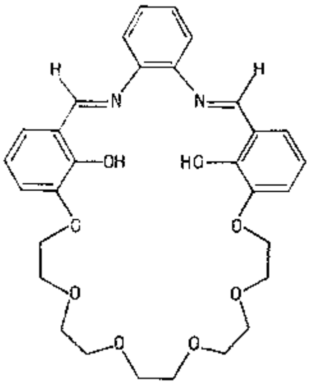
The tetra Schiff-base macrocycle formed by condensation of two molecules of 2,6-diformyl-5-methylphenol with two molecules of 2,6-bis(aminomethyl)-5-methylphenol has been reacted with Ni(II). The crystal and molecular structure of the resultant tetranuclear complex, $[Ni_4L(MeCO_2)_2(OH)(MeO\cdot H\cdot OMe)].4MeOH$, has been elucidated. The LNi_4 arrangement is essentially as shown in (**70**), but the four aromatic rings are inclined, all on the same side of the Ni_4 plane, at considerable angles to this plane [594]. The same group have extended this study by preparing the Ni_4 derivative of the macrocyclic tetra Schiff base (LH_4) formed by condensation of two molecules of 2,6-diformyl-4-methylphenol with two molecules of 2,6-bis(aminomethyl)-4-methylphenol. The crystal structure of this complex, $LNi_4(MeCO_2)_2(OH)(MeO\cdot H\cdot OMe)\cdot 4MeOH$, has also been determined, revealing four nickel atoms at the corners of a rectangle with edges 2.788(1) and 2.936(1) Å. The structure is also characterised by an unusual μ-4-hydroxo group located with its oxygen atom about 0.60 Å above the midpoint of the Ni_4 cluster [595].

Macrocycle ligands with different compartments in close proximity facilitate the formation of polynuclear complexes with different metal ions. This was shown in a paper which described the synthesis, complexation and X-ray structure of a new dinucleating macrocycle (**71**), incorporating both soft and hard ligating sites. Reaction of (**71**) with Ni(II) afforded the mononuclear complex with nickel coordinated to the *N,N'*-ethylenebis(salicylideneaminato) moiety, while reaction with Ba^{2+} resulted in a mononuclear complex with the Ba^{2+} ion located in the polyether cavity, as verified by its X-ray crystal structure. The heterobinuclear complex could also be prepared from either of the two mononuclear complexes by reaction with



(70)

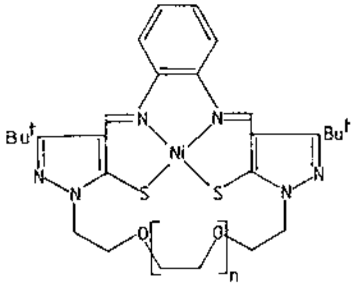
the appropriate ion [596]. The same group have extended this study by preparing a number of heterodinucleating ligands with both a cavity suitable for complexation with transition metal cations, and a cavity suitable for complexation with alkali- or alkaline earth-metal cations. In this study, a number of structures were verified by means of X-ray crystal structure determinations [597].



(71)

In a similar fashion, a series of novel macrocyclic systems have been prepared using 5-chloro-4-formyl pyrazoles (via selective N-1 alkylation) as heterocyclic building blocks. These macrocycles (**72**) also have two different compartments which can show metal ion selectivity. This has been confirmed by the synthesis of a dinuclear Ni(II)–Tl(I) complex [598].

Similarly, the preparation and characterisation of the mononuclear and dinuclear complexes of Ni(II) and UO_2 with the compartinental acyclic and macrocyclic



n = 1 - 5

(72)

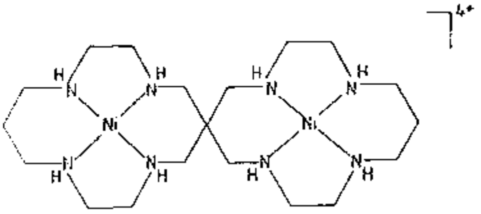
Schiff bases, obtained by condensation of 2,6-diformyl-4-chlorophenol and $NH_2(CH_2)_2X(CH_2)_2NH_2$ (X = NH, S), have been reported. Once again these ligands have two similar or dissimilar compartments in close proximity and can link two metal ions in an identical or different coordination mode [599].

The synthetic, structural, and spectroscopic results of a series mononuclear and dinuclear nickel(II) tropocoronand complexes have been presented. By increasing the lengths of the chains linking the two halves of the tropocoronand macrocycle (by adding methylene groups), it was shown that it was possible to alter the stereochemistry of the metal centre from square planar to distorted tetrahedral. Binuclear species were also obtained [600].

Another method of forming multiple coordination sites is to add pendant arms with donor atoms to macrocycle ligands. This is exemplified by the crystal and molecular structure of a novel mixed-spin binuclear nickel(II) complex with *N*,*N*′,*N*″,*N*‴-tetrakis(2-aminoethyl)-1,4,8,11-tetraazacycloteradecane (L). The complex cation, $[Ni_2(L)Cl]^{3+}$, isolated as its chloride salt, was found to have one nickel ion coordinated by the square planar N_4 donor set of the macrocycle, and the other by a distorted square-pyramidal N_4Cl donor set made up of the four pendent amine nitrogen atoms and the chloride ligand [601].

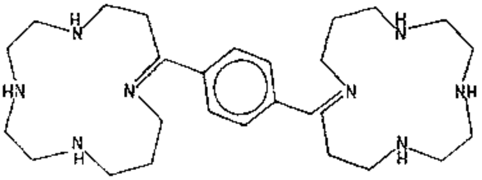
Related work has been carried out in an ongoing study of binuclear complexes with tetraazamacrocycle-*N*,*N*′,*N*″,*N*‴-tetraacetic acid ligands. Ligands investigated in this work include 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid, 1,4,8,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid, and 1,5,9,13-tetraazacyclohexadeca-*N*,*N*′,*N*″,*N*‴-tetraacetic acid. The crystal and molecular structures of the analogous Cu(II) complexes were determined [602].

Turning to bis(macrocycles), the synthesis and X-ray crystal structure of a C-spiro-bi-[cyclam nickel(II)] complex have been reported. Isolated as its perchlorate salt, the complex cation (73) macrocycle rings were found to deviate from orthogonality, which was attributed to a possible Ni Ni interaction [603]. The related ligand, 6,6′-bi(1,4,8,11-tetraazacyclotetradecane) (bicyclam), has been prepared and reacted with Ni(II) and Cu(II). Both homo- and hetero-binuclear complexes were isolated and their spectral and electrochemical properties investigated [604]. In addition, the same group have reported the preparation of a novel family of bis(macrocycles), in which two cyclam subunits are linked via nitrogen atoms by a carbon chain R of varying length (R = $-(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, *m*-xylyl, *p*-xylyl) [605].



(73)

Related to the above work, the two bis(macrocycles) (**74**) and (**75**), in which the tetraaza units are separated by a chain of different length, have been synthesized and complexed with Ni(II). Apart from spectral and electrochemical studies in solution, the X-ray crystal structures of the nickel(II) complexes of (**74**) and (**75**), isolated as their perchlorate salts, have been elucidated. In both complexes, the Ni(II) ions were found to have square planar geometry with coordination to the four N atoms of the macrocycle [606].



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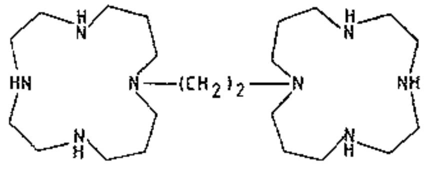


(75)

The new dinucleating ligand, *m*-xylylene bis(3,3′-bis(5,8-diaza-4,9-dimethyldodecane-2,11-dione) (H_4L), has been prepared and reacted with Ni(II). The resultant complex, NiL, was found to be dinuclear, with each nickel atom coordinated to a N_2O_2 donor set. The visible absorption spectrum strongly suggests a square planar coordination geometry about each of the nickel atoms [607].

N,N′-disalicylidene-ethylenediamine (salen) capped porphyrin and *N,N′*-disalicylidene-ethylene-diamine bridged porphyrin dimer ligands have been prepared and reacted with Ni(II) and Zn(II). It was found that in the capped complex, the nickel–salen moiety was held rigidly over the porphyrin ring, while the salen-bridged complexes, the preferred conformation was controlled by the metal complexation [608].

5. Nickel(II) polynuclear complexes

Polynuclear complexes continue to attract considerable interest. Aspects that have been investigated, apart form macrocycles as discussed earlier, include a variety of bridging agents, including Schiff-base and related ligands, mixed metal complexes, and multimetal complexes.

Halide and pseudo-halide ligands have been used as effective bridging agents. Table 10 lists a number of complexes that have F, Cl, Br and NCS as bridging moieties [609–622]. In addition, two crystal and molecular structures have been reported in which the CN^- ion bridges Ni atoms. These structures are of the homonuclear complex, *catena*-poly[bis(ethylenediamine)nickel(II)-μ-cyano-dicyanonickel(II)nickel]-μ-cyano] [623], and the heterodinuclear complex *catena*-poly[tri-μ-cyano-(ammine)(4-chloropyridine)cadmium-μ-cyano-nickel] [624]. Hydride ion has also fulfilled this function as verified by the polyhydride complex cation, $[(\text{triphos})\text{Rh}(\mu\text{-H})_3\text{Ni}(\text{triphos})]^{2+}$, which was isolated as its perchlorate salt [625].

A number of studies investigating nickel(II) phosphates and their compounds with hydrazine have been undertaken. These include a spectroscopic study, using electronic reflectance spectroscopy [626], and a study in which the equilibrium constants of the complexes have been determined [627].

Turning to hydrazide ligands, the 1:1 coordination polymers of azelaic acid-bis(phenylhydrazide) and azelaic acid-bis(2,4-dinitrophenylhydrazide) have been prepared by reaction of the ligands with nickel(II) acetate. Characterisation was carried out using elemental analysis, electronic reflectance and IR spectral methods, and magnetic moment data. The ligands were found to coordinate via carbonyl O and amino N atoms [628]. In addition, the dinuclear nickel(II) complexes, based on the condensation products of acetylpinacolone with the dihydrazides of oxalic and malonic acid, have been synthesized. The complexes have been assigned the dinuclear structure (**76**), with two equivalent square planar metal containing rings [629].

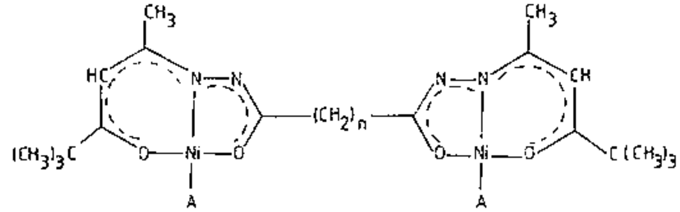
1-(Pyridinomethylcarbonyl)-4-phenylsemicarbazide chloride has been prepared and reacted with Ni(II). A number of analytical techniques have been used to characterise the resultant Ni(II) complex with its bridging tetradentate N,O,N,O donor ligand [630]. Similarly, a number of variously substituted thiosemicarbazides have been complexed with Ni(II). The resultant complexes, $NiLCl_2$ ($L = RC(O)NHNHC(S)NHR^1$; R = 2-furoyl, $R^1 = Ph$, $p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$), were found to be polymeric with didentate coordination of L via carbonyl O and thioketo S atoms [631].

