ELSEVIER

Coordination Chemistry Reviews 146 (1995)
1-90

COORDINATION
CHEMISTRY
REVIEWS

1. Nickel 1992

Gary A. Foulds

CONTENTS

SSDI 0010-8545(95)01195-1

INTRODUCTION

This review of nickel coordination chemistry essentially covers work published in 1992. It is based on a data search of the coordination complexes of nickel listed for 1992 in Chemical Abstracts, although the journals *Inorganic Chemistry, Inorganica Chimica Acta, Journal of the Chemical Society (Dalton Transactions and Chemical Communications), Journal of the American Chemical Society, Polyhedron, Journal of Coordination Chemistry, Acta Crystallographica and Coordination Chemistry Reviews* have been searched independently for the period January to end December 1992.

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

To introduce the review, two papers in which nickel chelate complexes have been used as catalysts for the oligomerization of olefins are noted. In the first paper, the olefin oligomerization and isomerization catalytic activities and selectivities of catalysts generated by combining the complexes $[Ni(RC(X)CHC(Y)R)_2]_n$ (R = Me, X = Y = O, n = 3; X = O, Y = NH, n = 1; X = O, Y = S, n = 1; X = Y = S, n = 1; and R = Bu^t, n = 1, X = Y = O; X = O, Y = S; X = Y = S) and $[Ni(CH_3C(S)CHC(S)CH_3)(PR_3)Cl]$ (R = alkyl, aryl) precursors with ethylaluminiumchloride cocatalysts have been compared. Catalytic activity and selectivity were found to be highly dependent on the donor atoms of the chelate ligands, while selectivity was found to be most dependent on substituent groups [1]. In the second, the perfluorinated ion-exchange polymer , Nafion-H^+, has been used as a Bronsted acid to activate $[Ni\{P(OEt)_3\}_4]$ and as a support for the resulting catalytically active cationic species Nafion-$[Ni\{P(OEt)_3\}_3]^+$ [2].

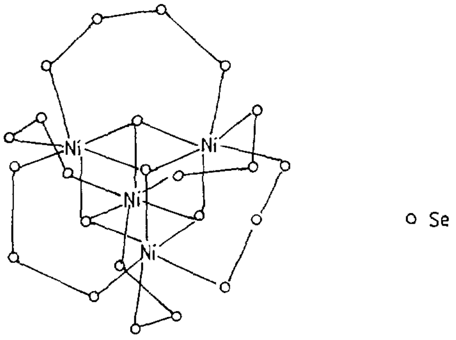
1.1 NICKEL(IV)

1.1.1 Complexes with sulfur, selenium and tellurium donor ligands

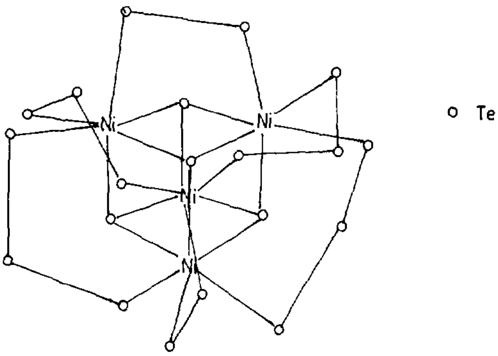
The compounds $[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_5.2dmf$ and $[Me_3N(CH_2)_4NMe_3]$-$[Ni(dmit)_2]_5.2CH_3CN$ have been prepared by electrochemical oxidation of

$[Me_3N(CH_2)_4NMe_3][Ni(dmit)_2]_2[Me_3N(CH_2)_4NMe_3]^{2+}$ ($dmit^{2-}$ = 4,5-dimercapto-1,3-dithiole-2-thionato). Single crystal X-ray measurements have been carried out for both compounds and it has been reported that several of the $Nidmit_2$ subunits show considerable deviation from planarity. Both compounds were found to behave as semiconductors, and the mean oxidation state of the metal centres is formally +3.6 [3].

Nickel(IV) cubane complexes of the type $[NEt_4]_4[Ni_4Se_4(Se_3)_5(Se_4)].xNEt_4Cl$ (x = 0, 1) and $[NEt_4]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]$ have been prepared from the reaction in dmf of $Ni(S_2COEt)_2$ with Li_2Se and Se or Li_2Te and Te respectively. The spontaneous assembly reaction was found to occur with oxidation of the Ni(II) centres to Ni(IV) with simultaneous reduction of the Se- or Te-containing species. $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ was found to possess a Ni_4Se_4 core (**1**), while $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ had a Ni_4Te_4 core (**2**). Structures were verified by single-crystal X-ray structure determinations. Ni-Se bond lengths were found to vary from 2.338(7) to 2.442(8)Å, while Ni-Te bond lengths were found to vary from 2.492(2) to 2.667(2)Å [4].



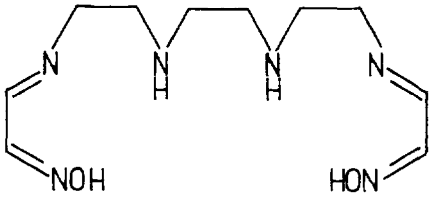
(**1**)



(**2**)

1.1.2 Complexes with nitrogen donor ligands

A review covering the reactions of L-Ascorbic acid with transition metal complexes has appeared as Polyhedron report number 41 [5]. A number of nickel complexes in higher oxidation states are reported for the oxidation of ascorbic acid including the nickel(IV) complex of the ligand (**3**), as well as a number of nickel(III) macrocyclic complexes.



(**3**)

Cyclic voltammetry and spectroscopic techniques have been used to study the electrochemical oxidation of $Ni(bipy)_3^{2+}$ in liquid sulfur dioxide. Four successive oxidations were observed, the first two of which were attributed to oxidation of the metal centre. The procedure for separation and purification of the very strong solid oxidant , $Ni(bipy)_3(AsF_6)_4$, has been described [6].

1.1.3 Complexes with oxygen donor ligands

$S_2O_8^{2-}$ has been used to oxidise Ni^{2+}(aq) in the presence of molybdate ion. The nickel(IV) product obtained was crystallized as $(NH_4)_6[NiMo_9O_{32}].6H_2O$. The crystal structure of this complex was determined revealing a severely distorted octahedral coordination environment for the Ni atom which is coordinated to six O atoms, with an average Ni-O bond length of 1.876(5)Å [7]. The structure of $(NH_4)_6[NiMo_9O_{32}].6H_2O$ was investigated simultaneously by an independent group who have also reported its crystal structure and electronic spectra. A similar Ni-O bond length of 1.872(2)Å was reported [8].

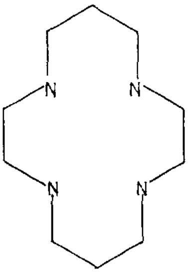
1.2 NICKEL(III)

By way of introduction to the Ni(III) oxidation state, a review with 22 references which describes multi-electron redox systems of a supramolecular nature, including Ni(III)/(II) complexes of cyclam and pyridine, has been published [9].

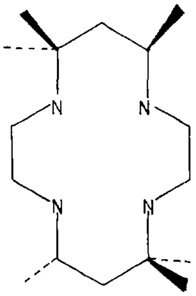
1.2.1 Complexes with nitrogen donor ligands

Nickel and bromine K-edge EXAFS data, combined with spectroscopic techniques have been used to study the Ni(II) complexes NiL_2X_2, and the Ni(III) complexes $[NiL_2X_2]X$ (L = the didentate ligands $NH_2CH_2CH_2NH_2$, $H_2NCHMeCH_2NH_2$, $H_2N(CH_2)_3NH_2$, $Me_2NCH_2CH_2NH_2$, $MeNHCH_2CH_2NHMe$, $Me_2NCH_2CH_2NHMe$; X = Cl, Br). The data indicated *cis*-N_4X_2 octahedral coordination for the Ni(II) complexes, and *trans*-N_4X_2 octahedral coordination for the Ni(III) complexes. Evidence has also been presented for the existence of a second Ni centre in some of the Ni(II) complexes, indicative of the existence of a halide-bridged dimer with the formula $[L_2Ni(\mu\text{-}X)_2NiL_2]X_2$ (X = halide) [10].

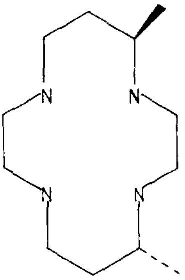
A number of Ni(III) macrocyclic complexes have been prepared by chemical oxidation of their corresponding Ni(II) complexes. The kinetics and mechanism of oxidation of $[Ni(II)L]^{2+}$ (L = (**4**), (**5**) and (**6**)) by $S_2O_8^{2-}$ have been determined in aqueous and binary solutions. It was found that reactions proceeded via an ion-pairing pre-equilibrium, followed by metal ion-assisted peroxy-bond fissure within the ion-pair solvent shell [11].



(**4**)



(**5**)



(**6**)

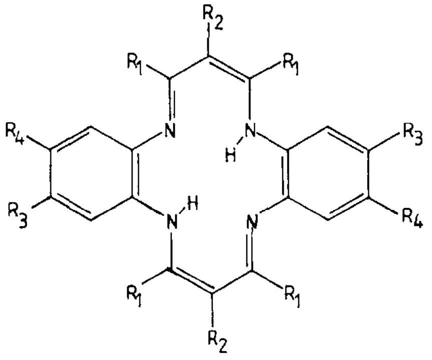
In addition, the mechanism of oxidation of (*meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) by HO_2 free radicals has been investigated in aqueous solution. Results indicated that the HO_2 radical reacts with the $[NiL]^{2+}$ complex in the ion pair $[NiL^{2+},X]$ to form the final Ni(III) products [12].

The macrocyclic complex bis(1,4,7-triazacyclononane)nickel(III) has been used to oxidise the thiosulphate anion in aqueous solution. The resultant products are the corresponding Ni(II) complex and $S_4O_6^{2-}$. A rate law was determined for the reaction, which was found to be first order in both Ni(III) complex and thiosulphate ion concentration [13].

In a related study, UV-Visible spectroscopy and stopped-flow techniques have been used to investigate the base promoted decomposition of bis(1,4,7-triazacyclononane)nickel(III) in aqueous solution. It has been suggested that the reaction is initiated by deprotonation of NiL_2^{3+} (L =

(1,4,7-triazacyclononane)), producing $NiLL'^{2+}$ (L′ = deprotonated L), which then decomposes further yielding $Ni(aq)^{2+}$ and $NiL(H_2O)_3^{2+}$. The reaction has been postulated to proceed via mono- and bimolecular pathways [14].

The electrochemistry of the planar Ni(II) complexes of a number of variously-substituted tetraaza[14]annulene ligands (**7**) has been reported. Cyclic voltammetry results showed the presence of both Ni(III)/(II) and Ni(II)/(I) couples for the planar ligands (R_1 = H; R_2 = CH_3; R_3 or R_4 = CH_3), with the Ni(III)/(II) couple being absent for the buckled non-planar ligand (R_1 = CH_3; R_2, R_3, R_4 = H) [15].

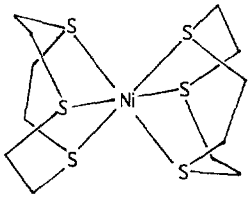


(R_1, R_2, R_3, R_4 = H; R_1 = CH_3, R_2, R_3, R_4 = H; R_2 = CH_3, R_1, R_3, R_4 = H)
(R_1 = H, R_2 = CH_3, R_3 or R_4 = CH_3; R_1 = H, R_2 = CH_3, R_3 = R_4 = CH_3)
(7)

1.2.2 Complexes with sulfur and selenium donor ligands

Dithiolate ligands continue to be used in the preparation of high oxidation state nickel complexes. Reactions leading to the formation of Ni complexes in the +3 oxidation state have been studied by ESR spectroscopy. Optimum conditions for the preparation of the Ni(III) complex of 1,2-dithiolate have been reported [16]. Similarly, the synthesis, structure and characterization of the thiolate dimer $[Ni_2\{P(o\text{-}C_6H_4S)_3\}_2]^{2-}$, as its tetrabutylammonium salt, has been reported. The complex was oxidized to give the mixed valence species [Ni(III)Ni(II)], as well as the [Ni(III)Ni(III)] species [17]. In addition, the mixed valence polynuclear thiolate complexes, $[Ni_4(SC_3H_7)_8Br]$ and $[Ni_4(SC_3H_7)_8I]$, have been prepared and characterized by single-crystal X-ray methods [18].