A range of Schiff-base and related ligands have been used to form polynuclear complexes. Work published in this area includes:

- The synthesis, structure and spectroscopic investigation of ethylenediamine-*N*,*N*′-

Table 10
Nickel(II) complexes with halide and pseudo-halide bridging groups

Bridging group	Complex	Comments	Ref.
F	$[(\mathrm{bipy})_2\mathrm{FNi\text{-}F\text{-}NiF}(\mathrm{bipy})_2]^+[\mathrm{F}(\mathrm{EtOH})_3(\mathrm{H_2O})_2]^-.\mathrm{H_2O}$	bipy = 2,2′-bipyridine; X-ray crystal structure determination. Three different F environments: ligand Ni–F = 2.005(4) Å, bridging Ni–F = 1.985(3) Å, and ethanol solvated ion.	[609]
	$\{\mathrm{R_2NiX}\}_2^{2-}$ (X = F,Cl,Br; R = $\mathrm{C_6F_5,SiCl_3}$)	X-ray crystal structure determinations of $[(\mu\text{-Cl})_2\mathrm{Ni_2(C_6F_5)_4}][\mathrm{Et_4N}]_2$, $[(\mu\text{-Cl})_2\mathrm{Ni_2(SiCl_3)_4}][(\mathrm{CH_3C})_2\mathrm{C_5H_3NH}]_2$, and $[(\mu\text{-F})_2\mathrm{Ni_2(C_6F_5)_4}][n\text{-}\mathrm{Bu_4N}]_2$.	[610]
Cl	$\{\mathrm{Ni_2Cl_4(H_2O)_6}].\mathrm{C_4H_{12}N_2^{2+}.2Cl^-}$	X-ray crystal structure determination. The structure consists of two edge-sharing $[\mathrm{Ni_2Cl_4(H_2O)_6}]$octahedra, piperazinium cations and isolated $\mathrm{Cl^-}$.	[611]
	$\mathrm{NiCl_2L}$ {L = 1,4-bis(4-pyridyl)butadiyne]	Polymeric octahedral structure as determined via solubility studies, together with spectral and magnetic properties.	[612]
	$\mathrm{NiL_2Cl_2}$ [L = 3-(3-pyridyl)acrylic acid]	Octahedral structures have been assigned on the basis of magnetic measurements, electronic and infrared spectral data.	[613]
	$\mathrm{NiCl_2.4L}$; $\mathrm{NiCl_2.2L}$ (L = urea, dimethyl- and diethylurea)	$\mathrm{NiCl_2\cdot 4L}$ complexes have been assigned octahedral structures, while $\mathrm{NiCl_2\cdot 2L}$ have been assigned polymeric structures with chloride bridges.	[614]
	$\mathrm{NiL_2Cl_2}$; $\mathrm{NiL_2(NO_3)_2.0.3EtOH}$ (L = 1,3-dimethylimidazoliumdithiocarboxalato)	Columnar structures have been proposed with chloro and nitrato bridging groups respectively.	[615]
	$[\mathrm{Ni(PHP6Me)X(H_2O)_4]X_3}$-solvent (X = Cl, Br) {PHP6Me = 1,4-bis[(6-methylpyridine-2- carboxaldimino)-amino]phthalazine}	X-ray crystal structure determination of the complex $[\mathrm{Ni(PHP6Me)Cl(H_2O)_4]Cl_3\cdot 4.6H_2O}$. Ni–Ni was found to be 3.678 Å.	[616]
Br	$[\mathrm{Ni(en)_2}]\,[\mathrm{PtBr_2(en)_2}](\mathrm{ClO_4})_4$	X-ray crystal structure determination.	[617]
NCS	$[\mathrm{NiL_2(NCS)_2}]$ (L = piperazine, N-methylpiperazine) $\{\mathrm{Ni(L)_2}][\mathrm{NCS}]_2$ (L = 1,4-diazacycloheptane)	Thermal investigation and stereochemical study of these thiocyanate bridged complexes in the solid state.	[618]
	$[\mathrm{NiL_3(NCS)_2}]$ (L = benzylamine)	Crystal and molecular structure determination.	[619]
	$[\mathrm{Ni(terpy)(NCS)_2}]_2$ (terpy = 2,2′:6′2″-terpyridine)	Dinuclear structure with metal centres linked via end-to-end NCS bridges.	[620]
	$\mathrm{Ni[Tl(SCN)(SeCN)]_2}$	NCS and NCSE coordinate to Ni via N and Tl via S or Se.	[621]
	$\mathrm{Ni(NCO)_2Tl_2(SCN)_2}$	This complex behaves as a Lewis acid and forms complexes with a variety of ligands.	[622]



A = NH_3, py, piperidine, PPh_3

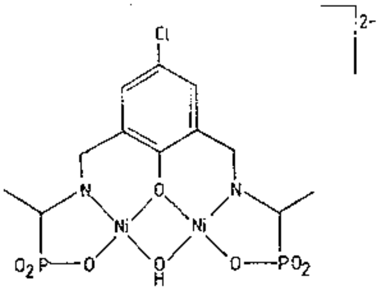
(76)

bis[1′-methyl-3′-oxo-3′-(2″-hydroxy-5″-methylphenyl)propenyl] and its mono and homodinuclear complexes with nickel(II) and copper(II). The crystal structure for the mononuclear complex was determined, while spectroscopic and magnetic data for the dinuclear complex, Ni_2L, were found to be consistent with an octahedral environment for the metal occupying the O_2O_2 site, and a square planar one for that occupying the N_2O_2 site [632].

- The preparation of dinuclear complexes formed by the reaction of nickel(II)(mesalen) [mesalen = *N,N′*-ethylenebis(2-hydroxyacetophenoneimine)] with the complexes bis[1,3-bis(2hydroxyphenyl)-1,3-propanedionate]metal(II), where metal(II) = Ni(II), Zn(II) and Mn(II). The Ni atom in the mesalen coordination sphere was found to be square planar, while the coordination geometry of the other metal ions was found to be dependent on the metal ion used [633].
- *N*-salicylidene-*o*-hydroxymethyleneaniline has been prepared by the condensation of *o*-aminobenzyl alcohol with salicylaldehyde. The tridentate ligand, when reacted with Ni(II), yielded the dinuclear complex, $[NiL(H_2O)_2]_2$, in which the nickel(II) ions were found to be in an octahedral environment [634].
- The Schiff base obtained by reacting 2′-aminoacetophenone with 2-aminoethanol has been reacted with nickel(II) chloride. The properties of the resultant complex, $[L_2Ni]_2$, were found to be fully consistent with a dinuclear structure [635].
- Two new dinucleating Schiff-base ligands, 5,8,20,23-tetraaza-4,9,19,24-tetramethylcosane-2,11,17,26-tetraone and 5,8,23,26-tetraaza-4,9,22,27-tetramethyltricontane-2,11,20,29-tetraone, have been prepared and their nickel(II) complexes synthesized and characterised. The binuclear complexes displayed magnetic and spectroscopic behaviour characteristic of square planar monomeric compounds with no significant metal–metal interaction [636].
- In a study of the synthesis and structural characteristics of Ni(II) complexes with Schiff bases, the dinuclear complexes, $Ni_2(H_2O)_4LL^2_1$ (H_2L = *o*-HOC_6H_4CH:-NRN:CHC_6H_4OH-*o*, R = ethylene, propylene, $HNCH_2CH_2$, H_2CCH_2NH-$CH_2CH_2NHCH_2CH_2$; HL^1 = anthranilic acid, BzOH) were isolated and characterised. In these complexes, the Schiff-base ligands were found to function as the bridging groups [637].
- *N,N′*-*o*-phenylenediiminebis(*o*-aminobenzaldehyde) (H_2L) has been reacted with Ni(II). A variety of polynuclear complexes were isolated including $Ni_2L_3 \cdot 3H_2O$, $[Ni_3L_2Cl_2] \cdot 5H_2O$ and $[Ni_3L_2(NO_3)thf]NO_3 \cdot thf$. The central

atoms in the trinuclear complexes were found to be magnetically non-equivalent [638].

- The nickel(II) complex anion (**77**), with the Schiff-base ligand containing "end-off" phosphoric acid groups, has been prepared and isolated as its sodium salt. The analogous sulphonic acid ligand complex was also prepared, as well as some structural analogues [639].

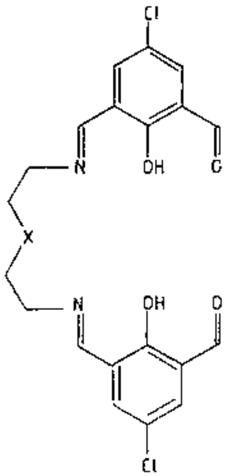


(77)

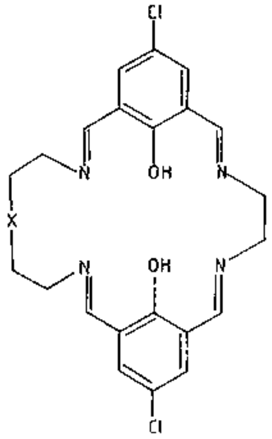
- In a study of Schiff-base complexes containing sulphur, the dinuclear complex, Ni_2L_2, where H_2L = *S*-methyl-*β*-*N*-(*o*-hydroxyphenylethylidene)dithiocarbazate, has been prepared and characterised by elemental analysis, molar conductance and IR spectroscopic measurement. In addition, its stability constant was determined as 2.9×10^{12} [640].
- The coordination compounds of Ni(II) with terephthalic acid hydrazide-bis-salicylidene (H_2L), terephthalic acid hydrazide-bis-2,3,4-trihydroxy phenacyclidene (H_2L') and terephthalic acid hydrazide-bis-2-hydroxy, 5-carboxy phenacyclidene (H2L″) have been synthesized and characterised via a range of analytical techniques. Spectral evidence indicates that the azomethine N and phenolic O atoms take part in coordination, while an octahedral polymeric structure has been assigned to the nickel(II) complexes, $NiL(H_2O)_2$, $NiL'(H_2O)_2$, and $NiL''(H_2O)_2$ [641].
- In an ongoing study of binuclear metal complexes, the mixed metal complexes, [Cu(samen)Ni(L)$_2$], where samen = *N*,*N*′-ethylenedisalicylamidato, and L = 2,2′-bipyridyl or 1,10-phenanthroline, have been synthesized. An antiferromagnetic spin-exchange has been suggested between the metal ions [642].
- The copper complex, [*N*-(1-methyl-3-oxobutylidene)-*N*′-salicylidene-ethylenediaminato]copper(II) (CuSA), has been reacted with nickel(II) nitrate. The resultant complex, $(CuSA)_2Ni(NO_3)_2 \cdot H_2O$, was found to be trinuclear with bridging occurring via the oxygen atoms of the quadridentate Schiff base [643].
- A series of heterobinuclear complexes have been prepared by the reaction of copper tetradentate Schiff-base complexes, Cu(TSB), with the metal hexafluoroacetylacetonates, M(hfa)$_2$ [M = Ni(II), Co(II), Fe(II), Mn(II)]. The Schiff-base ligands (H_2TSB) were prepared from the condensation of *o*-hydroxypropiophenone with ethylenediamine or 1,3-propylenediamine, respectively. Crystal struc-

tures of the Cu–Fe and Cu–Co analogues were elucidated as part of the structural characterisation [644].

- Twelve adducts of $SbCl_3$, $SbBr_3$, and $SbCl_5$ with the Ni(II) and Cu(II) chelates of tetradentate Schiff bases derived from the condensation of acetylacetone with ethylene- or propylenediamine, have been isolated. Spectral data indicate that in all the complexes the metal chelate is O,O bonded to the $SbCl_3$, $SbBr_3$, and $SbCl_5$, while the N atoms do not participate in coordination [645].
- The electrochemical behaviour of a series of mononuclear, homo-dinuclear and heterodinuclear complexes of dioxouranium(VI), nickel(II) and copper(II) ions with acyclic and cyclic compartmental ligands, derived from the condensation of 2,6-diformyl-4-chlorophenol and polyamines of the type $NH_2\text{-}(CH_2)_2\text{-}X\text{-}(CH_2)_2\text{-}NH_2$ (X = NH, S), has been reported. The structures of these ligands are shown below (**78**), (**79**) and (**80**) [646].



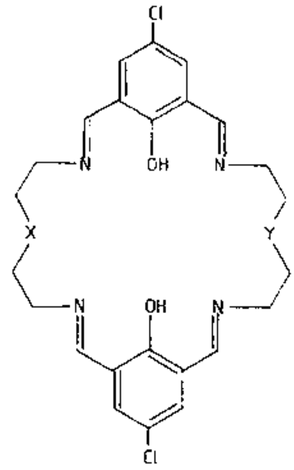
X = NH S
(78)



X = NH, S
(79)

- The polychelates of Ni(II), Cu(II), Co(II), Zn(II) and Mn(II) with the poly-Schiff base of 5,5′-methylenebis(3-bromosalicylaldehyde) with *o*-toluidine have been prepared. Structures have been proposed on the basis of their electronic and IR spectra, magnetic susceptibility data, and thermogravimetric and elemental analyses [647].

A number of hydrazone ligands have been used in the synthesis of polynuclear complexes. These include the aroylhydrazones, $H_2L = 4\text{-}RC_6H_4C(OH){:}CHCH{:}NN{:}C(OH)(CH2)mC(O)NHNH_2$ (R = Br, m = 1,4), which gave rise to the dinuclear complexes Ni_2L_2 [648], 3- and 5-substituted salicylaldehyde benzoyl hydrazones (HL with 3-NO_2, 3-MeO, 5-Cl, 5-Br, 5-Me, 5-NO_2), which yielded the dimeric, low-spin, five-coordinate complexes, $Ni(L)Cl \cdot 2H_2O$ [649], and bis(resacetophenone)-2,6-dipicolinoyldihydrazone (H4L), which functions as a tetra-



X = Y = NH; X = Y = S; X = S, Y = NH

(80)

basic nonadentate (N_5O_4) chelating agent giving rise to the trinuclear complex, $[Ni_3LCl_2(H_2O)_3]$ [650].

The related semicarbazone ligands, HL = 3-hydroxy-2-naphthaldehyde semicarbazone or *o*-hydroxyacetophenone semicarbazone have been prepared and reacted with nickel(II) acetate. The resultant complexes, $[NiL \cdot 2H_2O]_2$, were found to contain two tridentate ligands with each metal octahedrally coordinated by two water ligands, two bridging hydroxy O atoms, a keto O atom and an imino N atom [651].

In a study on the synthesis and properties of iodinated nickel imineoxime complexes, $Ni_2(L)_2X_2$ ($HL = HON{:}C(CH_3)C(CH_3){:}NCH_2CH_2NEt_2$; $X = I$, ClO_4) were reacted with I_2. The resultant complexes, $Ni_2(L)_2X_xZ_z$ (X and $Z = I$ or ClO_4), were assigned a binuclear skeletal structure, with oxidation states of ranging from diamagnetic to paramagnetic [652].

Thiolate and dithiolate ligands constitute an excellent source of S-bridging groups. Table 11 lists these ligands as well as their nickel(II) complexes [653–664]. X-ray crystal structure determinations have been used to a large degree in the structural characterisation of these complexes.

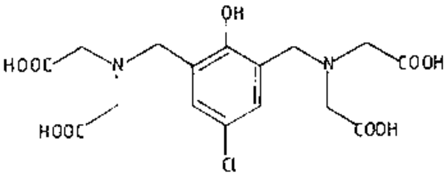
New complexes of nickel(II), cobalt(II) and copper(II) with silicon isothiocyanates of the type $R_2Si(NCS)_{4-x}$ (where $x = 0,1,2,3$) have been prepared and characterised. The nickel(II) complexes have been assigned a polymeric tetrahedral structure on the basis of elemental analysis, magnetic susceptibility measurements and spectral data [665].

The mixed metal complex anions, $Ni(Se_2)(WSe_4)^{2-}$ and $Ni(WSe_4)^{2-}$, have been synthesized and characterised via X-ray crystal structures of their tetraphenylphosphonium salts. $Ni(Se_2)(WSe_4)^{2-}$ was found to consist of a square planar Ni centre bound to a side-on Se_2 group and a nearly tetrahedral WSe_4 group, with two Se atoms functioning as bridging moieties. $Ni(WSe_4)^{2-}$ was found to consist of a square planar Ni atom coordinated to two essentially tetrahedral WSe_4 centres, with Se atoms once again functioning as the bridging groups [666].

Oxalic acid and its related ligands have been used widely in this regard. Table 12 lists complexes that have been prepared using oxalic acid [667–672], oxamide [673,674], and benzenetetracarboxylic acid [675] ligands.

A number of polynuclear complexes with bridging acetate and dithioacetate groups have been prepared and investigated. Studies include the crystal structure elucidation of $[Ni_2(L)(\mu\text{-OAc})](ClO_4)\cdot CH_3OH$ [676], a vibrational spectroscopic study of the complexes $[Ni_2(S_2CMe)_4]$ and $Ni_2(S_2CMe)_2I$ [677], as well as a solid-state high-resolution ^{13}C NMR spectroscopic study of the complex, $[Ni_2(S_2CMe)_4]$ [678].

Poly-amino-acetic acid ligands have been used to synthesize a range of polynuclear complexes. These include *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetic acid (H_4L), which was used to prepare the mixed-metal complexes, $[(H_2O)_4Cu(L)Ni]\cdot 3H_2O$ and $[(H_2O)_5Ni(L)Cu]\cdot H_2O$ [679], 2,5-toluenediamine-*N,N′*-disuccinic acid, whose complexing properties with Ni(II) were investigated in aqueous solution [680], and the related ligand 1-oxy-2,6-di(*N,N′*-biscarboxymethyl)aniinomethyl)-4-chlorobenzol (H_5L) (**81**), which gave rise to the dimetallic complex, $Ni_2(HL)\cdot 4H_2O$ [681].



(81)

In addition, the thiopoly carboxylic acid, 2,2′,2″,2‴-pentane-1,5-diylidenetetrthio)tetrapropionic acid (H_4L), has been prepared and complexed with Ni(II), yielding the high-spin octahedral dinuclear complex, $Ni_2L\cdot 4H_2O$ [682], while diethylenetriamine-*N,N,N′,N′,N′*-penta(methylene-phosphoric acid) formed the polynuclear complex, $Ni_5L\cdot 20H_2O$ [683].

The synthesis, characterisation, structure and magnetism of the homo- and heteronuclear complexes, $M_2(\mu\text{-OH}_2)(\mu\text{-O}_2CR)_2(O_2CR)_2(tmen)_2$ (where M = Ni(II), Co(II); R = CH_3, CH_2Cl, $CHCl_2$, and CCl_3; tmen = *N,N,N′,N′*-tetramethyl-1,2-diaminoethane) have been reported. These complexes contain bridging carboxylato groups and a rather unusual bridging water molecule, as verified by the X-ray crystal structure determination of $NiCo(\mu\text{-OH}_2)(\mu\text{-O}_2CCH_2Cl)_2\text{-}(O_2CCH_2Cl)_2(tmen)_2$ [684].

Bridging hydroxide ion has been observed in a variety of polynuclear complexes. Complexes that have been reported include $[\{Ni(bppte)(\mu\text{-OH})\}_2](ClO_4)_2\cdot$ acetone, the crystal structure of which was determined, revealing two bridging hydroxide groups [685], $[Ni_2(\mu\text{-OH})(\mu\text{-CH}_3CO_2)_2L_2](ClO_4)\cdot H_2O$ (where L = *N,N′,N″*-trimethyl-1,4,7-triazacyclononane), the crystal structure of which has also been determined, confirming a bridging hydroxide group and two bridging

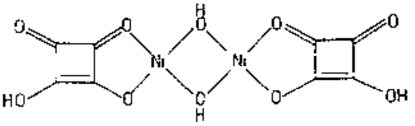
Table 11
Nickel(II) complexes with thiolate bridging centres

Ligand	Complex	Comments	Ref.
Methanethiol (HL)	$[Ni_3(\mu_3\text{-}S)(\mu\text{-}SMe)_3(SMe)_3]^{2}$	X-ray crystal structure of the anion isolated as its tetramethylammonium salt.	[653]
Ethanethiol (HL)	$[NiL_2]_6$	X-ray crystal structure of the triclinic form and re-determination of the monoclinic form.	[654]
1,2-Ethanedithiol (H_2L)	$(Ph_4P)_2[Ni_4(S)_2L_4]\cdot MeOH$	X-ray crystal structure of the mixed disulphide-thiolate anion isolated as its tetraphenylphosphonium salt.	[655]
1,2-Ethanedithiol (H_2L)	$[Ni_2L_3]^{2}$ $[Ni_3L_4]^{2-}$	X-ray crystal structure determination of both complex anions, isolated as their tetraphenylphosphonium salts.	[656]
1,2-Ethanedithiol (H_2L)	$[Ni_3L_4]^{2}$	X-ray crystal structure determination of complex anion isolated as its tetraphenylphosphonium salt.	[657]
1,3-Propanedithiol (H_2L)	$[Ni_6L_7]^{2-}$	X-ray crystal structure determination of complex anion isolated as its tetraphenylphosphonium salt.	[657]
o-Xylene-α,α′-dithiol (H_2L)	$[Ni_3L_4]^{2}$	X-ray crystal structure determination of complex anion isolated as its tetraphenylphosphonium salt.	[657]
1,5-Diamino-3-pentane-thiol (HL)	$[Ni_2L_2]Br_2$	X-ray crystal structure determination. The complex has a thiolate-bridged structure with square planar coordination for each Ni atom.	[658]
2-Mercapto-*N*,*N*′-bis(pyridin-2-ylmethyl)-butanediamide (H_3L)	LNi_2X	X = acetate, trimethylacetate, and the conjugate base of pyrazole.	[659]
N,*N*′-3-mercaptopentane-1,5-diylbis-(salicylideneimine) (H_3L)	$[Ni_2L(pz)]$ (pz pyrazolate)	X-ray crystal structure determination. The first example of a binuclear Ni(II) complex bonded to binucleating Schiff-base ligands containing an endogenous alkanethiolato-bridging sulphur atom.	[660]
N,*N*′-2-mercapto-5-methyl phenyl-1,3-diylbis(4,6-di-*tert*-butylphenol-2-imine) (H_3L)	$[Ni_2L(pz)]$ (pz pyrazolate)	Electrochemical reduction and oxidation study in noncoordinating and coordinating solvents of the binuclear complex containing the endogenous thiolato-bridging sulphur atom and its oxygen analogue.	[661]
N-(2-mercaptopropionyl)glycine	$[Ni_3(C_5H_6NO_3S)_3]^{3}$	X-ray crystal structure. Coordination geometry about each Ni atom is square planar.	[662]
Me_3SiCH_2SH (HL)	$[Ni(L)_2]_5$	X-ray crystal structure. Pentagon of Ni atoms bridged by pairs of L.	[653]
3-Dimethylamino-1-propanethiol (HL)	$[Ni_6(L)_{12}]$	X-ray crystal structure.	[654]