The electrochemistry of $[NiL_2]^{2+}$ (L = 1,4,7-trithiacyclononane) has been re-examined in acetonitrile solution. Oxidation of $[NiL_2]^{2+}$ in perchloric acid yielded the corresponding Ni(III) cation, $[NiL_2]^{3+}$, which was isolated as $[NiL_2][H_5O_2][ClO_4]_6$. The single-crystal X-ray structure of this complex was determined confirming octahedral homoleptic thioether coordination (**8**). Ni-S bond lengths (2.3129(25)Å) for the Ni(III) complex cation were found to be considerably shorter than those for the corresponding Ni(II) complex cation, thereby confirming its formulation as a mononuclear Ni(III)-thioether complex cation [19].

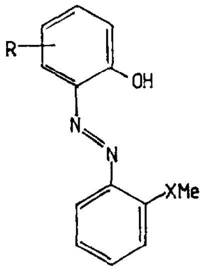


(8)

The crystal structures of the two phases (α and β) of $[Bu_4N]_2[Ni(dsit)_2]_2$ (dsit = 1,3-dithiole-2-thione-4,5-selenolate) have been reported. Both crystal structures were found to differ only slightly, with the Ni atom square pyramidally coordinated by five selenium donor atoms. Ni-Se distances were found to range from 2.316(1) to 2.480(1)Å for the α-complex, while distances for the β-complex ranged from 2.317(2) to 2.472(2)Å [20].

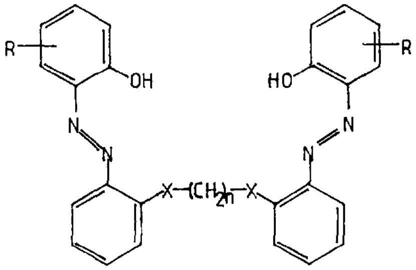
1.2.3 Complexes with nitrogen-oxygen, nitrogen-sulfur and nitrogen-oxygen-sulfur donor ligands

The tridentate ligands (**9**) and the hexadentate ligands (**10**) have been complexed with Ni(II), and the resultant distorted octahedral complexes, $[NiL_2]$ (HL =(**9**)) and [NiL] (H_2L = (**10**)), oxidised coulometrically in dichloromethane solution. It was found that the thioether complexes were easily oxidised to the Ni(III) species, with the tridentate nickel(III) complexes being less thermally stable than the hexadentate complexes. The corresponding ether complexes were more difficult to oxidise than their thioether analogues, and the nickel(III) species were not tractable. None of the Ni(III) species were isolated [21].



(R = 5-Me, 5-Cl, 5,6-C_4H_4; X = S or O)

(9)



(R = 5-Me, 5-Cl; X = S or O; n = 2 or 3)

(10)

Four bisdipeptide nickel(III) complexes, $[Ni(H_{-1}GG)_2]^-$, $[Ni(H_{-1}GA)_2]^-$, and $[Ni(H_{-1}AA)_2]^-$ (GH = glycine, AH = (*S*)-alanine), have been used to oxidise the cobalt complex $[Co(edta)]^{2-}$ in 0.1M perchlorate media at 25°C. Kinetic studies indicated that the reactions are first order in each reagent and have a complex dependence on pH [22].

The mixed donor macrocycle 8-aza-1,5-dithiacyclodecane (L) and the related macrobicycle 1,2-bis(8-aza-1,5-dithiacyclodecanyl)ethane (L′) have been prepared and complexed with nickel(II) perchlorate. The resultant complexes, $[NiL_2](ClO_4)_2.2CH_3CN$ and $[NiL'](ClO_4)_2.2CH_3CN$ respectively, were isolated and their single-crystal X-ray structures determined. Both complex cations could be oxidised, either by chemical or electrochemical methods, to their corresponding Ni(III) complex cation species, as verified by ESR measurements [23].

1.3 NICKEL(II)

1.3.1 Complexes with nitrogen donor ligands

By way of introduction to this section, the equatorial-axial interactions of the nitrogen donor ligands in solid nickel(II) isothiocyanato complexes of the type $[NiL_4(NCS)_2]$ (L = monodentate N-donor ligand), $[NiL_4(NCS)_2].nG$ (G = guest molecule in the inclusion compound), $[NiL_2(NCS)_2]$ (L = didentate N-donor ligand), and $[NiL(NCS)_2]$ (L = tetraazamacrocyclic ligand), have been studied. It was shown that the mean interatomic distances in the axial directions are mutually dependent with those in the equatorial plane [24].

Continuing with thiocyanato complexes, the electrosynthesis of thiocynato and mixed-ligand thiocyanto complexes of transition metals by the sacrificial dissolution of metal anodes has been reported. The complexes $(Me4N)_2[Ni(NCS)_6]$ and $[Ni(bipy)_2(NCS)_2]$ have been prepared in this fashion, with yields of over 60% being obtained [25].

Pyridine and substituted-pyridine complexes of nickel(II) continue to attract interest. These include *trans*-$[Ni(py)_4Cl_2]$, the crystal structure of which has been determined [26], the Werner Clathrate complex $[Ni(4\text{-vinylpyridine})_4(NCS)_2]$ [27], and the complexes $[Ni(py)_2X_2]$ and $[Ni(py)_4X_2]$, where X = $Ph_2P(S)NCN$ [28]. In addition, in an ongoing study of steric hindrance in 2,6-disubstituted pyridines, the complexes *trans*-$[Ni(L)_2Cl_2]$ (L = 2,6-dimethylpyridine or 2,4,6-trimethylpyridine) have been prepared and their structures determined by single-crystal X-ray methods. Square planar coordination geometry was found in both cases with Ni-Cl = 2.1940(8)Å and Ni-N = 1.935(1)Å when L = 2,6-dimethylpyridine, and Ni-Cl = 2.1953(8)Å and Ni-N = 1.928(2)Å when L = 2,4,6-trimethylpyridine. In both complexes the plane of the substituted pyridine ring was found to be almost normal to the $NiCl_2N_2$ plane [29].

The synthesis and X-ray crystallographic characterization of the methazolamide complex, $[NiL_2(py)_2(OH_2)_2]$ (L = [*N*(4-methyl-2-sulphamoyl-Δ^2-1,3,4-thiodiazolin-5-ylidene]acetamide), has been described. The coordination geometry about Ni(II) was found to be almost regular octahedral with two pyridine nitrogen atoms and two sulphonamido nitrogen atoms occupying the equatorial sites, with two water molecules in *trans*-apical positions completing the coordination sphere. Relevant data are Ni-N(py) = 2.136(3)Å, Ni-N(sulphonamido) = 2.090(3)Å, and Ni-O = 2.073(3)Å [30].

3,5-Dimethylpiperidine (L) has been complexed with nickel(II)isothiocyanate. The crystal structure of the resultant complex, $[NiL_3(NCS)_2]$, has been determined, revealing a tetragonal pyramidal geometry about Ni(II). The basal plane of the tetragonal pyramid is occupied by two nitrogen donor atoms of the *trans* NCS ligands (Ni-N = 1.97(2) and 1.95(2)Å) and two nitrogen donor atoms of two 3,5-dimethylpiperidine ligands (Ni-N = 2.05(1) and 2.10(1)Å). The apex of the pyramid is occupied by the remaining 3,5-dimethylpiperidine ligand (Ni-N = 2.04(1)Å) [31].

A review of model systems containing pyrazole chelates and related ligand groups has been published. A wide range of pyrazole- and imidazole-containing ligands and their nickel(II) complexes are included in the review [32].

The complex $[Ni(N\text{-MeIm})_6]S_8$ (*N*-MeIm = *N*-methylimidazole) has been prepared in over 50% yield via a novel procedure in which $Ni(CO)_4$ and S_8 are contacted in *N*-methylimidazole. Reaction of this complex with $Fe(CO)_5$ in *N*-methylimidazole produced the mixed metal complex $[Ni(N\text{-MeIm})_6]Fe_2S_{12}$ [33].

Several tetracoordinate nickel aryl and aroyl complexes containing bulky bis- or tris-(3-*tert*-butylpyrazolyl)borate ligands have been prepared. In each of the complexes it was found that the poly(pyrazolyl)borate ligands adopted monohapto coordination, both in solution and the solid state [34].

Turning to didentate ligands, variable-temperature and variable-pressure multinuclear magnetic resonance has been employed to study solvent exchange between ethylenediamine molecules in the bulk solvent and ethylenediamine (en) molecules coordinated to the Ni(II) ion. These studies have been carried out in neat ethylenediamine and in mixtures involving dmf as diluent. The exchange rate constant at 298K and the activation parameters were determined. Results indicated that the exchange reaction is independent of the concentration of en in the solvent and that reaction proceeds via a dissociative mechanism [35].

Ethylenediamine has been complexed with Ni(II) in the presence of other ligands. The formation constants of the mixed-ligand complexes of Ni(II) with en and thiosalicylic acid have been determined in aqueous ethanol using potentiometric methods [36], while the electrochemical behaviour of the complexes $[Ni(diamine)(\beta\text{-diketonate})](Ph_4B)$ (diamine = tetramethylethylendiamine, trimethylethylenediamine, tetraethylethylendiamine, triethylethylenediamine; β-diketonate = acac, trifluoroacetylacetonate, 1-phenylpropane-1,3-dionato, 1,3-diphenylpropane-1,3-dionato, 1,3-ditertiarybutyl-1,3-dionato) has been investigated in a variety of nonaqueous solvents at different temperatures [37].

A full infrared assignment (4000 to $50cm^{-1}$) has been published for the metal complexes $[M(bpy)_3](ClO_4)_2$ and $[M(phen)_3](ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn) and their fully deuterated analogues. Ni-N stretching modes have been assigned on the basis of isotopic labelling and metal ion substitution [38].

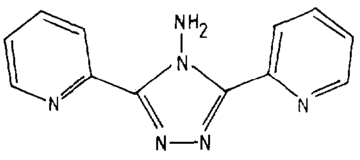
In a rather unusual application, 2,2′-bipyridine has been complexed with Ni(II) located in Ni(II)-exchanged montmorillonite clay. The intercalated resultant Ni-bipy complex was found to be very similar to the more conventional complex, on the basis of elemental analysis, infrared spectroscopy, magnetic studies and X-ray diffraction [39].

The diastereoisomeric complexes δ,λ-$[\mathrm{Ni(phen)_2}(S\text{-ala})]\mathrm{X}$ (*S*-ala = *S*-alaninate, X = Br, Cl, OAc, SO_4, variously-substituted benzoates, *m*- and *o*-phthalate, *R,S*-mandelate, *S*-alaninate) have been prepared as methanolic solutions and characterized by spectral and conductance methods. A predominance of the λ-isomer was observed in solution [40].

1-(2-Pyridinyl)ethanone oxime has been complexed with Ni(II) at varying pH. Two complexes were isolated, one at pH 3, and the other at pH 6, and characterised by single-crystal X-ray crystallography. The first complex, dibromobis(1-(2-pyridinyl)ethanone oxime)nickel(II), was found to have a *cis*-octahedral structure with the Br ions *cis* to each other (Ni-Br = 2.57(2)Å), two pyridine nitrogen atoms *cis* to each other (Ni-N = 2.091(9)Å) but *trans* to the Br ions, with the two oxime nitrogen atoms, which complete the coordination sphere (Ni-N = 2.043(7)Å), *trans* to each other. The second complex, diaquo(1-(2-pyridinyl)ethanone oxime)(1-(2-pyridinyl)ethanone oximato)nickel(II) nitrate, was also found to exhibit octahedral coordination about Ni(II). In this complex coordination was completed by two planar didentate amine oxime ligands with *cis* oxime groups (Ni-N(pyridine) = 2.109(5)Å; Ni-N(oxime) = 2.037(6)Å) and two *trans* water molecules above and below this plane (Ni-O = 2.069(5)Å) [41].