Table 12
Nickel(II) polynuclear complexes with oxalate and related bridging ligands

Complex	Comments	Ref.
$Ni(C_2O_4).H_2O$	L = 4-methoxy-2-(5-methoxy-3-methylpyrazol-1-yl)-6-methylpyrimidine. Oxalate acts as a didentate bridge to form a suggested polymeric structure.	[667]
$[Ni_2(cyclam)_2(C_2O_4)](NO_3)_2$	X-ray crystal structure determination. Structure consist of centrosymmetrical [μ-oxalato nickel(II) binuclear units with noncoordinated nitrate anions. Each nickel atom has a distorted octahedral coordination environment.	[668]
$[(M^IL)Ni(H_2O)_2C_2O_4]$	M^I = Li, Na, K; HL = 8-hydroxyquinoline. Oxalate group functions as bridging group. Electronic spectral and magnetic moment data indicate that polymeric octahedral complexes $[Ni(H_2O)_2\ C_2O_4]$ are converted to tetrahedral ions in their alkali metal adducts.	[669]
$[\{Ni(MePMe_3)\}_2(C_2O_4)]$	X-ray crystal structure determination. Complex consists of two nickel(II) atoms bridged by the oxalato ligand [Ni–O = 1.990(3) and 1.961(3) Å]. The coordination geometry about each Ni atom was found to be square planar.	[670]
$\{Cr[(C_2O_4)Ni(L)]_3\}(ClO_4)_3$	L = (+)-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane. Spectroscopic data indicate a central Cr(III) ion linked to three Ni(II) ions via oxalato bridges.	[671]
$[\{Ce(H_2O)_3(O_2CCH_2CH_2\ NH_3)\}_2(C_2O_4)]–$ $[Ni(S_2C_2O_2)_2]_2.6H_2O$	X-ray crystal structure determination. Both ligands, β-alanine and oxalate, were found to bridge several positions bi-dimensional along the [100] axis. The bis(dithiooxalato)nickelate(II) anions and inserted water molecules were found to occupy the interlayer spaces.	[672]
$NiCu(L).6H_2O$	L = oxamidobisbenzoato. X-ray crystal structure has been elucidated. L functions as the bridging group with two O atoms coordinated to Ni(II) and two N atoms and two O atoms coordinated to Cu(II). The coordination sphere about Ni is completed by four water ligands, and was found to be distorted octahedral. The Cu environment is essentially square planar.	[673]
NiLNi, CuLNi	H_4L = *N,N'*-bis(4-methylaza-3-hepten-2on-7-yl)oxamide. New synthetic method that utilises the *cis–trans* isomerisation of the oxamido group.	[674]
$[Ni_2(L)(en)_2(H_2O)_6].4H_2O$	L = 1,2,4,5-benzenetetrqcarboxylato(4-); en = ethylenediamine. L functions as the bridging group, with each Ni atom octahedrally coordinated, the remaining coordination sites being occupied by the N atoms of en and the O atoms of two water molecules.	[675]

acetate groups [686], $[(C_6F_5)_2Ni(\mu\text{-}OH)_2Ni(C_6F_5)_2]^{2-}$, isolated as its tetrabutylammonium salt, and used as a precursor for the synthesis of μ-pyrazolate derivatives, $[(C_6F_5)2Ni(\mu\text{-}pz)(\mu\text{-}OH)_2Ni(C_6F_5)_2]^{2}$ and $[(C_6F_5)_2Ni(\mu\text{-}Pz)_2Ni(C_6F_5)_2]^{2-}$ [687], and $Na[Ni_2(\mu\text{-}OH)(L)(L^1)(H_2O)_4]$ (where H_3L = nitrilotriacetic acid; L^1 = uracil or thymine) [688]. In addition, reaction of squaric acid with nickel(II) bromide has resulted in the formation of $[Ni(\mu\text{-}OH)(HC_4O_4)]_2.C_3H_7OH$, which has been assigned the structure (**82**) [689]. A structurally related complex, $[Ce_2(H_2O)_{14}(sq)]$-$[Ni(dts)_2]_2 \cdot 4H_2O$, where H_2sq = squaric acid and H_2dts = dithiosquaric acid has also been reported [690].



(**82**)

The synthesis and characterisation of $Ni(OCH_3)(OCH_2CCl_3)$ have been reported. The compound has been assigned a polymeric structure in the solid state with methoxide bridging groups. Characterisation was carried out via infrared and mass spectroscopic data as well as magnetic susceptibility measurements [691].

A thermodynamic and spectrophotometric study of copper(II)–citrate heterobinuclear complexes with nickel(II) has been carried out in aqueous solution. The different binary and ternary systems were characterised by potentiometric measurements as well as visible spectra [692].

Linear heterodinuclear complexes of the type UO_2-M-UO_2 (M = Ni, Co, Zn) have been prepared with the trinucleating synthesis-directing ligand, 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (H_3L). The crystal structure of the nickel-containing complex, $[(UO_2)_2Ni(L)_2]$.6py, has been elucidated. The nickel(II) ion was found to have distorted octahedral coordination geometry, with coordination to two pyridine groups in the axial direction and four oxygen atoms of the β-diketone moieties of the two L^{3-} ligands in the basal plane [693]. In addition, the mixed coordination compounds of lanthanides and nickel(II) with hydroxyphenylacetic acid, $[Ln_2NiL_8] \cdot nH_2O$ (Ln = La, Sm, Ho, Er; HL = hydroxyphenylacetic acid), were synthesised and characterised [694].

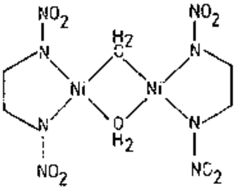
Homo- and heterodinuclear complexes of composition $[M_2L_2](ClO_4)_2 \cdot 4H_2O$, $[CuML_2](ClO_4)_2 \cdot nH_2O$ (M = Ni, Co or Mn; L = L^1 or L^2), and $[CuML^2Cl^2] \cdot 2H_2O$ (M = Ni or Co), have been synthesized with the dinucleating ligands 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde (HL^1) and 1,3-diacetyl-2-hydroxy-5-methylbenzene (HL^2). The complexes were characterised and their reactivities and electrochemical behaviour investigated [695].

Polynuclear alkali-metal complexes with nickel(II) and cobalt(II) salicyladehyde have been synthesized and characterised. The resultant complexes, $ML_2.2M^1L^1$ (M = Ni, Co; HL = salicylaldehyde; HL^1 = 1-nitroso-2-naphthol or 8-hydroxyquinoline), were found to have Ni and Co in tetrahedral coordination environments, with the alkali metals coordinated to salicylaldehyde through O atoms [696].

The practical limit of direct, stoichiometric transmetallation of the tetranuclear copper(II) complexes (μ_4-O)(N,py)$_4$Cu$_4$Cl$_6$ (N = monodentate *N,N'*-diethylnicotinamide, py = pyridine) with M(NS)$_2$ (M = Ni, Co, Zn, Cd, Hg, Sn; NS = *S*-methyl isopropylidenehydrazinecarbodithioate), to give the heterotetranuclear products, (μ_4-O)(N,py)$_4$(Ni, Co, Cu, Zn)$_4$Cl$_6$, has been found to be reagent dependent. All of the complexes were found to have a (μ_4-oxo)metal core structure [697].

Cotton and co-workers have investigated formanidinato complexes of nickel and palladium. In this regard, they have reported the synthesis, molecular structure and physicochemical properties of M$_2$(form)$_4$ (M = Ni, Pd; form = *N,N'*-di-*p*-tolylformamidinato). The crystal structure of the dinickel complex confirms that the two nickel centres are bridged by four formamidinato ligands, with four N atoms around each metal atom in a square planar configuration. The most interesting feature was found to be the Ni–Ni distance of 2.622(3) Å [698,699].

Brill and co-workers have investigated the synthesis and modes of coordination of energetic nitramine ligands in nickel(II) complexes. A wide variety of metal–ligand coordination modes were revealed by X-ray crystal structure determinations. The nitaminatio ligands were found to be able to bond through the O or N donor sites alone, or chelate via coordination at both the O and N sites. Crystal structures that have been elucidated include those of the polymeric complex, poly{[Ni(H$_2$O)$_2$N(NO$_2$)(CH$_2$)$_4$N(NO$_2$)]}, the dimeric complex, [Ni(NH$_3$)$_3$-(O$_2$NNCN$_4$)]$_2$, and the monomeric complex, β-[Ni(H$_2$O)$_4$(L)] (H$_2$L = ethylenedinitroamine) [700]. In addition, they have looked at the thermolysis of these complexes under conditions that simulate combustion. The condensed-phase decomposition of the two polymorphs of [Ni(H$_2$O)$_4$(L)] (H$_2$L = ethylenedinitroamine) was studied. Only water was liberated under 140°C giving a dehydrated product with two suggested structures, a water bridged dimer (**83**), or the polymeric structure (**84**) [701].



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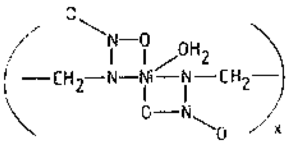

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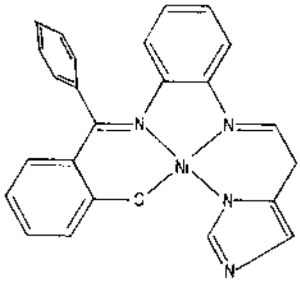
The structure of bis(2,2',2''-triaminotriethylamine-*N,N',N''*)-μ-(triethylenetetramine-*N,N',N'',N'''*)dinickel(II) tetraperchlorate has been reported. It consists of pairs of octahedrally coordinated Ni(II) complex cations and isolated perchlorate anions. Each tren ligand (tren = 2,2',2''-triaminotriethylamine) occupies four coordination sites on each Ni(II) ion, spanning a pair of adjacent octahedral faces. The trien ligand (trien = triethylenetetramine) bridges between two Ni ions, with two N atoms coordinating in a *cis* fashion to each Ni atom, thereby completing the coordination sphere [702].

Nickel(II) complexes of the Schiff base formed by sequential condensation of

5-chloro-2-hydroxybenzophenone, 1,2-diamino benzene, and imidazole-4-carboxaldehyde, NiIm (**85**), have the ability to function as imidazole-like ligands towards iron(II) porphyrin complexes. The Ni–Fe–Ni system was expected to give an all-diamagnetic trinuclear species and the Cu–Fe–Cu system magnetically isolated Cu(II) centres separated by diamagnetic Fe(II). These expectations have been realised by the isolation of Fe(TPP)(NiIM)$_2$ and Fe(TPP)(CuIM)$_2$, where TPP = tetraphenylporphyrinate [703].



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The preparation and spectroscopic and electrochemical properties of some new 2,2'-benzimidazolate (L) bridged binuclear complexes have been reported. These complexes have the general formula $[(bpy)_2M(L)M'(bpy)_2]^{n+}$ (M = Ru, Os; M' = Ni, Ru, Os, Co). The nickel-containing complex was found to be paramagnetic, suggesting that high-spin octahedral nickel(II) exists within the complex [704].

Nickel hexafluoroacetylacetonate, Ni(hfac)2, has been reacted with the nitronyl nitroxide radical 4,4,5,5-tetramethyl-2-ethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl-3-oxide (NITEt), giving the dinuclear species, $[Ni(hfac)_2(NITEt)]_2$. The structure of the cobalt(II) analogue has been determined, showing the nitronyl nitroxide radical bridging the two different Co(II) centres, with coordination occurring via its oxygen atoms [705].

The potentially decadentate ligand, 1,1,4,7,10,1O-hexakis(3,5-dimethyl-1-pyrazolylmethyl)1,4,7,10-tetraazadecane (tthd), has been synthesized and reacted with a variety of metal salts. A number of dimeric complexes have been isolated, including $Ni_2(tthd)(H_2O)_8(ClO_4)_4$, $Ni_2(tthd)Cl_2(ClO_4)_2(H_2O)_8$, and $Ni_2(tthd)(NCS)_2(ClO_4)_2(H_2O)_8$. The crystal structure of the cobalt complex, $CO_2(tthd)(H_2O)_2(ClO_4)_2(MeOH)$, was determined, showing that the tthd ligand functions as a decadentate, dinucleating ligand, with each distorted octahedral Co atom bound to five N atoms of the ligand and one water molecule [706].

A number of triazole and tetrazole ligands have been complexed with nickel(II). ^{1}H NMR spectroscopy has been used to study the complexation of nickel(II) perchlorate with 4-amino-1,2,4triazole at 313-333 K [707]. Similarly, IR and ^{13}C NMR spectra have been used to study the complexes $NiCl_2.L$ (L = 3-vinylthio-1,2,4-triazole) and $NiCl_2.L^1$ (L^1 = 3-vinylthio-5-methyl-1,2,4-triazole). Coordination in these complexes was found to occur via the N4 atom [708]. In addition, the soluble, polymeric 5-(*p*-nitrophenyl)- and 5-(*p*-methylphenyl)tetrazolate (L) complexes of nickel(II) have been prepared and characterised. These complexes have the general formula $[NiL3^-]_n$ [709].

The synthesis of a series of polynuclear complexes of general formula, $[M(tP)_2(NCS)_2]_n$ (M = Ni, Fe, Co, Mn and tp = [1,2,4]triazolo[1,5-*a*]pyrimidine) has been described. All complexes were found to be IR and X-ray isostructural. The structure of the Fe analogue was elucidated, revealing octahedral Fe coordinated to two monodentate NCS groups, and to four N atoms from four symmetry-related tp molecules. Each tp ligand bridges two metal atoms through both non-bridgehead tdazole N atoms [710].

Bis-pyridazinecarboxamide complexes of the type ML (M = Ni, Cu; H_2L = *N,N'*-bis(3'-pyridazinecarboxamide)1,3-propane) have been used as N,N-donor ligands and reacted with $Ni(hfacac)_2$ (hfacac = hexafluoroacetylacetonate). The resultant dimetallic complexes, $MLNi(hfacac)_2$, have been assigned high-spin coordination geometry on the basis of their magnetic moments [711].

A series of complexes of the type $MX_2(L)_2(A)$ and $MX_2(L)$ (B), where M = Ni(II), Co(II) or Cu(II), X = Cl, Br, I, and L = 4,4'-dithiopyridine, have been prepared and spectroscopically characterised. The chloride and bromide complexes were found to be of type (A) and were assigned a polymeric octahedral structure, whereas the iodide complexes were of type (B) and have been assigned a polymeric tetrahedral structure [712].

Dimeric amidine complexes of nickel(II) and platinum(II), $\{M[R'NC(R)NR']_2\}_n$ (M = Ni, Pt; R,R' = allyl or aryl), have been prepared and studied. The nickel(II) complexes were found to be dimeric in the solid state, but monomeric with chelating amidino-groups in solution. In contrast, for the platinum complexes, monomeric structures were observed both in the solid state and in solution [713].

A complete series of homo- and heterodimetallic complexes of the type $[MM'(dppm)_2(CH_3CN)_2](BF_4)_2$ (M,M' = Ni, Pd, Pt; dppm = $Ph_2PCH_2PPh_2$) have been prepared by conproportionation of appropriate M(O) and M'(II) complexes. These complexes have been characterised by ^1H and ^{31}P NMR spectroscopy, which showed that the acetonitrile ligands are labile for all complexes containing nickel and palladium. For certain hetero-dimetallic complexes, a second isomer was observed involving one bridging and one chelating dppm ligand, with preservation of the metal–metal bond [714].

In an ongoing study of dimetallic systems, a number of nickel(II) mercury(II) acetylide complexes containing bridging $Ph_2PCH_2PPh_2$ ligands (dppm), have been prepared. Complexes isolated include $[(RC{=}C)_2Ni(\mu\text{-dppm})_2HgX_2]$ (X = Cl, Br, I), as well as $[(RC{=}C)_2Ni(\mu\text{-dppm})_2Au]Cl$ [715].

Stanley and co-workers have been investigating the coordination properties of dinucleating hexaphosphine ligand systems. In their studies, they have isolated and determined the crystal structure of the $Ni_2Cl_2(eHTP)^{2+}$ cation $\{EHTP = (Et_2PCH_2CH_2)_2PCH_2PCH_2CH_2PEt_2)_2\}$, both as its chloride and tetrafluoroborate salts. The coordination sphere about both of the Ni atoms was found to be distorted square planar, with the EHTP ligand coordinating in a symmetrical bischelating, tridentate fashion [716]. In addition, they have prepared the dinucleating tertiary phosphine ligand system $(R_2PCH_2CH_2)(Ph)PCH_2P(Ph)(CH_2CH_2PR_2)$ (R = Et {eLTTP} and Ph {phLTTP}) and reacted it with Ni(II). They have elucidated the crystal and molecular structures of two of the complexes, *rac*-Ni_2Cl_4(eLTTP) and *meso*-Ni_2Cl_2(eLTTP) [717].

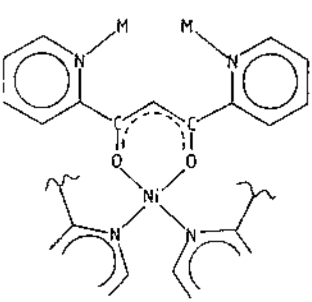
The complex formation equilibria of Ni(II) with 2-(dialkylamino)acetamidoxime (H_2L) have been studied in aqueous solution. The best model was found to be one that included $Ni(HL)^{2+}$, together with the hydrolysed dinuclear $Ni_2(H_2L)^{2+}$ and tetranuclear $[Ni_4(HL)_2(L)_2]^{2+}$ complex cations [718].

Pyridine-2-aldoxime (HL) complexes of the type Cu(HL)LCl and $Ni(HL)_2Cl_2$ have been reacted with nickel(II) and copper(II). Homo- and heterodinuclear complexes having the molecular formula $[M^1(ML_2)Cl_2 \cdot nH_2O]$, where M^1 = Ni, Cu and $n = 0$, 2, 4, were isolated and their thermochemistry investigated [719].

Coordination polymers of bis(8-hydroxy-5-quinolylmethylene)sulphide have been prepared with Ni^{2+}, Co^{2+}, Cu^{2+}, Zn^{2+} and Mn^{2+}. The coordination polymers were characterised by elemental analyses, IR and diffuse reflectance spectral studies, and magnetic moment data. The metal content in all polymers was found to be 1:1 (metal:ligand) stoichiometry [720].

The synthesis of the new dinucleating ligand, 3,3'-[5-(1,1-dimethylethyl)-1,3-phenylenebis(methylene)bis(4-amino-3-penten-2-one) (H_2L), and the properties of three of its five possible cofacial binuclear metal complexes have been described. A crystal structure determination of the nickel complex, $[Ni_2L_2]$.2dmf, showed that the complex consists of centrosymmetric Ni_2L_2 units with a *cis–anti* structure. The coordination geometry about each nickel atom was found to be nearly planar with a Ni···Ni distance of 4.4305(7) Å [721].

Complexes of transition metal ions with the oxygen–nitrogen-containing ligands, 1,3-bis(pyridyl)-1,3-propanedione (HL), and *N,N'*-dimethyl-1,3-bis(pyridyl)-1,3-propanedione (HL^1), have been prepared and characterised. Complexation of HL with nickel(II) yielded complexes with the composition Ni(L)X (X = Cl, Br, NCS), while complexation with HL^1 gave complexes of composition $(L^1)_2NiX_4$. The authors concluded that in the first case, the ligand L has coordinated to the metal ion via the pyridine N and the *β*-diketone units (**86**), while in the second case the ligand L^1 has coordinated only through the *β*-diketone unit [722].



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The coordination behaviour of 5-(*p*-sulphonatophenyl)-1,3,4-oxadiazole-2-thione (UL) with nickel(II), cobalt(II), manganese(II), copper(II) and zinc(II) has been investigated. The nickel complex, $NiLCl_2 \cdot 2H_2O$, was assigned a polymeric structure on the basis of its elemental analyses, conductance, magnetic moment, thermal decomposition, IR and electronic spectral and ESR spectral data [723].

A number of nickel(II) halide complexes with hypoxanthine and xanthine have been synthesised. The complexes, $Ni(HL)_3(L)X$ (HL = hypoxanthine or xanthine; X = Cl, Br or I), have been assigned a linear chain-like polymeric structure, with didentate monoanionic L^- ligands singly bridging between adjacent Ni(II) ions. The coordination number of 6 about each Ni(II) ion is completed by the presence of three terminal unidentate HL ligands and one halide ligand [724].

In a continuing study of sulphur ligands, the reactions of $[Ni(S_2CNPr^i_2)(Ph_2PO)_2H]$ with some transition metal and main group acetylacetonate complexes have been investigated. Complexes that have been isolated include $\{M'[(OPPh_2)_2Ni(S_2CNPr^i_2)]_n\}$ (M′ = Pd(II), $n = 2$; M′ = Ga(III), $n = 3$; M′ = In(III), $n = 3$; M′ = Al(III), $n = 3$) and $\{Ni[(OPPh_2)_2Pd(S_2CNPr^i_2)]_2\}$. The nickel atom was found to be square planar in each of the compounds [725].