The oxime ligands RC(CN):NOH (R = 2-quinolinyl, 2-thiazolinyl) have been prepared and characterized by spectroscopic and X-ray methods. The ligands were complexed with a variety of Ni(II) salts and stability constants were also determined [42].

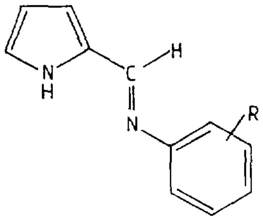
3,5-Bis(pyridin-2-yl)-4-amino-1,2,4-triazole (abpt =(**11**)) has the potential to function in a multidentate fashion. The complex $\mathrm{Ni(abpt)_2(TCNQ)_2}$ (TCNQ = 7,7′,8,8′-tetracyanoquinodimethane) has been prepared and characterised. On the basis of its isostructural Cu analogue, *trans*-octahedral coordination geometry was assigned to this complex, with (**11**) functioning in a didentate fashion, coordinating via the two nitrogen atoms as shown, while TCNQ coordinates in a rather novel monodentate fashion to Ni(II) [43].



(**11**)

3,5-Dimethyl-1-(*o*-aminophenyl)pyrazole (L) has been complexed with different nickel(II) salts. The complexes $[NiL_2X_2]$ (X = Br, I, NO_2, NCS) have been assigned tetragonally distorted octahedral structures on the basis of magnetic and spectral data, as well as the crystal structure of the thiocyanate complex. Vibrational spectral data have indicated that L functions in a didentate fashion (Ni-N(L) = 2.140(4), 2.125(5), 2.110(50) and 2.179(3)Å, Ni-NCS = 2.054(4) and 2.041(4)Å). Similarly, the complexes $[NiL_2(H_2O)_2]X_2$ (X = Cl, ClO_4, BF_4) have been assigned an octahedral coordination sphere. This has been verified by the single-crystal X-ray structure of $[NiL_2(H_2O)_2]Cl_2$ (Ni-N(L) = 2.101(2), 2.167(2), 2.094(2) and 2.126(1)Å, Ni-O = 2.096(1) and 2.124(2)Å). In both crystal structures the configuration of the NCS and H_2O ligands was found to be *cis* [44].

A series of 17*N*-arylpyrrole-2-aldimine ligands (**12**) has been synthesized by condensation of pyrrole-2-carboxaldehyde and variously-substituted anilines. Complexation with Ni(II) yielded complexes of the type $[NiL_2]$ (L = (**12**)). These complexes exhibit square-planar or tetrahedral geometry or eventually present an equilibrium mixture of both in the solid state, depending on the substituent R. Attempts at chemical oxidation indicated the existence of nickel(III) in solution [45].



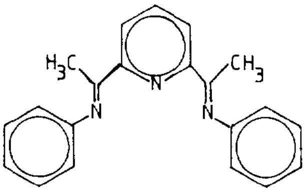
(R = H, CH_3, OCH_3, OC_2H_5, Cl, Br, NO_2 in *o*-, *m*- or *p*- positions)

(12)

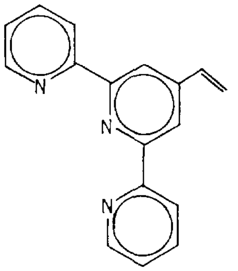
A number of tris- and bis-pyrazol-1-yl-borate ligands have been complexed with Ni(II). These include dihydrobis(1-pyrazolyl)borate [46], 1,5-cyclooctanediylbis(pyrazol-1-yl)borate [47], hydrotris(3-neopentylpyrazol-1-yl)borate [48], hydrotris(3-isopropyl-4-bromopyrazol-1-yl)borate and hydrotris(3-*tert*-butyl-5-methylpyrazol-1-yl)borate [49]. In the nickel(II) complexes, the bis(1-pyrazol-1-yl)borate ligands were found to function as didentate nitrogen donors, while the tris(1-pyrazol-1-yl)borate ligands were found to function as tridentate nitrogen donors.

Progressing to terdentate ligands, a thermodynamic evaluation of the chelate effect has been undertaken for Ni(II) complexes of 2,6-di(aminomethyl)pyridine and 2,6-di(aminoethyl)pyridine. Interestingly, mono and bis complexes were obtained with 2,6-di(aminomethyl)pyridine, while only the mono complex could be obtained with 2,6-di(aminoethyl)pyridine [50].

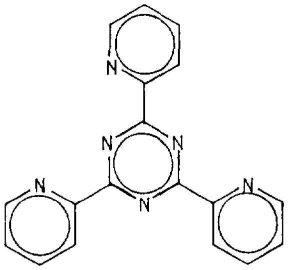
A number of terdentate nitrogen donor ligands (**13**), (**14**), (**15**), (**16**), (**17**) and (**18**) have been complexed with Ni(II) with a view to using the resultant complexes as models for the catalytic reduction of carbon dioxide. Complexes of the type $NiL_2(PF_6)_2$ were formed with ligands (**13**) to (**17**), while the complex $NiL(PF_6)_2$ was formed with (**18**) [51].



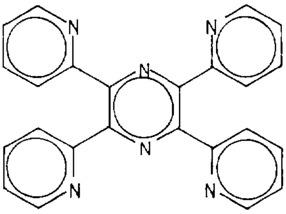
(**13**)



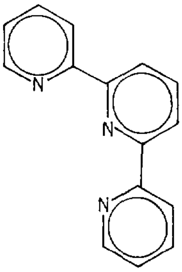
(**14**)



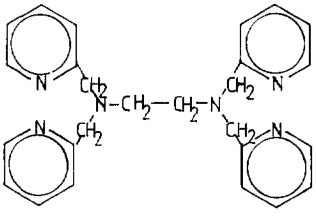
(**15**)



(**16**)



(**17**)



(**18**)

A series of variously-substituted *N,N'*-bis(8-quinolyl)malonamide ligands (H_2L) has been complexed with Ni(II) in an attempt to examine the effect of the substituents on metal ion extraction. The ligands were all found to function in a dibasic tetradentate fashion with coordination occurring via the four nitrogen donor atoms, yielding complexes of the type NiL [52].

The reaction of (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene)nickel(II) with formaldehyde has been studied spectrophotometrically. Reaction was found to occur at the highly reactive C12 position of the tetradentate ligand yielding a dimeric species as an intermediate which reacted further to give two molecules of the complex with primary alcohol groups substituted at the C12 position [53]. Similarly, the same workers have effected electrophyllic substitution of an acetyl group onto the C12 position of (2,2,3,9,10,10-hexamethyl-5,7-dioxa-6-hydra-1,4,8,11-tetraazacyclotetradeca-3,8,11,13-tetraene)nickel(II). The position of substitution was verified via a single-crystal X-ray structure determination. Relevant data are Ni-N = 1.861(4), 1.861(4), 1.840(4) and 1.836(4)Å [54].

1.3.2 Complexes with phosphorus donor ligands

$[Ni(PEt_3)_4]$ has been reacted with Buckminsterfullerene to yield the complex $(PEt_3)_2Ni(\eta_2\text{-}C_{60})$, which was characterised by Raman spectroscopy [55]. This reaction has been extended to multiple metal addition, and the complex $[(PEt_3)_2Ni]_6(\eta_2\text{-}C_{60})$ has been reported [56].

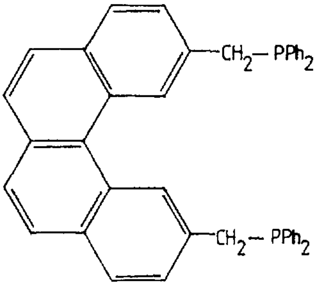
Complexes of the type *trans*-$[Ni(CH_2R)X(PMe_3)_2]$ (R = CO_2Et, X = Cl; R = CN, X = Cl; R = OMe, X = Br) have been prepared by oxidative addition of $ClCH_2CO_2Et$, $ClCH_2CN$ and $BrCH_2OMe$ to $[Ni(cod)_2]$ respectively. The interaction of these complexes with carbon monoxide has been studied [57]. Similarly, the stepwise reaction of the dibromides *m*- and *p*-$BrCH_2C_6H_4Br$ with $[Ni(cod)(PMe_3)_2]$ afforded the mononuclear complexes *trans*-$[Ni(CH_2C_6H_4Br)Br(PMe_3)_2]$ (*meta*) or (*para*), and the dinuclear species *trans, trans*-$[(Me_3P)_2BrNi(\mu\text{-}\sigma{:}\sigma\text{-}CH_2C_6H_4)NiBr(PMe_3)_2]$ (*meta*) or (*para*). In addition, a crystal structure determination of *trans, trans*-$[(Me_3P)_2BrNi(\mu\text{-}\sigma{:}\sigma\text{-}CH_2C_6H_4)NiBr(PMe_3)_2]$ (*para*) was reported, revealing distorted square planar geometry for both Ni atoms [58].

The photochemistry and stereochemistry of *trans*-$(Et_3P)_2Ni(N_3)_2$ have been investigated in the solid state. In addition, its crystal and molecular structure have been determined by single-crystal X-ray diffraction. The complex is essentially square planar, with Ni-P bond lengths of 2.226(2) and 2.225(2)Å, and N-N bond lengths of 1.872(5) and 1.867(6)Å respectively [59].

Diphenylphosphinoacetone (HL = Ph_2PCH_2COMe) has been reacted with nickel(II)chloride. Two complexes, $[NiCl_2(HL)_2]$ and $[NiL_2]$, were isolated and their crystal and molecular structures determined. The first complex has a *trans* square planar configuration, with HL functioning as a P-donor ligand (Ni-P = 2.224(1)Å, Ni-Cl = 2.165(1)Å). In the second complex, which has *cis* square planar geometry, L functions as a monobasic P,O-donor ligand (Ni-P = 2.185(1)Å, Ni-O = 1.893(3)Å) [60].

The crystal and molecular structure of dibromobis(ethyldiphenylphosphine)nickel(II) has been reported. The asymmetric unit was found to comprise of two mononuclear complexes, one with a twofold and the other with a pseudo-twofold axis passing through Ni. Coordination about Ni is essentially tetrahedral with Ni-P bond lengths ranging from 2.306(3) to 2.316(3)Å, and Ni-Br lengths ranging from 2.339(2) to 2.362(2)Å [61].

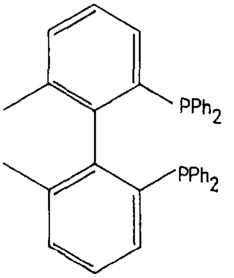
2,11-Bis(diethylphosphinomethyl)benzo[*c*]phenanthrene (L) has been reacted with a number of group VIII metal ions. The crystal and molecular structure of the nickel(II) complex, [$NiLCl_2$], reveals a rather unusual *trans* square planar geometry for the Ni ion, with L functioning as a didentate P-donor ligand which spans a diagonal of the complex (**19**). Relevant data are Ni-P = 2.214(2)Å, Ni-Cl = 2.167(2)Å [62].



(**19**)

$NiCl_2$ and $NiBr_2$ complexes of the diphosphine ligand 3,4-dimethyl-3′,4′-bis(diphenylphosphino)-tetrathiafulvalene (L) have been prepared and characterized. The crystal structure of the nickel(II)bromide complex, [$NiLBr_2$], was determined, revealing essentially square planar geometry about Ni with some tetrahedral distortion. L functions as a didentate ligand with Ni-P = 2.145(4) and 2.139(4)Å, and Ni-Br = 2.331(2) and 2.328(2)Å [63].

(6,6′-Dimethyl-1,1′-biphenyl-2,2′-diyl)bis(diphenylphosphine) (**20**) has been reacted with bis(2-methylallyl)nickelbromide. The resultant complex, [NiL(2-methylallyl)]Br (L = (**20**)) was used as a precursor for the analogous perchlorate complex, [NiL(2-methylallyl)](ClO_4), the crystal structure of which has been determined. Distorted square planar geometry for Ni was reported, with Ni-P = 2.201(8) and 2.184(7)Å [64].



(**20**)

Finally, a review covering the synthesis and reactivity of small mixed clusters formed by transition metals and main group elements has been published. The review, amongst other things, examines the Ni complexes of triphos and structurally related ligands such as tris(2-diphenylphosphinoethyl)amine and their arsenic analogues [65].

1.3.3 Complexes with arsenic donor ligands

Cyclic voltammetry has been used to investigate the electronic properties of the bis-triarsine complex cations, $[Ni(mtas)_2]^{2+}$ (mtas = bis(2-methylarsinophenyl)methylarsine) and $[Ni(ptas)_2]^{2+}$ (ptas = bis(2-methylarsinophenyl)phenylarsine), in acetonitrile. These studies reveal an extended metal-centred electron-transfer series with reversible interconversion of all nickel oxidation states from 0 to IV [66].

1.3.4 Complexes with oxygen donor ligands

The coordination of water with Ni(II) continues to attract interest. The structure of diammonium hexaaquanickel(II) bis(monofluorophosphate) has been reported, and consists of $Ni(H_2O)_6{}^{2+}$ and $NH_4{}^+$ cations and PO_3F^{2-} anions held together by hydrogen bonds involving all H atoms except the one belonging to the ammonium cation. Ni(II) was found to be octahedrally coordinated by the six water ligands with Ni-O bond lengths ranging from 2.034(1) to 2.079(1)$\mathring{A}$ [67]. In addition, full geometric optimizations have been carried out on high-spin hexaaqua complexes of first row transition metal ions, including Ni^{2+}. In this study the optimized octahedral molecular arrangement of the water ligands around Ni^{2+} was found to be regular [68].

The rather unusual complex, $[(H_2O)_5Ni(NC_5H_5)]_2(Na)$[calix[4]arene sulfonate].3.5H_2O, has been prepared by reaction of $Ni(NC_5H_5)_3(NO_3)_2$ with Na_5[calix[4]arene sulfonate] in deionized water. The crystal and molecular structure revealed two different $[(H_2O)_5Ni(NC_5H_5)]^{2+}$ cations. The Ni atom in both cations was octahedrally coordinated with four water molecules in the equatorial plane and a fifth water molecule and pyridine ligand occupying the axial positions. However, one cation had the pyridine ligand complexed in the hydrophobic cavity of the calixarene, while in the other it was located between two calixarene ligands [69].

Single-crystal High-Order X-ray diffraction has been used to determine the structure of tetraaquabis(hydrogen maleato)nickel(II). The complex has a *trans*-octahedral geometry with four water ligands occupying the equatorial positions (Ni-O = 2.089(1) and 2.025(1)$\mathring{A}$), and the mono-coordinated hydrogen maleato ligands occupying the *trans* axial sites (Ni-O = 2.078(1)$\mathring{A}$). The hydrogen bonding scheme, which was accurately determined, reduces the symmetry of metal coordination from O_h to C_i [70].

3-Hydroxy-4-methoxy-benzoic acid (hmba) and 3-methoxy-4-hydroxybenzoic acid (mhba) have been reacted with Ni(II). Only 1:1 complexes of the formulae Ni(hmba).3H_2O and Ni(mhba).4H_2O were isolated. Electronic spectral studies indicated octahedral geometry for both complexes, while infrared spectra showed bands attributed to metal-bound water molecules and carboxylate O-atoms [71].

The synthesis of a rather novel complex, which contains ethanol as a ligand, has been reported. $[Ni(EtOH)_6](BF_4)_2$ has been prepared by the reaction of $[Ni(H_2O)_6](BF_4)_2$ with $HC(OEt)_3$. Further reaction of $[Ni(EtOH)_6](BF_4)_2$ with Ph_2SO afforded the complex $[Ni(Ph_2SO)_6](BF_4)_2$ [72].

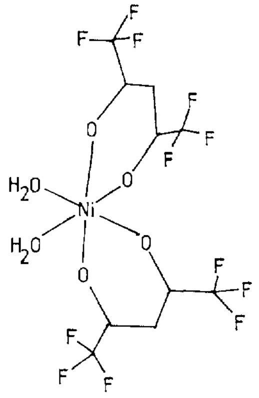
A model of selective energy transfer has been applied to explain the isokinetic temperature found for some substitution and exchange reactions of the hexasolvated complex of Ni(II) in dmso solutions e.g.

$$Ni(dmso)_6^{2+} + L \Leftrightarrow Ni(dmso)_5L^{2+} + dmso$$

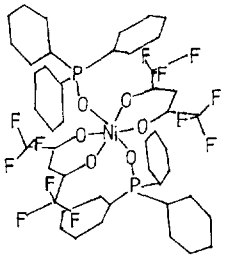
Results from this study suggest that the reaction coordinate can be described as an expansion of one face of the octahedron, where the reactant enters, and the corresponding contraction of the opposite face [73].

N,N-dimethylformamide has been complexed with a variety of nickel(II) salts. Complexes that have been isolated and characterized using spectroscopic, X-ray, themogravimetric and conductivity methods, include $NiX_2.4dmf.2H_2O$ ($X = Cl, NO_3$) and $[Ni(dmf)_6]_3[Cr(SCN)_6]$ [74].

β-Diketone and related ligands, their Ni(II) complexes, and uses, continue to attract considerable interest. The structure of *cis*-diaquabis(hexafluoroacetylacetonato)nickel(II) has been reported. It was found that the Ni atom possesses octahedral geometry with the O atoms of the chelate ligands occupying both axial and equatorial positions (Ni-O = 2.029(3) and 2.027(2)Å), while the two water molecules complete the coordination sphere in a *cis* configuration (Ni-O = 2.054(3)Å) (**21**) [75]. The crystal and molecular structure of the related complex, bis(hexafluoroacetylacetonato)bis(tripehylphosphine oxide)nickel(II), has been determined by the same group. Once again the Ni atom was found to possess octahedral geometry, but in this case the two chelate ligands occupy the equatorial coordination sites (Ni-O = 2.041(3) and 2.048(2)Å), while the tripehylphosphine oxide ligands occupy the *trans* axial sites (Ni-O = 2.058(3)Å) (**22**) [76].



(21)



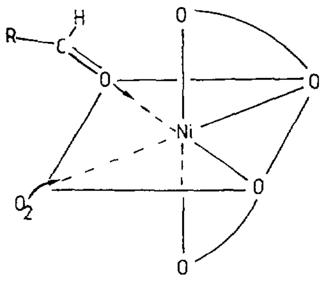
(22)

Nickel(II) hexafluoroacetylacetonate derivatives of imino nitroxides have been synthesized and their crystal and molecular structures determined. In the complex $Ni(hfacac)_2(H_2O)_2(IMPh)_2$ (hfacac = hexafluoroacetylacetonate; IMPh = 2-phenyl-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl), it was found that IMPh is not coordinated to Ni, the coordination sphere being made up of four O-atoms belonging to the didentate hfacac ligands and two O-atoms from the water ligands, in a *trans*-octahedral arrangement. The structure of the second complex, $Ni(hfacac)_2(IM2\text{-}py)_2$ (IM2-py = 2-(2-pyridyl)-4,4,5,5-tetramethyl-4,5-dihydro-1*H*-imidazol-1-oxyl), reveals a *cis*-octahedral configuration about Ni, in which the hfacac ligands function as didendate O,O-donor ligands, while IM2-py functions as a didentate N,N-donor ligand. Finally, for the third complex, $Ni(hfacac)_2(IMMe)_2$ (IMMe = 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazol-1-oxyl), a *trans*-octahedral configuration about Ni was observed, with two hfacac ligands coordinated in a didentate fashion in the equatorial plane, and two IMMe ligands functioning in a monodendate N-donor fashion, occupying the *trans* axial coordination sites [77].

In a study of the solubilities and solvation of β-diketonate complexes, the solubility of $Ni(acac)_2$ was investigated in binary aqueous solvent mixtures with co-solvents including methanol, isopropanol, *t*-butyl alcohol, dioxan and dmso. The solubilities of the bis-trifluoroacetylacetonate, bis-hexafluoroacetylacetonate, and bis-dibenzoylmethane complexes were also determined in methanol/water [78].

The β-diketonate-containing mixed-ligand nickel(II) complexes, [Ni(L)(diam)]X (L = β-diketonate; diam = *N,N'*-polyalkylated ethylenediamine; X = ClO_4, Ph_4B), have been utilised in the preparation of potential hydrogen phosphate ion-sensing electrodes. $[Ni(L)(diam)](ClO_4)$ was found to produce an electrochemical response to hydrogen phosphate, while the tetraphenylborate analogue did not [79].

$Ni(acac)_2.2H_2O$ and $Ni(dbm)_2.2H_2O$ (dbm = dibenzoylmethane) have been mixed with a variety of aldehydes in 1,2-dichloroethane. The resultant mixture was shown to have extremely good activity for the formation of an active oxygen species. It has been suggested that dioxygen is activated *via* coordination to the Ni atom, with bound aldehyde promoting this coordination, as shown in (**23**) [80].

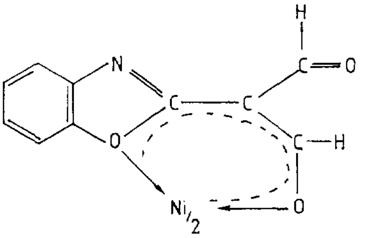


(**23**)

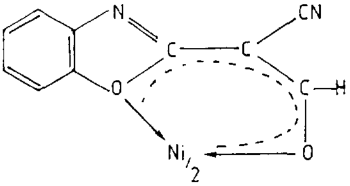
Linkage isomerization in β-diketonates, resulting from sterically induced intramolecular rearrangements in metal-ligand bonding, has been observed during phenyl isocyanation of β-diketonato and β-ketoimino complexes of Ni(II). It has been suggested that steric repulsion between γ-CONXPh (X = H or halide) and the α-methyl or α-phenyl substituents of the β-diketonate chelate rings has lead to a rearrangement in which the metal-ligand bonding has changed from Ni-O(diketonate) to Ni-O(amide) [81].

The formation constants of binary and ternary complexes of the type NiL, NiL_2 and NiAL (L = 1,2,3-triketo hydrindane hydrate; 2,2-dihydroxy-1,3-indandione; A = alanine, valine, en, bpy, oxalic acid, catechol) have been determined potentiometrically in aqueous media. The stabilities of the various ternary complexes have been compared with the corresponding binary complexes [82].

2-(2-Benzoxazolyl)malonaldehyde (2-BOMA) and 2-(2-benzoxazolyl)cyanoacetaldehyde (2-BOCA) have been complexed with Ni(II). The resultant complexes, NiL_2 (HL = 2-BOMA, 2-BOCA), were characterised using a number of spectroscopic techniques. On the basis of these data, both ligands have been assigned as didentate, with coordination to the metal occurring via the oxygen donor atoms as shown (**24**), (**25**) [83].



(**24**)

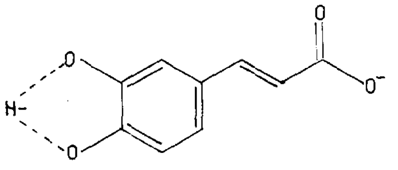


(**25**)

The stability constants of the Ni^{2+} complexes of 3-(4′-chlorophenyl)-1-(2′-hydroxynaphthyl)-2-propen-1-one) have been determined in 75% (v/v) dioxane/water. Comparison of the Ni^{2+} complexes with a variety of other M^{2+} complexes yielded results in fair agreement with the Irving-Williams order [84].