The preparation and crystal structure determination of tetraethylammonium {monochloro-bis[bis-*μ*-thiazoline-2-thionatonickelate(II)]} have been reported. The complex was found to have a novel dinuclear structure in which one Ni atom assumes square planar coordination, bonded to an S_4 donor set, while the other exhibits square-based pyramidal coordination, bonded to four N atoms and a chloride ligand. While a relatively short Ni···Ni distance of 2.648(2) Å was observed, the authors concluded that a metal–metal interaction was not occurring and that the resultant room temperature magnetic moment of the complex is simply the result of the two coordination spheres [726].

Bis-*N*-acylthiourea ligands have the potential, after deprotonation, to function as bis-didentate S,O ligands towards polyvalent metal ions, and can form oligomeric or polymeric, cyclic or chain-like chelates. 1,1,1′,1′-Tetraalkyl-3,3′-terephthaloyl-bis-thiourea ligands (H_2L) were found to yield the oligomeric triangulometalla macrocycles Ni_3L_3 and Cu_3L_3. A crystal structure of the nickel complex (alkyl = ethyl) showed that these complexes contain perimetric 27-membered rings, counting the internal oxygens, or 39-membered rings with the external sulphur atoms, i.e. equal chalcogen atoms are in *cis*-positions within each chelate unit around the three metal ions [727].

The donor ability of *μ*-oxobis(tri-*n*-butyltin) towards nickel(II) and cobalt(II) has been studied. Complexes of the type NiX_2L_4 ($L = (Bu_3Sn)_2O$; X = Cl, Br, I, NO_3, NCS) were isolated and characterised. The nickel complexes were found to possess octahedral coordination geometry [728].

The organometallic ligand, bis[(1-methyl-1-benzoylhydrazoneethyl)-cyclopentadienyl]iron (H_2L), has been complexed with a number of transition metal ions. Nickel-containing complexes that were synthesised include NiL and $Ni(H_2L)Cl_2$. Both complexes have been assigned a polymeric structure with tetracoordinate and hexacoordinate environments about the nickel ion, respectively [729].

6. Nickel(II) complexes with biological ligands

The complexation of a range of amino acid and amino acid derivatives with nickel(II) has been investigated. Of general interest is an article which reports a general method of asymmetric synthesis of α-amino acids via alkylation of chiral glycine–nickel(II) complexes. This method has been applied to the asymmetric synthesis of (*S*)-alanine, (*S*)-valine, (*S*)-tryptophan, (*S*)-phenylalanine, (*S*)-norleucine, and (*S*)-3,4-dimethoxyphenylalanine [730]. This work has been extended to include the synthesis of optically pure aspartic acid [731].

More specifically, studies involving amino acids and their derivatives that have been reported include:

- The synthesis of nickel(II) complexes with *N*-protected amino acids. This includes the preparation of bis(*N*-acetylglycinato)tetraaquanickel(II) [732] and its crystal and molecular structures [733].
- Reaction of a number of *N*-substituted glycines with Ni(II) including N-(substituted phenyl) glycines [734], *N*-Me-, *N*-Et-, *N*,*N*-di-Me-glycine [735], *N*-benzoylglycine (and L-leucine) [736], *N*-(2-hydroxy-5-sulpho)benzylglycine [737], *N*-(2-hydroxy-1-naphthylidene)glycine [738], *N*,*N*-bis(carboxymethyl)-glycine [739], and glycine itself with bis(3-aminopropyl)aminonickel(II) [740].
- Regarding alanine, studies that have been undertaken include: (a) the comparative stability of complexes of divalent transition metal ions with the amino acids α-alanine, β-phenyl-α-alanine and β-alanine [741]; (b) the complexing characteristics of L-α-alaninehydroxamic acid with Ni(II) [742]; (c) an electronic spectral study of nickel(II) alanine complexes [743], the binary and ternary complexes of DL-α-alanine with Ni(II) by pH potentiometric titration [744]; (d) the protonation and complex formation of the *cis* and *trans* isomers of alicyclic β-amino acids, including β-alanine [745]; (e) the mixed-ligand complexes of the type [MAL], where M = Ni(II), Cu(II), Zn(II) or Cd(II), A = α,α′-bipyridyl and L = α-alanine, β-phenylalanine or tryptophan [746]; and (f) the hydrophobic interaction in binary and ternary complexes of the type [MAL], where M = Ni(II) or Cu(II), A = 5-nitro-1,10-phenanthroline or 2,2′-bipyridylamine and L = 3,4-dihydroxyphenylalanine, tyrosine, phenylalanine or tryptophan [747].
- The stability constants of *N*-isobutyroyl-L-lysine and poly(*N*-methacryloyl-L-lysine) complexes with Ni(II) have been determined by potentiometry in aqueous solution [748]. In addition, a potentiometric and spectrophotometric study of nickel(II) and copper(II) complexes with δ-hydroxylysine has been reported. Binary and ternary homo- and heteronuclear complexes were observed in solution [749].
- A number of studies of transition metal complexes with amino acids and peptides containing a thioether group have been reported. In an ongoing study, the stability constants of nickel(II) complexes of the amino acids, *S*-methyl-L-cysteine and methionine (Met), as well as the peptides, Met–Gly, Gly–Met, Met–His and His–Met (Gly = glycine, His = histidine), have been determined [750]. Similarly, the coordinating abilities of the thioamide analogues, leucine-*N*-methylamide, methionine-*N*-methylamide, their thiocarbonyl analogues, and for (phenylalanyl)-

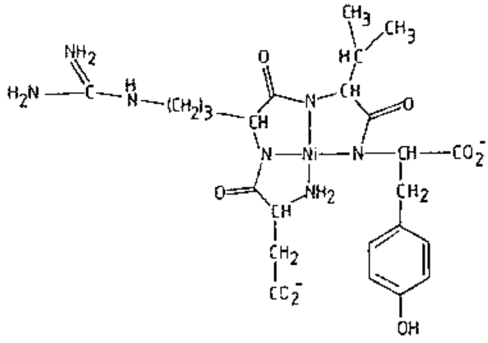
methionine-*N*-methylamide have been investigated via potentiometric and spectroscopic methods [751]. In addition, the behaviour of the Ni(II), Co(II) and Cu(II) complexes with cystine, cysteine and methionine ligands have been studied in aqueous solution over 25–40 °C [752], as have the *N*-benzenesulphonamide ligands derived from the amino acids, serine, threonine and methionine [753].

- Barium salts of the dithiocarbamate derivatives of the amino acids, DL-valine, L-valine, DL-leucine, DL-isoleucine and L-proline have been prepared, and the anions have been used to obtain the nickel(II) complexes in acid form. The complexes, [NiL_2], were found to be diamagnetic, with coordination taking place via the sulphur atoms of the dithiocarbamate moiety [754].
- Nickel(II) chlorides have been reacted with an excess of cystamine in ethanol. The resultant complex, bis(cystamine)nickel(II), appears to have a distorted octahedral structure. In aqueous solution, the metal-S(disulphide) interaction promotes nucleophilic scission of the sulphur–sulphur bond, leading to the formation of *trans*-[$Ni(SCH_2CH_2CH_2)_2$], which has been characterised by single-crystal X-ray diffraction [755].
- The formation constants of ternary and quaternary complexes containing the ligands imidazole, glycylglycine and pyridoxamine with Ni(II) have been determined by pH-metric titration in aqueous solution [756].
- The stability constants of the complexes formed by Ni(II), Co(II) and Cu(II) with L-threonine have been determined ph-potentiometrically in aqueous solution. Both 1:1 and 1:2 (metal:ligand) complexes were found to form [757]. In addition, the effect of Ni(II) on the rate of racemisation of L-serine and L-threonine has been investigated in aqueous solution [758].

Leporati and co-workers have investigated a number of hydroxamic acid derivatives and their complexes with Ni(II). These include 2-amino-*N*,3-hydroxybutanamide [759] and 2-amino-*N*-hydroxy-3-phenylpropanamide [759,760], 2-amino-*N*-hydroxy-3-(*p*-hydroxyphenyl)propanamide [761], α-amino-*N*-hydroxy-1*H*-imidazole-4-propanamide [762], and *N*-hydroxy-D-asparagine [763]. All of these studies have been undertaken in aqueous solution using potentiometric methods.

Turning to peptides, a potentiometric and spectroscopic study of nickel(II) complexes with sulphhydryl-containing peptides has been reported [764]. This study showed that the sulphhydryl group is a very effective binding group in Ni(II) complexes with L-cysteine-containing ligands. Similar potentiometric and spectroscopic studies have been undertaken for vasopressin-like peptides [765], thiocarbonyl-containing dipeptides [766], histidylphenylalanine and histidyltyrosine [767], and angiotensin II and its peptide fragments [768]. The proposed structure for the complex with Asp–Arg–Val–Tyr shows tetra-coordination via four N atoms (**87**).

Nickel(II) and iron(III) complexes of glycylglycinehydroxamic acid and triglycinehydroxamic acid have been prepared and fully characterised. The ligands were found to coordinate via the ketonic carbonyl O atom and the deprotonated hydroxamate O atom in the metal complexes [769]. In addition, a study of the kinetics of acid dissociation of oligopeptide complexes of Ni(II) and Cu(II) has been reported [770].



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A spectroscopic study of nickel(II)–bovine serum albumin binding and reactivity has been undertaken. The pH dependence of the UV/visible and CD spectra of the 1:1 complex in aqueous solution has been interpreted in terms of a major square planar form and an octahedral form [771]. Similarly, the isolation and two-dimensional ^{1}H NMR spectra of peptide [1–24] of dog serum albumin and its complexation with nickel(II), studied by NMR spectroscopy and CD, have been reported.

Complexation in this case, was found to occur via the α-NH_2, three deprotonated amide N atoms of Ala-2, Tyr-3, and Lys-4 residues [772].

Nickel(II)-substituted myoglobin and horseradish peroxidase have been oxidised with iridate to investigate whether porphyrin-π-cation radical is formed in these hemoproteins. UV visible and ESR spectra confirmed that porphyrin-π-cation radical formed in all of the hemoproteins [773].

Nickel metalloenzymes have attracted considerable attention. This is manifested by a general article entitled "Nickel Enzymes" which has appeared in Perspectives in Biochemistry [774].

A variety of hydrogenases have been studied. These include an EPR study of the enzyme from *Wolinella succinogens*, enriched in ^{33}S, in which direct evidence for sulphur as a ligand was observed [775], and the preparation and characterisation of Ni(II)-substituted rubredoxins from *Desulphovibrio vulgaris* and *Chlostridium pasteurianum* [776]. In this last study, the nickel coordination sites were found to be high spin and have been interpreted in terms of a tetragonally distorted thiolate coordination sphere.