The rate constants for the formation and dissociation of the nickel(II) complexes with 3-nitro- and 4-nitrophthalate and phenylmalonate, as well as the activation parameters, have been measured in aqueous solution using the pressure-jump relaxation method. Results obtained suggest that the rates of formation of the Ni(II) complexes are controlled by both solvent exchange and chelate ring closure [85].

Aqueous solution equilibria have been investigated for the metal(II) complexes of caffeic acid (*trans*-3-(3,4-dihydroxyphenyl)-propenoate) by means of glass electrode potentiometry. By defining the ligand species as the dianion (**26**), in conjunction with the titration data, it was concluded that the metal coordinates to the catecholate site of the caffeate ion [86].



(**26**)

The dissociation of C.I. Mordant Orange 35 (MO 35) in H_2O and its complexation with a variety of metal(II) ions, have been investigated. Spontaneous complexation was found to occur, and structures for the complexes have been suggested on the basis of IR spectral data. Indications were that the ligand coordinates in a didentate O,O-donor fashion [87].

Finally, a review on the magnetic properties of complexes containing paramagnetic ions bound to polyoxolene radicals has been published. The complexes have been divided into simple 1:1 complexes and metal-polyoxolene complexes of varying complexity. Mononuclear nickel complexes that have been included in the article are $Ni(CTH)(DTBSQ)PF_6$ (CTH = dl-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; DTBSQ = 3,5-di-tert-butylbenzosemiquinonate), $Ni(CTH)(TCSQ)ClO_4$ (TCSQ = 3,4,5,6-tetrachlorosemiquninonate), $Ni(n_3)(DTBSQ)ClO_4$ (n_3 = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene), $Ni(n_3)(TCCat)(TCQ)ClO_4$ (TCCat = 3,4,5,6-tetrachlorocatecholate, and $Ni(n_3)(TCSQ)(TCQ)$ (TCQ = 3,4,5,6--tetrachloroquinone). In addition, the dinuclear complexes $Ni(phenSQ)(py)_2$ (phenSQ = 9,10-phenanthrenesemiquinonate) and $Ni_2(CTH)(PTHF)(ClO_4)_2$ (PTHF = 9-phenyl-2,3,7-trihydroxy-6-fluorone) have also been discussed [88].

1.3.5 Complexes with sulfur donor ligands

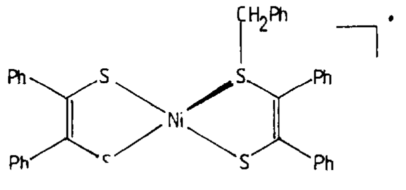
Thiolate and dithiolate complexation with Ni(II) continues to dominate this area of research, as manifested by a review of the chemistry of the ubiquitous ligand 1,3-dithiole-2-thione-4,5-dithiolate (dmit) [89]. Material presented in this review covers the synthesis of dmit, its conversion into a number of organic derivatives, its coordination with Ni(II) including bis- and tris-chelates, as well as mixed-ligand chelates, its conversion into 1,2-dithiole-3-thione-4,5-dithiolate (dmt) and its corresponding Ni(II) chelates. In addition, preparation of the analogous ligand 1,2-dithiole-2-one-4,5-dithiolate (dmid) and its complexation with Ni(II) has also been included.

The crystal and molecular structure of the semiconductive salt, $(ImH)[Ni(dmit)_2]_2$, has been determined. $Ni(dmit)_2$ molecules were found to be dimerized and stacked in columns with two types of columnar interaction through an imidazolium counter cation. The coordination sphere about the Ni centres is square planar with Ni-S bond lengths ranging from 2.154(2) to 2.170(2)Å [90].

The mixed valence radical salts $[smdt][Ni(C_3S_5)_2]_2$, $[dmp][Ni(C_3S_5)_2]_2$ and $[dmm][Ni(C_3S_5)_2]_2$ ($C_3S_5^{2-}$ = dmt; smdt = *S*-methyl-1,3-dithianium; dmp = *N,N*-dimethylpyrrolidinium; dmm = *N,N*-dimethylmorpholinium) have been prepared electrochemically from the corresponding [cation]$[Ni(C_3S_5)_2]$ complexes in acetonitrile. Single-crystal structure determinations of the three complexes revealed that all three crystallise in essentially the same packing mode, with anionic diads stacked face-to-face along one direction. Coordination about Ni was found to be essentially square planar in all three cases, with Ni-S bond lengths varying from 2.153(4) to 2.179(5)Å ($[smdt][Ni(C_3S_5)_2]_2$), 2.160(1) to 2.170(1)Å ($[dmp][Ni(C_3S_5)_2]_2$) and 2.145(2) to 2.161(2)Å ($[dmm][Ni(C_3S_5)_2]_2$) [91].

Dissociation of the nickel(II) arenethiolate complex anions, $[Ni(RS)_4]^{2-}$ (RSH = p-$CH_3C_6H_4SH$, m-$CH_3C_6H_4SH$, C_6H_5SH, p-ClC_6H_4SH, p-$NO_2C_6H_4SH$), has been investigated in dmso using spectrophotometric methods. Dissociation was found to proceed with generation of the diamagnetic species $[Ni(RS)_3(dmso)]^-$ and $[Ni(RS)_2(dmso)_2]$ [92].

The photodissociation of bis(*S*-benzyl-1,2-diphenyl-1,2-ethylenedithiolato)nickel has been investigated using time-resolved EPR and UV-Vis absorption spectroscopy. Results obtained in this study indicate that the radical species (**27**) is formed as an intermediate in the dissociation reaction before finally decaying to give the resultant complex bis(1,2-diphenyl-1,2-ethylenedithiolato)nickel [93].

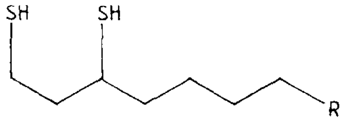


(**27**)

Trimethylene-bis(*cis*-stilbene-1,2-dithiolato)nickel(II) and tetramethylene-bis(*cis*-stilbene-1,2-dithiolato)nickel(II) have been synthesized and characterized by single-crystal X-ray methods. Trimethylene-bis(*cis*-stilbene-1,2-dithiolato)nickel(II) was found to have a *cis-syn* configuration with respect to the Ni-S(CH$_2$)- bonds, with the coordination geometry of Ni being essentially square planar (Ni-S = 2.174(4)Å, Ni-S(CH$_2$) = 2.162(5)Å). Tetramethylene-bis(*cis*-stilbene-1,2-dithiolato)-nickel(II), on the other hand, was found to exhibit a *cis-anti* configuration with respect to the Ni-S(CH$_2$)- bonds, with the coordination geometry about Ni being slightly distorted towards tetrahedral (Ni-S = 2.156(5)Å, Ni-S(CH$_2$) = 2.153(9)Å) [94].

A study has been carried out on the thermodynamic characteristics of the formation of transition metal complexes with the unithiolate ligand 2,3-dimercaptopropanesulfonate. The stability constants were calculated for both the 1:1 and 1:2 complexes with Ni(II) [95].

Dihydrolipoic acid, H_3L = (**28a**), and dihydrolipoamide, H_2L' (**28b**), have been prepared and complexed with Ni(II). Both ligands were found to function in a didentate S,S-donor fashion. Complexes were characterized by potentiometric and spectroscopic methods [96].



(**a**, R = COOH; **b**, R = CONH$_2$)

(**28**)

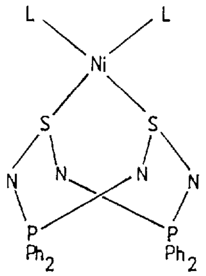
$NiCl_2$, PPh_3 and Na_2edt (edt^{2-} = $SCH_2CH_2S^{2-}$), when reacted in methanol, resulted in cleavage of the C-S bond and the formation of the mixed-ligand complex, [Ni(PPh_3)(tpt)] (tpt^{2-} = $SCH_2CH_2SCH_2CH_2S^{2-}$). The crystal and molecular structure of this complex revealed a distorted square planar geometry for the Ni atom, with tpt functioning as a tridentate ligand, with the fourth coordination site occupied by the phosphine ligand. Ni-S distances were found to be 2.150(2), 2.168(2) and 2.180(2)Å, while the Ni-P distance was 2.187(2)Å [97].

An excellent review of thio-oxalates, which discusses their ligand properties and coordination chemistry, has been published. Topics that are incorporated into the review include the synthesis of the ligands, the modes of ligation in thio-oxalate complexes, and the coordination of mono-thio-oxalate, 1,1-dithio-oxalate, 1,2-dithio-oxalate, trithio-oxalate and tetrathio-oxalate ligands with metal ions, including Ni(II). In addition, the physical methods used to characterize the complexes are also discussed [98].

The synthesis and solid-state characterisation of 3-aminopyridinium bis(dithiooxalato)nickelate(II) have been described. A square planar coordination geometry, with the ligand functioning in a S,S didentate manner, has been assigned to the complex on the basis of the crystal structure of its Pd(II) analogue [99]. The same group have published the crystal structures of the analogous tetraphenylarsonium and tetraphenylphosphonium bis(dithiooxalato)nickelate(II) complexes. In both complexes, the coordination geometry about Ni(II) was found to be square planar, with the ligand functioning as a S,S didentate chelate. Ni-S bond lengths varied from 2.15(1) to 2.188(2)Å [100].

In a review entitled "Transition metal liquid crystals: advanced materials within the reach of the coordination chemist", the application of Ni(II) complexes with sulfur donor ligands and Schiff base imines to the area of liquid crystals has been discussed. Sulfur donor ligands that were included consisted of alkyldithiocarboxylates, xanthates and dithiolenes [101].

$Li_2[1,5\text{-}Ph_4P_2N_4S_2]$ has been reacted with $NiCl_2$(diphos) (diphos = 1,2-bis(diphenylphosphino)ethane). The resultant complex, $[Ni(diphos)(1,5\text{-}Ph_4P_2N_4S_2)]$, has the proposed tetra-coordinate structure (**29**), in which $1,5\text{-}Ph_4P_2N_4S_2^{2-}$ functions as a S,S didentate ligand [102].



(**29**)

A series of 3,4-bis(alkylamino)-3-cyclobuten-1,2-dithiones (alkyl = cyclohexyl, cyclopentyl, *n*-butyl) (*cis*-dithiosquaramides, LH_2) have been reacted with nickel(II) acetate, yielding neutral complexes of the general formula $Mi(II)(LH_2).xH_2O$. The ligands were found to bind in a didentate S,S fashion, yielding a square planar coordination sphere for Ni(II) [103].

1.3.6 Complexes with selenium donor ligands

The crystal structure of the mixed ligand complex anion, $[Ni(C_3S_5)(C_3Se_5)]^{2-}$, has been determined as its tetra-*n*-butylammonium salt. The complex is essentially square planar with the positions of the S and Se atoms being disordered. Ni-S/Se distances were found to range from 2.229(3) to 2.245(1)Å, close to those found for the analogous bisthionato complex [104].

Similarly, the crystal and molecular structure of the bisselenolato complex anion, $[Ni(C_3Se_5)_2]^{2-}$, has been reported both as its potassium and tetramethylammonium salts. The structure of the anion was found to be identical in both cases, with the coordination geometry about Ni being square planar. Ni-Se bond lengths varied from 2.305(1) to 2.315(2)Å, which are considerably longer than those found in the analogous bisdithionato complexes [105].

1.3.7 Complexes with nitrogen-oxygen donor ligands

Schiff bases, hydrazones, carbazones, semi-carbazones, oximes, hydrazides and 8-hydroxyquinoline and its variously-substituted derivatives constitute the bulk of ligands that complex with Ni(II) *via* the N,O donor group.

A review has been published which discusses the coordination compounds of copper, nickel and iron with Schiff base ligands derived from hydroxynaphthaldehydes and salicylaldehydes. Apart from general remarks about the ligands, the review also looks at the electronic and electrochemical properties of the Ni(II) complexes in solution, and some spectroscopic and magnetic properties in the solid state [106].

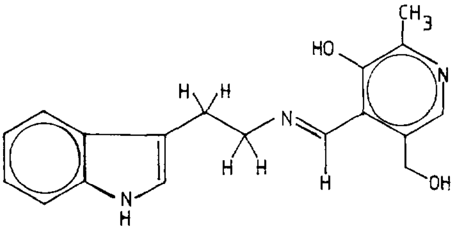
The general use of salicyladehyde in the preparation of Schiff base ligands is exemplified by the number of reports describing Ni(II) complexation with ligands of this type. Compounds that have been isolated in the solid state include the complexes [NiL_2] (HL = *m*-methoxy-, *m*-cloro- and *m*-nitrophenylsalicylaldemine), which were prepared in methanol [107], [$NiL(py)_3$] (H_2L = salicylideneglycine), the crystal structure of which has been determined [108], [NiL] (H_2L = 2-$HOC_6H_4CH{:}NC_6H_4CO_2H$-2, 2-$HOC_6H_4CH{:}NC_6H_4N{:}CHC_6H_4OH$-2, 2-$HOC_6H_4CH{:}NCH_2CH_2$-$N{:}CHC_6H_4OH$-2), prepared via solid state reaction [109], and mononuclear and dinuclear nickel(II) complexes of poly(5-vinylsalicylidene-2-aminopyridine) [110].

Ni(II) complexes of the Schiff bases derived from 3-amino-1,2,4-triazole and salicyladehyde (HL1), p-hydroxybenzaldehyde (HL2), and vanillin (HL3), have ben prepared and investigated spectrophotometrically, conductometrically, and by elemental analysis. All of the ligands were found to function in a didentate fashion, with L1 coordinating via its imino N and phenolic O atoms, and L2 and L3 via their imino N and one ring N atoms [111].

The synthesis, acid-base equilibria, and metal ion chelating tendencies of 2,5-pyrrolediylbis[*N*-(*o*-hydroxyphenylaldimine)] (H_2L), have been reported. Stability constants of the metal complexes, including Ni(II), were determined in dioxan-water. The use of H_2L as an analytical reagent for the spectrophotometric determination on Ni(II) has also been discussed [112].

Electronic spectrophotometry has been used to study the mechanism of transamination in bis(*N*-alkylsalicylaldiminato)nickel(II) complexes (alkyl = Me, Et, Pr^i, Pr^n, Bu^n). Results indicated that the reaction is biphasic, with fast addition of ammonium and slow elimination of alkylammonium ions [113]. Furthermore, in an extension of these studies, the reaction of bis(*N*-phenylsalicylaldiminato)nickel(II) and ammonium or ammonium-like ions has been studied kinetically in acetonitrile. The results of this study showed that the protonable groups of the Schiff base are involved in an acid-base equilibrium with ammonium ions, in a complex stepwise reaction mechanism [114].

The didentate ligand *N*-[2-(3-ethyl-indole)]pyridoxaldimine, H_2L = (**30**), prepared by the 1:1 Schiff base condensation of 3-(2-amino-ethyl)indole with [3-hydroxy-5-(hydroxy-methyl)-4-pyridinecarboxaldehyde], has been complexed with Ni(II). A single-crystal X-ray structure of the complex [$NiHL_2$] was determined confirming a *trans* square planar configuration about Ni(II), with the monoanionic ligand coordinated *via* the deprotonated hydroxyl O (adjacent to the methyl group) and imine N atoms. The Ni-O and Ni-N bond lengths were 1.841(1) and 1.926(2)Å respectively [115].

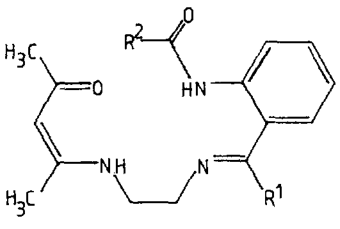


(30)

Bis-chelates of *N*-R-1-hydroxy-2-naphthylstyrylketoimines (R = H, Me, Et) with nickel(II) have been synthesized *in situ via* the ring opening reaction of 7,8-benzoflavanone with $NiCl_2$ and the corresponding aliphatic monoamine. It was found that changing the substituent R from H to Et through Me, resulted in the coordination geometry of Ni(II) changing from *trans* square planar to tetrahedral *via* a quasi-octahedral structure. Similarly, the *N,N'*-ethylene-bis(1-hydroxy-2-naphthylstyrylketoimine)- and *N,N'*-propylene-bis(1-hydroxy-2-naphthylstyrylketoimine)-nickel(II) complexes were prepared in the same way using 1,2-ethanediamine and 1,3-propanediamine as the amine respectively. The former complex was assigned *cis* square planar geometry and the latter octahedral [116].

The structure of the Schiff base complex, (diethylamino){1-[(2-hydroxyphenyl)iminomethyl]-naphthalen-2-olato-*O,O',N*}nickel(II), has been reported. Coordination about Ni was found to be essentially square planar with Ni-O distances of 1.820(3) and 1.842(3)Å, and Ni-N distances of 1.849(3) and 1.955(4)Å respectively. Interestingly, the ethylamino ligand is fully extended perpendicular to the Ni coordination plane [117].

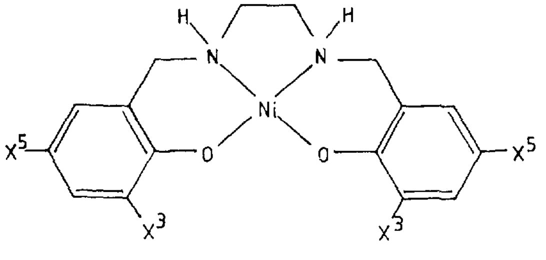
Nickel(II) has been complexed with a series of unsymmetrical tetradentate Schiff base ligands having a pendant *N*-acyl substituent (**31a,b,c**). An unusual temperature-dependent proton NMR spectrum was found for the complex [NiL] (H_2L = (**31c**)), which indicated a substantial energy barrier for enantiomer interconversion of the chiral complex molecule at moderate temperatures. A crystal structure determination of this complex revealed a fluorine-nickel interaction which may be responsible for this phenomenon. Relevant data are Ni-O = 1.835(3)Å, Ni-N = 1.908(3), 1.863(3) and 1.857(3)Å [118].



(**a**: $R^1 = H$, $R^2 = CH_3$; **b**: $R^1 = H$, $R^2 = CF_3$; **c**: $R^1 = CH_3$, $R^2 = CF_3$)

(**31**)

Ni(II) complexes of the open chain, variously-substituted, tetrahydrosalen ligands (**32a-d**) have been prepared and tested for O_2 activation. Oxygen addition was found to take place at low temperature, the rate of uptake being influenced by the nature of the substituents. In addition, the coordination geometry about Ni(II) is affected by the nature of the substituents and introduction of the bulky *tert*-butyl group (**32b-d**) appears to contribute to the square planar coordination found for these complexes. The crystal and molecular structure of (**32b**) confirms square planar coordination for Ni(II) with Ni-O = 1.866 and 1.850Å, and Ni-N = 1.930 and 1.890Å [119].



(**a**: $X^3 = H$, $X^5 = H$; **b**: $X^3 = t\text{-Bu}$, $X^5 = H$)

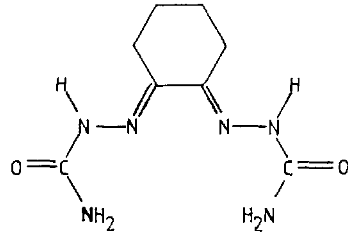
(**c**: $X^3 = t\text{-Bu}$, $X^5 = CH_3$; **d**: $X^3 = t\text{-Bu}$, $X^5 = Cl$)

(**32**)

In a study investigating the reaction of divalent metal ions with ethyl-2,3-dioxobutyrate-2-*p*-bromophenylhydrazone, the complexation of Ni(II) with this ligand has been studied potentiometrically in ethanol/water (50 vol%). Ligand field stabilization energies were calculated for each of the 3d transition metals [120].

2-Hydroxyphenylhydrazoacetylacetone has been complexed with Ni(II) in 75% (vol./vol.) dioxane/water. The stepwise stability constants of the 1:1, 1:2 and 1:3 complexes have been determined at various temperatures, and the thermodynamic parameters calculated [121].

The chelating properties of the potentially tetradentate ligand cyclohexane-1,2-dione bis(semicarbazone) (H_2L) have been investigated. Reaction with nickel(II)nitrate yielded the complex $[Ni(H_2L)_2][NO_3]_2.2H_2O$, the crystal structure of which has been determined. It was found that the Ni(II) ion is octahedrally coordinated *via* two ligands functioning in a terdentate fashion, with one of the urea group nitrogen atoms free (**33**). Relevant data are Ni-N = 2.093(4), 2.000(5), 2.141(5) and 1.992(4)Å, while Ni-O = 2.128(4) and 2.116(3)Å [122].



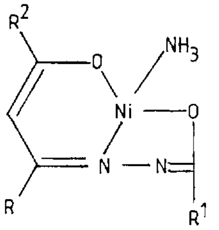
(**33**)

In an on-going study of the solid state reactions of coordination compounds, the solid state reaction of salicylaldoxime (HL) with anhydrous nickel(II) acetate has been investigated at 30°C. The resultant complex, *trans*-$[NiL_2]$, was obtained in 99% yield and characterised by X-ray diffraction, IR spectroscopy and elemental analysis [123].

The nickel(II) complexes of a series of *ortho*-quinone monoxime ligands, $[NiL_2]$ (HL = 4-methyl-*o*-quinone, 4-chloro-*o*-quinone, 4-tertiarybutyl-*o*-quinone, 4,6-dimethyl-*o*-quinone, 4-chloro-5-methyl-*o*-quinone, 4,6-ditertiarybutyl-*o*-quinone), have been prepared and their monomer-dimer equilibrium in solution examined. The temperature and concentration dependant equilibria exhibited by these complexes in non-coordinating solvents were shown for the first time to involve only paramagnetic dimers and diamagnetic monomers [124].

Ni(II) has been complexed with 2,4-dichloro- and 2-methyl-4-chlorophenoxyacetic acid hydrazide. The resultant complexes were characterised by TGA, electronic and infrared spectral data [125].

A number of benzoic acid hydrazide derivatives of 1,3-diketones and their nickel complexes have been synthesized. Spectral studies have revealed that the ligands exist exclusively as cyclic tautomers and undergo a ring-opening reaction on chelation with nickel to form complexes of the type (**34**). In addition, a crystal structure of the complex in which R^1 = p-F-C_6H_4, R = C_6H_5 and R^2 = p-F-C_6H_4, has been reported. The coordination geometry about nickel was found to be square planar with Ni-O = 1.822(2) and 1.835(2)Å, Ni-N = 1.827(3)Å, and Ni-NH_3 = 1.927(2)Å [126].