Turning to dehydrogenases, X-ray absorption spectroscopic evidence for a unique nickel site in *Chlostridium thermoacetium* carbon monoxide dehydrogenase has been obtained. Square-pyramidal and distorted square planar geometries have been suggested on the basis of this evidence [777]. A similar study using EXAFS has been undertaken on *Chlostridium therinoacetium* strain DSM. This study indicated the presence of iron sulphur centres, as likely Fe_4S_4 clusters, as well as nickel surrounded by four sulphur atoms at approximately 2.16 Å [778]. In addition, the isolation of an enzyme complex with carbon monoxide dehydrogenase activity, containing corrinoid and nickel from acetate-grown *Methanosarcina thermophia*, has been reported. UV visible spectra suggested the presence of Fe S centres, while the EPR spectra indicated the involvement of Ni in the spectrum [779]. In terms of understanding the mode of action of the enzyme carbon monoxide dehydrogenase, the reduction of coordinated carbon dioxide to carbon monoxide via protonation by thiols and other Brønsted acids, has been investigated [780].

The spectroscopic and magnetic properties of iron-activated alcohol dehydrogenase from *Zymomonas mobilis* have been studied. Magnetic susceptibility, ESR, Mossbauer and electronic spectral data indicate the presence of high-spin six-coordinate sites influenced by a ligand field close to octahedral. Three or four of the ligands have been assigned to histidyl N atoms, while the rest of the coordination sphere is made up of O donor atoms from water, aspartate, glutamate or tyrinosate ligands [781].

Similarly, the magnetic properties of the nickel enzymes urease, nickel-substituted carboxypeptidase and nickel-substituted carbonic anhydrase have been investigated. This work has revealed that urease has a binuclear Ni active site, possibly with a unique Ni–thiolate interaction [782].

Factor 430, the nickel tetrahydrocorphinoid cofactor, and some of its structurally related compounds found in many methanogenic bacteria, have been the subject of a number of studies. These include:

- The use of Raman difference spectroscopy to investigate the axial ligation-induced structural changes in nickel hydrocorphinoids related to coenzyme F_{430} [783]. The same group have published a review on axial coordination in nickel porphyrins and nickel-reconstituted heme proteins, investigated by Raman difference and transient Raman spectroscopy [784].
- The use of resonance Raman spectroscopy to study the four- and six-coordinate forms of a Ni(II) hydrocorphinate model of cofactor F_{430} of the methyl-coenzyme M methylreductase [785].
- A report on the photodynamics of a nickel hydrocorphinoid model of F_{430} [786].
- A study of coenzyme F_{430} from methanogenic bacteria, in which methane formation by reductive carbon–sulphur bond cleavage of methyl sulphonium ions, catalysed by F_{430} pentamethyl ester, was observed [787].
- A low-temperature investigation of the magnetic and electronic properties of *Methanobacterium thermoautotrophicum* (strain δH) methyl coenzyme M reductase and its nickel tetrapyrrole cofactor F_{430}, using circular dichroism [788].
- An investigation of the reductive chemistry of nickel, in which evidence for a biologically significant difference between porphyrins, hydroporphyrins and other tetrapyrroles such as cofactor F_{430} was presented [789].
- An investigation in which both the mono- and divalent oxidation states of the water soluble complex, Ni(dioxo[16]aneN_5), was found to catalyse methyl coenzyme M to methane and coenzyme M [790].
- A study of chlorophyll model compounds in which the effect of low symmetry on the resonance Raman spectra and normal mode descriptions of Ni(II) dihydroporphyrins have been reported [791].

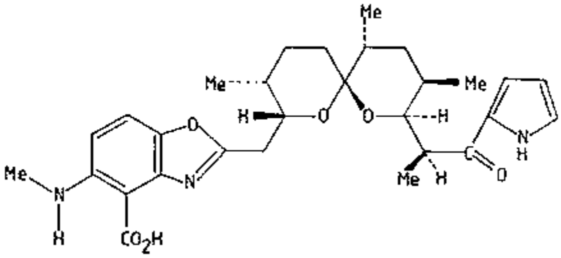
Ni(II) has been substituted into bovine copper zinc superoxide dismutase, Cu_2Zn_2SOD, to give two new derivatives, Cu_2Ni_2SOD and Ag_2Ni_2SOD. In the first complex, it was found that Ni(II) occupies the native Zn(II) site without migration of Cu(II), while the second derivative contains Ag(I) ions in the native copper site and Ni(II) ions in the native zinc site [792].

D-Penicillamine and its complexation with Ni(II) has been studied in aqueous media both potentiometrically [793], and using the pressure jump technique [794]. It was found that D-penicillamine coordinates to the nickel(II) ion via its S and N donor atoms at pH 9.2. Decreasing the pH was found to inhibit the ability of the mercapto group to participate in bonding.

In an ongoing series, Evans and Martin have published two articles in which the complexation of phytic acid with metal ions has been studied. The first is a titrimetric, calorimetric and binding study with nickel(II) and cobalt (II) [795], while the second is a calorimetric study of its interaction with nickel(II), cobalt(II), zinc(II) and magnesium(II) [796].

The complexation of citric acid with Ni(II) has been investigated both in the solid state and solution. Complexes of the type $M[BL_2]_2 \cdot 8H_2O$ (M = Ni, Fe; H_2L = citric acid), in which the citrate ion coordinates in a didentate fashion through the deprotonated hydroxide and adjacent carboxylato groups, have been isolated and characterised [797]. In addition, the kinetics of complexation of nickel(II) by DL-isocitric acid have been studied in aqueous solution using stopped-flow methods [798].

Similarly, stopped flow methods have been used to determine the formation and dissociation rate constants of the nickel(II) complexes of the ionophore A23187 (**88**) in 80% methanol–water at 25 °C. First-bond formation involving the carboxylate,oxygen atom of the anionic form of the ionophore has been proposed as the rate determining step [799].



(**88**)

Aqueous solutions containing triethylenetetramine, thiolactic acid, perchlorate ions and Ni(II), Co(II) or Zn(II) have been investigated by potentiometric methods. The 1:1:1 complexes were detected and their formation constants determined [800].

In a study aimed at predicting metal complex formation with drugs and their undesirable side effects, the Mellor–Maley rule has been used to predict the stability constants of a number of drugs with metal ions, including Ni(II). The complex forming properties of tetracyclines, nalidixic acid and methicillin have been predicted, based on the known complex forming behaviour of ethylenediamine, dipyridyl and dithizone, respectively [801]. In addition, the chelates of tetracycline (tc) with first row transition metal perchlorates have also been prepared and characterised. Coordination in the nickel(II) complex, $Ni(tc)_2(ClO_4)_2$, was found to occur via the protonated hydroxyl and amide carbonyl oxygen atoms [802].

Turning to purine base and related ligands, a paper has been published which describes the synthesis of compounds of Ni(II) with uracil, uridine and the nucleotides 5′UMP, 5′GMP and 5′IMP, and their characterisation which was carried out by elemental analysis, IR and diffuse electronic spectral methods, and conductivity measurements [803]. Similarly, mixed complexes of Ni(II) with 6-aminopurine and uracil have been prepared from aqueous solution and characterised [804], while the crystal and molecular structure of tetraaqua(uracil-6-carboxylato)nickel(II) monohydrate have been determined [805].

The stability constants of the 1:1 complexes formed between Ni(II) and a range of other metal(II) ions, with $2'AMP^{2-}$, $3'AMP^{2-}$ or $5'AMP^{2-}$ (AMP = adenosine monophosphate) have been determined by potentiometric pH titration [806]. Potentiometric equilibrium measurements have also been made at 35 °C for the interactions of 5′-cytidine monophosphate and Ni(II) with the biologically important secondary ligands, glycine, oxalic acid, histidine and histamine [807]. In addition, the ternary nucleotide complexes, $[Ni(en)_{1.3}(H_2O)_{1.4}(H_2O)_2][Ni(5'\text{-}dGMP)_2\text{-}(en)_{0.7}(H_2O)_{0.6}(H_2O)_2]\cdot 7H_2O$ and $[Ni(en)_2(H_2O)_2][Ni(5'\text{-}GMP)_2(H_2O)_4]\cdot 6H_2O$ (en = ethylendiamine, 5′-dGMP = 2′-deoxyguanosine 5′-monophosphate, 5′-GMP = guanosine 5′-monophosphate), have been prepared and their crystal and molecular structures determined [808].

Four metal complexes of the anti-hypseruricema drug, allopurinol, have been synthesised and characterised. The complexes were found to have the general formula $M(II)(allopurinol)_2SO_4\cdot 4H_2O$ (M = Ni, Co, Zn, Cd), as verified by the crystal structures of the Zn and Cd complexes [809]. In addition, the crystal and molecular structures of the complex, bis(allopurinol)diaquadichloronickel(II), have been reported. The coordination sphere in this complex was found to be octahedral, with all of the ligands in the *trans* configuration [810].

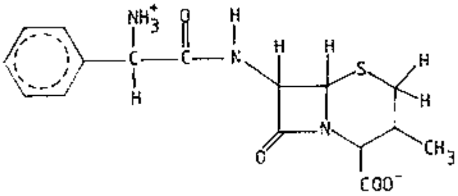
The crystal structure of bisacetodiaquabis(isonicotinamide)nickel(II) has been elucidated. The Ni atom was found to be octahedrally coordinated by two N atoms from the two isonicotinamide ligands, two O atoms from two acetates, and two O atoms from two water ligands, all of which are in *trans* positions [811].

Cyanuric acid has been complexed with nickel(II). The resultant complex, $NiL_2\cdot{=}7H_2O$, was postulated as the octahedral complex $[NiL(H_2O)_5]L\cdot 2H_2O$. Successive dehydration of this complex led to the formation of octahedral $NiL_2\cdot 4H_2O$ and tetrahedral NiL_2 [812].

Nickel(II) has been complexed with 6-hydroxypurine (L). The resultant complex, $Ni(L)SO_4\cdot 5H_2O$, was found to be octahedral with coordination occurring via five O atoms of five water ligands and the N(7) atom of L. This structure was assigned on the basis of thermal analysis, IR and electronic spectral studies and the crystal structure of the isostructural Co analogue [813].

The complexing properties of the antibiotic, Cephalexine (**89**), with Ni(II) have been studied in aqueous solution using potentiometric techniques. In addition, the complex, $[Ni(L)(H_2O)_4]BPh_4$ {HL = (**89**)}, has been isolated and characterised.

L^- was found to function as a didentate ligand coordinating via the carbonyl and amino-NH_2 groups of the side chain [814].



(89)

Three different types of Ni(II)-creatinine complex species have been prepared in non-aqueous media. These complexes have the molecular formulas $[Ni(L)_4(H_2O)_2](NO_3)_2.2H_2O$, (L = creatinine), $[Ni(L)_3(H_2O)_3](NO_3)_2 \cdot H_2O$ and $[Ni(L)_6](NO_3)_2 \cdot 4H_2O$, respectively. All of the complexes were assigned octahedral coordination on the basis of spectroscopic, magnetochemical and thermogravimetric methods [815].

Pyridoxine (L) has been complexed with Ni(II). Two complexes were isolated, namely $NiLCl_2$ and $NiL(glycinate)_2$. The formation constants of these complexes were also determined in water and 80% dioxane [816].