(R^1 = C_6H_5, p-F-C_6H_4; R = CH_3, C_2H_5, p-F-C_6H_4;)
(R^2 = p-F-C_6H_4, 3-CH_3-4-F-C_6H_4)

(34)

Nickel β-diketonate complexes, [NiL_2] (HL = acetylacetone, benzoylacetone, dibenzoylmethane), have been reacted with benzoylcyanide to give C-C bond formation between the methine and cyano carbon atoms. The resultant compounds were found to be square planar iminodiketonato complexes, suggested catalytic intermediates in the synthesis of β-enaminodiones from β-diketones and PhCOCN. The acetylacetonato derivative, [Ni(acac.PhCOCN)$_2$], was isolated as two forms in the solid state, the crystal structure of the more stable form being reported. Surprisingly, the nickel atom was found to be centrosymmetrically coordinated to the ligand in a N,O bonding configuration, which appears to be preferred to O,O coordination in all cases. Relevant data for [Ni(acac.PhCOCN)$_2$] are Ni-O = 1.832(7) and 1.836(9)Å, Ni-N = 1.822(8) and 1.828(8)Å [127]. The same group have re-determined the solid-state structure of the iminodiketonato complex, obtained by the reaction of cyanogen with [Ni(acac)$_2$] under improved conditions. It was found that the N,O coordination mode yielded a better fit than the previously postulated O,O coordination mode and, in addition, clearly indicated the presence of the imino hydrogen. Relevant data for [Ni(acac.C_2N_2)$_2$] are Ni-O = 1.816(1) and 1.818(3)Å, Ni-NH = 1.833(4) and 1.847(3)Å [128].

The coordination of a selection of indolic acid ligands with Ni(II) has been investigated. Complexes of the type, $NiL_2.2H_2O$ (HL = indole-3-carboxylic acid, indole-3-acetic acid, indole-*N*-acetic acid, indole-*N*-methyl-2-carboxylic acid) were isolated. Spectroscopic and magnetic susceptibility data indicated that the complexes have a distorted octahedral structure [129].

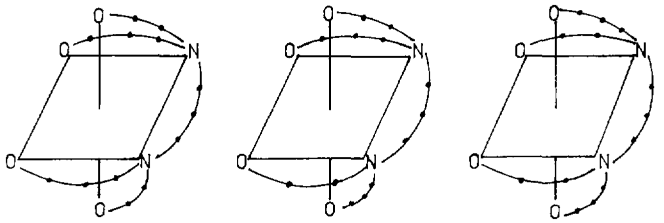
The kinetics and mechanism of Ni(II) binary complexation with the variously-substituted iminodiacetic acid ligands, *N*-(*p*-R-phenyl)iminodiacetic acid (R = OMe, Me, H, Cl), have been determined as a function of pH. It was found that the ligand anions and zwitterions were both complexing species [130].

Ethylenediaminedisuccinic acid lactam has been complexed with Ni(II) in aqueous solution. Complexation was studied calorimetrically, pH-metrically and spectrophotometrically. The stability constants for the nickel complexes, as well as the thermodynamic parameters for complexation, have been reported [131].

Synthesis of the bis chelates of Ni(II) with *o*-[[chloro(thien-2-yl)methylene]amino]benzoic acid, 3-[[chloro(thien-2-yl)methylene]amino]propanoic acid and *o*-[[1-(furan-2-yl)ethylidene]-amino]benzoic acid has been published. The complexes were characterised using magnetic, conductance and spectral techniques. In addition, the stability constants of these complexes were determined potentiometrically in 30% (v/v) aqueous ethanol [132].

Potentiometric titration, in the pH range 2-11, has been utilised to study the coordination equilibria of Ni(II) with a number of 2-(polyhydroxyalkyl)thiazolidine-4-carboxylic acid (polyhydroxylalkyl = L-arabinose, D-xylose, D-glucose, D-galactose, L-rhamnose, D-ribose, D-arabinose, D-lyxose, D-mannose) ligands. The ligands were found to function as O,N or O,N,O donor ligands, depending on the nature of the sugar and the pH. Mixed-ligand complexes involving hydroxide ion coordination and/or further deprotonation of the alcoholic hydroxy groups of the sugar moieties were observed at pH > 6 [133].

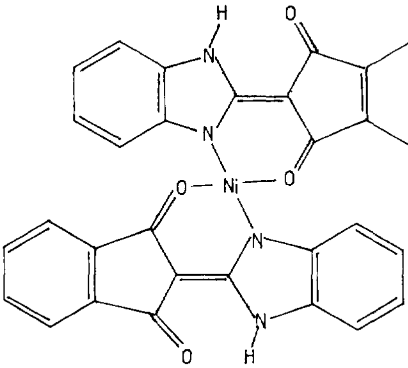
Complex formation between nickel(II) and the potentially hexadentate ligand, 1,3-propanediamine-*N*,*N*′-diacetate-*N*,*N*′-di-3-propionic acid (H_4L), has been studied by emf glass electrode and spectrophotometric methods. In addition, the complex $Na_2[NiL]$ has been synthesized and characterized by elemental analysis and visible and IR spectroscopy. Three possible geometrical isomers of $Na_2[NiL]$ have been suggested (**35**) [134].



(35)

3-Benzimidazolylcoumarin (L) has been complexed with a selection of nickel(II) salts. Complexes of the type NiL_2X_2 (X = Cl, Br, NO_3, NCS) were prepared and characterized by IR and electronic spectra, thermal analysis, and magnetic moment measurements. The complexes have been assigned octahedral coordination geometry with L functioning in a didentate fashion, coordinating *via* the pyridine N atom of the benzimidazolyl group and the exocyclic O atom of the coumarin group [135].

2-(1,3-Dioxo-2-indanylidene)benzimadazoline, H_2L, has been reacted with $(P\textit{n}Bu_3)_2NiCl_2$ in the presence of NaH. The resultant complex, *trans*-$[Ni(HL)_2]$, has been isolated and characterized. The ligand was found to function in a N,O donor fashion, with coordination occurring *via* a deprotonated amino N atom and its adjacent ketone O atom (**36**) [136].



(**36**)

3,6-Dihydroxypyridazine has been complexed with a number of 3d transition metal ions. The overall stability constants of the complexes were found to follow the Irving-Williams order. Log K_1 and K_2 values (298K) found for the Ni(II) complexes were 6.60 and 4.11 respectively [137].

Bis(*P*,*P*-di-*tert*-butylphosphinic-*N*-isopropylamidato-*N*,*O*)nickel(II) has been prepared and its crystal and molecular structure determined. The complex is unusual in that it shows Curie-Weiss behaviour in both the solid state and solution, as is usually observed for tetrahedral Ni(II) complexes. The crystal structure, however, reveals a *trans* square planar coordination geometry for Ni(II), with the ligands functioning in a N,O donor didentate fashion. This appears to be the first example of a paramagnetic planar Ni(II) complex whose coordination geometry has been confirmed by X-ray crystallography [138].

The new, potentially N,N,O-tridentate ligand 6-(2-hydroxyphenyl)-2,2'-bipyridine (HL) has been prepared and reacted with nickel(II) acetate. The resultant complex, $[NiL_2].HPF_6$, was precipitated with KPF_6, and characterized using FAB mass spectroscopy. The structure is presently being further confirmed by single-crystal X-ray methods [139].

8-Hydroxyquinoline and its variously-substituted analogues continue to be a much used source of potential N,O donor ligands. The stability constants and thermodynamic parameters of the binary complexes of 5-phenylazo-8-quinolinol and its 5-(4-R-substituted-phenylazo)-8-quinolinols (R = OMe, Me, NO_2) with Ni(II) have been determined potentiometrically in 50% dioxane. Both 1:1 and 1:2 chelates were formed [140].

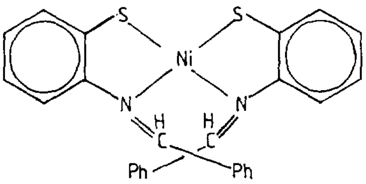
The rate of formation of Ni(II) complexes with 8-quinolinol and 5-alkyloxymethyl-8-quinolinol (alkyl = methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl [141] and octyl [142]) ligands, has been investigated in nonionic surfactant micellar systems. Ni(II) complexes were found to form in both phases, the reaction rate in the micellar phase being about one tenth of that found in the aqueous phase. In addition, the same group have studied the extraction of Ni(II) using 2-methyl-8-quinolinol (HL) in chloroform as extractant. An equilibrium analysis revealed that the neutral complexes Ni_2L_4 and Ni_3L_6 were responsible for extraction from sulfate solutions, whereas the ion-pair species, $[Ni_3H(L)_6](ClO_4)$ and $[Ni_2H_3(L_6)](ClO_4)$, were predominant with perchlorate solutions. X-ray crystal structures showed that the complexes $[Ni_3L_6].2C_2H_5OH$ and $[Ni_3H(L)_6](ClO_4).C_2H_5OH$ have discrete bent trimeric structures, with the octahedral coordination sphere maintained by two μ- and two μ_3-bridging phenolate O atoms. In the $[Ni_2H_3(L_6)](ClO_4)$ complex each Ni atom was found to be coordinated to three ligands in a *fac* configuration, with three hydrogen bonds connecting the two octahedrons [143].

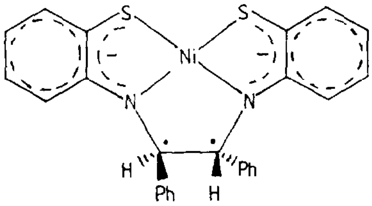
In similar work to the above, the complexation of nickel(II) to a variety of azophenol ligands has been investigated in aqueous and micellar solutions of a nonionic surfactant. Stopped-flow spectrophotometry was used to determine the kinetics of formation of the 1:1 complexes [144].

1.3.8 Complexes with nitrogen-sulfur donor ligands

A review has been published which discusses organodisulfide complexes. Sections of the review have been devoted to the complexes of amine disulfides, ligands which lend themselves readily to the N,S mode of coordination. Ligands that have been included are 2-aminoethyl-alkyldisulfides and related ligands, cystamine and its derivatives, bis(2-aminophenyl)disulfide and its derivatives, and pyridyldisulfides [145].

2-Phenylbenzothiazoline has been complexed with nickel(II) acetate. The resultant complex, *cis*-bis[2-*N*-(phenylmethylideneamine)benzenethiolato]nickel(II) (**37**), was found to undergo C-C bond formation upon heating, and yielded the complex (**38**), which contains two chiral centres. The crystal structures of both (**37**) and (**38**) have also been reported. Both complexes were found to exhibit essentially square planar structures ((**37**): Ni-S = 2.180(1)Å, Ni-N = 1.962(2)Å; (**38**): Ni-S = 2.126(1) and 2.129(2)Å, Ni-N = 1.830(5) and 1.826(4)Å) [146].

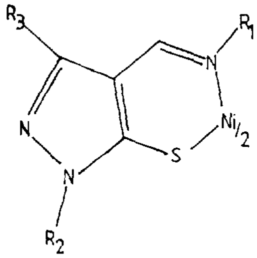




(37) (38)

The crystal and molecular structure of the nickel(II) complex of methyl-2-amino-1-cyclopentenedithiocarboxylate (L) has been reported. [NiL_2] was found to have a *trans*-square planar configuration, with L functioning in a didentate N,S donor fashion. The Ni-S and Ni-N bond lengths of 2.183(2) and 1.863(4)Å are consistent with planar structures of this type, while the Ni-S distances are longer than those found in the corresponding *cis* complexes [147].

A comparative study involving the racemization kinetics and spin states of tetra-coordinate nickel(II) complexes with didentate N,S donor ligands has been undertaken. Nine complexes of the type (**39**) were synthesized for the study. In addition, the X-ray structure of bis(1,3-dimethyl-5-thiolato-pyrazol-4-isopropylaldimino-*N*,*S*)nickel(II) has been determined. A near tetrahedral coordination geometry for Ni(II) was found, with Ni-S = 2.249(1)Å and Ni-N = 1.989(3)Å. Each complex was found to be almost totally high spin [148].