A study of the chelation behaviour of bivalent metals with the biologically active ligand, 2-hydroxy-1,4-naphthaquinone monoxime (HL), has been undertaken in dioxane–water mixtures. Potentiometric methods were used to determine the equilibria between the metal ions and the ligand, L [817].

Glufosinate has the ability to function as a tridentate or tetradentate ligand at near-neutral pH to form complexes with many of the metals found in ground-water, including Ni(II). In the case of Ni(II), IR and UV–visible spectroscopy has been used to establish that coordination occurs via the amine N atom, carboxylate O atom, and phosphonate O atoms of the ligand [818].

The formation constants of the heterocyclic sulphonamide ligands, sulphadiazine, sulphamerazine and sulphasomidine with Ni(II) have been determined in 50% aqueous ethanol, using pH-metric titration [819]. This work has been extended by the same group to a study involving the coordination of these ligands in the same solvent over a range of temperature [820].

Acetazolamide (L), one of the most potent inhibitors of carbonic anhydrase enzyme, has been complexed with Ni(II). The resultant complex, $[Ni(L)_2(NH_3)_4]$, has been isolated and its crystal structure determined. L was found to coordinate via the N(2) atom of the heterocyclic ring [821].

Glutathione (H_3L), when reacted with Ni(II), yielded the complex, $Ni(HL) \cdot 2H_2O$, which was characterised by IR and electronic spectra, magnetic moment measurements and thermal analysis. It was found that the complex is octahedral with both water molecules coordinated, and that HL is functioning as a tetradentate ligand [822].

A new series of polymeric complexes $[M(Neom)H_2O_x]_n$ have been prepared, where M = Ni(II), Co(II), Cu(II), or Zn(II), Neom = neomycin and $x = 2$–4. The complexes were characterised by elemental analysis, conductance and magnetic moment measurements. IR spectra indicated that coordination between neomycin takes place through M–O bonds [823].

^{13}C NMR spectroscopy has been used to study the C-2 epimerisation of aldoses using combinations of certain metals, including Ni(II) and diamines such as *N,N,N'*-trimethylethylenediamine and *N,N,N',N'*-tetramethylethylenediamine. This reaction was found to involve a novel rearrangement of the carbon skeleton, with exchange of the C-1 and C-2 atoms by inversion of the C-1-C-2 aldose [824]. This newly discovered C-2 epimerisation of aldoses promoted by nickel(II) diamine complexes has been investigated in detail by the same group using ^{13}C-enriched D-glucose, ^{13}C NMR spectroscopy, and EXAFS analysis. Aldoses treated with the nickel(II) diamine complexes in methanolic solutions were found to be rapidly epimerised at C-2 giving equilibrium mixtures where the ratio of C-2 epimers shifts to the side of the naturally rare mannose-type aldoses having the *cis* arrangement of C-2 and C-3 hydroxyl groups [825]. A similar ^{13}C NMR spectroscopic study has been carried out utilising [1-^{13}C]-D-glucose, catalysed by $[Ni(H_2O)_2(tmen)_2]Cl_2$ (tmen = *N,N,N'*-trimethylethylenediamine). This study showed that the apparent C-2 epimerisation proceeds via a molecular rearrangement in which the C-1 carbon label was found at the C-2 position of the product mannose [826]. In addition, an unprecedented dinuclear nickel(II) complex containing two types of N-glycosides formed from *N,N'*-dimethylethylenediamine (*N,N'*-Me$_2$-en) and D-mannose (D-Man) has been synthesised, and its crystal and molecular structure determined. The complex, (μ-Man)[Ni$_2$(CH$_3$OH)(*N*-(D-Man)-*N,N'*-Me$_2$-en)(*N,N'*-(D-Man)$_2$-*N,N'*-Me$_2$-en)]Cl$_2$ · 2CH$_3$OH · H$_2$O, was found to be a dinuclear structure in which the two nickel centres are bridged by a mannose residue. Both Ni atoms were found to have distorted octahedral coordination geometry [827].

The potentiometric and spectroscopic results for the Ni(II), Cu(II) and Co(II) ion complexes with D-glucosamine have been reported and discussed. Cu(II) and Ni(II) were found to form two major complex species, ML$_2$ and ML_2H_{-2} [828]. Similarly, the complexation behaviour of galactose oxime with Ni(II), Cu(II) and Co(II) has been investigated ph-metrically in aqueous solution. Complex formation was found to occur in a stepwise fashion, with formation of the ML^+ and ML$_2$ complexes [829].

7. Nickel(I)

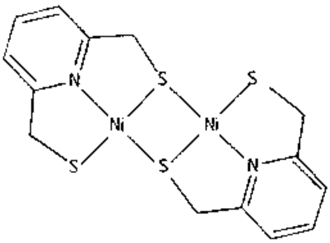
Macrocycles have the ability to stabilise Ni in the +1 oxidation state as well as the higher oxidation states. An example of this is the monovalent nickel complex formed by the reduction of the β-isomer of the complex of C-5, 12-racemic-1,4,5,7,7,8,11,12,14,14-decamethyl-1,4,8,11-tetraazacyclotetradecane nickel(II). The half-life of the resultant monovalent complex was found to be longer than 90 h [830].

In a study of the reductive chemistry of nickel hydroporphyrins, the synthesis and reactivity of the nickel(I) octaethylisobacteriochlorin anion, Ni^{I}(OEiBC)$^-$, has been reported [831]. In particular, its reaction with alkyl halides have been studied in some detail. The complex was found to mediate electrolytic reduction of the alkyl halides and methyl-*p*-toluenesulphonate, producing methane as a product [832].

Reduction of the nickel(II) complex of 5,10,15,20-tetraphenyl-21-thiaporphyrin yielded the corresponding Ni(I) complex, which was isolated and characterised. Reaction of this complex with sulphur dioxide produced a paramagnetic five-coordinate Ni(I)–SO_2 adduct, while reaction with nitrogenous base ligands (amines, pyridines, imidazoles) yielded five- and six-coordinate complexes, respectively [833]. In addition, the crystal structure of nickel(I) diphenyldi-*p*-tolyl-21-thiaporphyrin has been determined. The coordination geometry about the nickel centre was found to be essentially square planar with extremely short Ni--N and Ni–S bonds [Ni–N = 2.015 (2), 2.014 (12) and 1.910 (14) Å and Ni–S = 2.143 (6) Å] [834].

The nickel(I) tetraazamacrocycle, $Ni(tmc)^+$, has been reacted with a number of variously substituted disubstituted alkanes, including 1,4-dihaloalkanes [835], 1,5-dihaloalkanes [836], 1,2-disubstituted alkanes, 1,3-disubstituted alkanes, 1,4-disubstituted alkanes, 1,5-disubstituted alkanes and 1,6-disubstituted alkanes [837]. Reaction products ranged from ethylene to cyclopentane depending on the disubstituted alkane employed. The same group have also examined the effect of steric crowding on the rates of reaction of the nickel(I) tetraaza macrocycle complex, $Ni(dmc)^+$ (dmc = decamethylcyclam), with organic halides and hydroperoxides. Reaction with this complex was found to be about 104 times as slow than with the corresponding $Ni(tmc)^+$ complex [838].

The first extensive study of the reactivity of nickel in a classical coordination environment containing mainly thiolate ligands has undertaken to examine the factors affecting the stability of Ni(III) in hydrogenases. In this study, reaction of $Ni(acac)_2$ with pyridine-2,6-dimethanethiol (H_2pdmt) yielded $[Ni(pdmt)]_2$ (**90**). This complex was electrochemically reduced to form the mixed valence Ni(II,I) complex, $[Ni(pdmt)]_2^-$, which could then be cleaved with thiolate to afford $[Ni(pdmt)(SR)]^-$ (R = Ph, Et) [839].



(**90**)

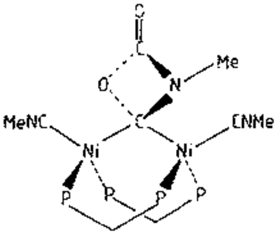
The synthesis and properties of some novel alkali metal alkoxonickelates have been reported. Spectroscopic and magnetic data indicate that these complexes have tetrahedral geometries. Reaction of these complexes with phosphines and phosphates give hydridonickel, Ni(I) and Ni(0) ligand complexes. These complexes react with CO_2 and CS_2, opening up new synthesis possibilities [840].

8. Nickel(0)

In an ongoing study of the spectroscopy and photochemistry of nickel(0)-α-diimine complexes, the structural differences among the complexes NiL_2 and $Ni(CO)_2L$ (L = α-diimine) have been examined via molecular orbital calculations and electronic absorption Raman resonance studies [841,842]. A theoretical study on the coordination of dinitrogen and related molecules to Ni(0) has also been reported. *Ab initio* calculations on the model compounds $[Ni(PH_3)_2(N_2)]$, $[Ni(PH_3)_2(NCH_2)]$, and $[Ni(PH_3)_2(N_2H_2)]$ were undertaken [843]. Similarly, extended Hückel theory has been used to investigate the dependence of the mode of sulphur dioxide coordination in the complexes $NiL_3(SO_2)$ (L = PF_3, CO, CNME, PH_3, PMe_3) [844].

The dinuclear Ni(0) "cradle" complex, $Ni_2(\mu\text{-CNMe})(CNMe)_2(PPh_2CH_2PPh_2)_2$, has been reacted with CO_2. The complex, $Ni_2(\mu\text{-CNMeCO}_2)(CNMe)_2(PPh_2CH_2PPh_2)_2$, forms initially, while prolonged exposure to CO_2 results in the formation of $Ni_2(\mu\text{-CO})(CO)_2(PPh_2CH_2PPh_2)_2$ [845]. In addition, another synthetic route to the Ni(0) cradle complex $Ni_2(\mu\text{-CO})(CO)_2(PPh_2CH_2PPh_2)_2$ has been reported. This convenient synthesis involves the simultaneous reaction of $Ni(COD)_2$ with CO and dppm [846].

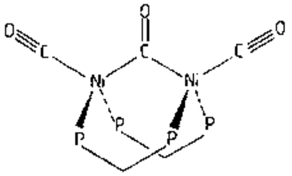
The photochemical activation of CO_2 has been effected using the ligand centred charge-transfer excited state of the binuclear Ni(0) complex, $Ni_2(\mu\text{-CNMe})(CNMe)_2(PPh_2CH_2PPh_2)_2$. The product of the photochemical reaction, (**91**), is the first example of a bimolecular association of CO_2 to an excited state of a transition metal complex [847].



(**91**)

$Ni(CO)_2[HC(PPh_2)_3]$ has been used to prepare the nickel(O) dimer, $Ni_2(CO)_3(PPh_2CH_2PPh_2)_2$. The crystal structure of this complex has been determined, showing approximate tetrahedral geometry about each of the nickel atoms, with an unusual *cis* arrangement of the two bridging dppm ligands, one bridging CO ligand and two terminal CO ligands (**92**) [848].

Water soluble, zero valent Ni, Pd and Pt complexes of the type, $[M\{P(CH_2OH)_3\}_4]$ (M = Ni, Pd, Pt), have been prepared. These complexes are catalysts for the addition of PPh_3 to CH_2O. The crystal structure of the Pd complex has also been reported. A tetrahedral coordination geometry about Pd was observed [849].



(92)

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