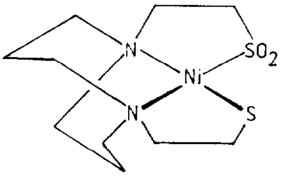
($R_2 = R_3$ = Me; R_2 = Ph, R_3 = Me; R_2 = Me, R_3 = Ph; $R_2 = R_3$ = Ph; R_2 = Me, R_3 = *p*-Cl-Ph)
(R_2 = Me, R_3 = *p*-NO_2-Ph; R_2 = Me, R_3 = *p*-MeO-Ph; R_2 = Ph, R_3 = *p*-Cl-Ph; R_2 = Ph, R_3 = *p*-MeO-Ph)

(39)

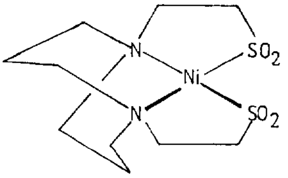
In a continuing study of 1,3,4-thiadiazole derivatives, the coordination compounds of 1-(5-mercapto-1,3,4-thiadiazol-2-yl)-2-methyl-4,6-diphenylpyridinium, $(HL)^+$, perchlorate with divalent metal cations, including Ni^{2+}, have been prepared. The resultant complexes, $[ML_2(ClO_4)_2]$, were characterized using chemical analysis, thermogravimetric, magnetic, and a variety of spectroscopic techniques [149].

The complexation behaviour of diacetylmonoxime thiosemicarbazone and diacetylmonoxime-4-phenylthiosemicarbazone with Ni(II) have been investigated in 50% (v/v) aqueous ethanol using Calvin-Bjerrum pH-titration techniques. Stability constants and thermodynamic parameters for the coordination complexes were determined [150].

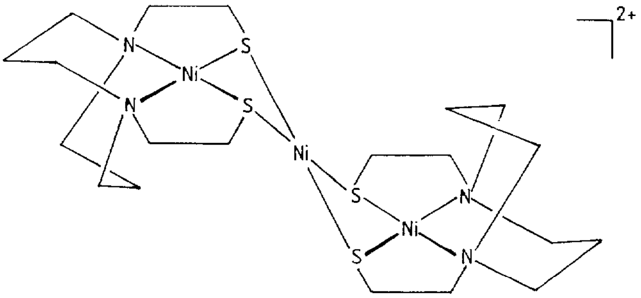
Molecular oxygen has been reacted with [*N*,*N*′-bis(mercaptoethyl)-1,5-diazacyclooctane]-nickel(II) to produce two oxygenates, [(mercaptoethyl)(sulfinatoethyl)diazacyclooctane]nickel(II) (**40**) and [bis(sulfinatoethyl)diazacyclooctane]nickel(II) (**41**), and the trimetallic complex, (**42**). The molecular structures of (**40**) and (**42**) were determined by X-ray crystallographic methods. Complex (**40**) was found to have a pseudo square planar configuration with *cis* sulfur donor atoms (Ni-S = 2.140(1)and 2.163(1)Å, Ni-N = 2.000(2) and 1.982(2)Å), while complex (**42**) had a staircase-like structure with the central Ni atom coordinated to four S atoms in a planar configuration [151].



(**40**)



(**41**)

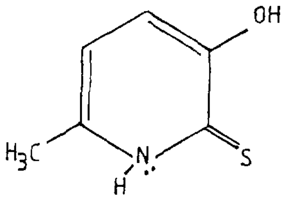


(**42**)

The synthesis, X-ray crystal structures, and electronic spectra of two nickel complexes with tripodal N,S donor ligands have been reported. Reaction of the tripodal ligand tris{[2-(2-aminophenyl)thio]ethyl}amine (L^1) with nickel(II) perchlorate yielded the complex $[NiL^1(ClO_4)](ClO_4)$, in which the nickel atom is bound equatorially to two S and two N atoms from two arms of the tripod, while the remaining two axial coordination sites are occupied by the bridgehead N atom and an O atom from a coordinated perchlorate ligand. Relevant crystallographic data are Ni-S = 2.363(3) and 2.393(3)Å, Ni-N = 2.081(6), 2.081(7) and 2.167(6)Å, and Ni-O = 2.249(7)Å. On the other hand, reaction of tris{[2-(2-aminoethyl)thio]ethyl}amine (L^2) with nickel(II) perchlorate afforded the complex $[NiL^2](ClO_4)_2$. In this case all three arms of the tripodal ligand were found to be coordinated to Ni(II), providing a distorted octahedral S_3N_2 donor set. Relevant structural data are Ni-S = 2.461(1), 2.490(9) and 2.478(1)Å, Ni-N = 2.132(3), 2.120(3) and 2.102(3)Å [152].

1.3.9 Complexes with oxygen-sulfur donor ligands

3-Hydroxy-6-methylpyridine-2-thione (**43**) has the potential to coordinate in a chelating fashion *via* its N and S atoms, or its S and O atoms. A crystal structure of its bis complex with nickel(II), bis(6-methylpyridine-2-thion-3-olato)nickel(II) bis(dimethylformamide) has been determined, revealing coordination *via* the O and S atoms. The complex exhibits slightly distorted *trans* square planar geometry with Ni-S = 2.204(1)Å and Ni-O = 1.856Å [153].



(**43**)

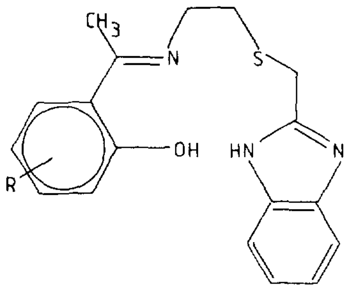
The formation of mixed-ligand complexes of Ni(II) with thiosalicylic acid (H_2L) and ethylenediamine has been investigated in 50% (v/v) aqueous ethanol using potentiometric methods. Thermodynamic parameters of the complexes were also determined [154].

1.3.10 Complexes with nitrogen-oxygen-sulfur donor ligands

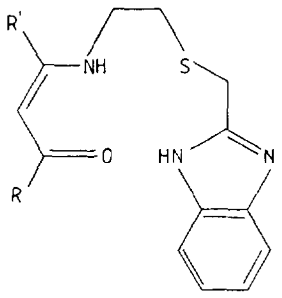
A potentiometric study of the chelation behaviour of 2-hydroxy-1-naphthaldehyde thiosemicarbazone towards divalent metal ions has been undertaken in 75% (v/v) dioxan/water. Stability constants were determined for the complexes, the order being $Mg^{2+} < Mn^{2+} < Cd^{2+} < Pb^{2+} < Zn^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < UO_2^{2+}$ [155].

Continuing with thiosemicarbazone ligands, 2-oxoglutaric acid thiosemicarbazone (HL) has been complexed with Ni(II). The resultant complex, $NiL_2.5H_2O$, was characterized by elemental analysis, solubility, conductivity, magnetic moment, and IR and UV-visible spectroscopic methods [156].

The synthesis of the asymmetrical tetradentate Schiff-base ligands containing benzimidazole and thioether groups, (**44**) and (**45**), and the electrochemical preparation of their electrically neutral complexes, $[NiL].nH_2O$, have been reported. Spectroscopic and magnetic data indicated that the ligands function in a dianionic tetradentate fashion, with coordination occurring *via* the four O,N,S,N donor atoms [157].



(**44**)



(**45**)

1.3.11 Complexes with nitrogen-phosphorus donor ligands

A review of the structural and bonding capabilities of the potentially tripodal ligand, tris(2-diphenyl-phosphinoethyl)amine (np_3), has been published. Areas relevant to Ni(II) that are covered in the review include diamagnetic trigonal bipyramidal complexes of the type $(np_3)ML$, trigonally elongated high-spin complexes of the type $(np_3)ML$, trigonal pyramidal complexes with no coligand $(np_3)M$, complexes with a total electron count exceeding 18, and pseudo-tetrahedral $(np_3)ML$ complexes [158].

1.3.12 Complexes with phosphorus-oxygen donor ligands

The preparation, properties, and X-ray crystal structure of the nickel(II) hydroquinonylphosphine complex, *cis*-$[Ni(HL)_2].H_2O.2(CH_3)_2NCHO$ (H_2L = hydroquinonylphosphine), have been reported. The complex displays distorted square planar coordination geometry with two *cis*-coordinated monobasic hydroquinonylphosphine ligands. Relevant structural data are Ni-P = 2.138(6) and 2.159(6)Å, Ni-O = 1.90(1) and 1.87(1)Å [159].

1.3.13 Complexes with phosphorus-sulfur donor ligands

Bis{2-(dimethylphosphino)ethane-1-thiolato}nickel(II) has been prepared and its crystal and molecular structure determined. The geometry about Ni(II) was found to be square planar with a *trans(P,P)* arrangement of the ligands. Relevant structural data are Ni-P = 2.162(4) and 2.171(4)Å, Ni-S = 2.178(4) and 2.179(4)Å [160].

1.3.14 Complexes with halide or pseudo-halide ligands

The X-ray crystal structure of 2-aminophenyltriphenylphosphonium tetrachloronickelate(II) has been reported. The $[NiCl_4]^{2-}$ dianion was found to exhibit tetrahedral coordination geometry, with Ni-Cl bond lengths varying from 2.240(2) to 2.279(2)Å. The bromide analogue, 2-aminophenyltriphenylphosphonium tetrabromonickelate(II) was also prepared [161].

Spectrophotometry and calorimetry have been used to study the formation of nickel(II) chloro complexes in *N,N*-dimethylacetamide (DMA). Formation constants, reaction enthalpies and entropies, and electronic spectra have been determined for four mononuclear complexes, $[NiCl_n]^{(2-n)+}$ (n = 1-4). These data indicate octahedral coordination geometry for $[Ni(DMA)_6]^{2+}$, and tetrahedral geometry for $[NiCl_3(DMA)]^-$ and $[NiCl_4]^{2-}$. In addition, it has also been suggested that the steric requirements of the acetyl and methyl groups of the DMA molecules lead to the formation of the unusual coordination geometries, penta-coordinate $[NiCl(DMA)_4]^+$ and $[NiCl_2(DMA)_3]$, and tetrahedral $[NiCl_2(DMA)_2]$ [162].

Similarly, electronic absorption spectra have been obtained of nickel(II) bromide in solutions of polyethyleneglycol, with a view to determining the coordination environment. Results obtained indicate that Ni(II) is partitioned between octahedral and tetrahedral complexes, the former being of the type $[NiO_6]^{2+}$, or as a variation including some Br^- ions, the latter appearing to be free ions in the form of $[NiBr_4]^{2-}$ [163].

In addition, structural changes occurring during the stepwise formation of halo and thiocyanato complexes of Ni(II) in aqueous and nonaqueous solutions have been observed using spectroscopic, calorimetric and solution X-ray diffraction data. The structures of $[NiX_n]^{(2-n)+}$ (n = 1 - 4) and the bond length variations due to structural changes were determined *via* solution X-ray diffraction. Spectroscopic and structural data were also used to monitor the change from octahedral to tetrahedral coordination geometry [164].

The crystal and molecular structure of $NiCl_2.4H_2O$ has been determined by single-crystal X-ray methods. Surprisingly, the coordination geometry about Ni(II) was found to be distorted octahedral, with a *cis* configuration with respect to the chloride ions. Relevant structural data are Ni-O = 2.058(3), 2.075(3), 2.080(3) and 2.070(4)Å, Ni-Cl = 2.374(1) and 2.397(1)Å [165].

1.4 NICKEL(II) MACROCYCLE COMPLEXES

By way of introduction to this well researched area of nickel(II) chemistry, a number of articles of general interest have been published in 1992. One review discusses the redox processes in supramolecular coordination compounds, including a variety of biscyclam complexes [166], while a second review examines the coordination chemistry of a number of didentate medium ring ligands (mesocycles). Ligands and their complexes included in this review consist of 1,5-diazacyclooctane, 1,4-diazacycloheptane and their derivatives, 1,4-dithiacycloheptane, 1,5-dithiacyclooctane and their derivatives, 5-methyl-1-thia-5-azacyclooctane, 5-phenyl-1-thia-5-phosphacyclooctane and 1,5-diphenyl-1,5-diphosphacyclooctane [167].

The effect of coordination number in macrocyclic nickel(II) complexes has once again attracted interest. One study has investigated the influence of coordination number on the peroxydisulfate oxidation of nickel(II) macrocyclic complexes. It was shown, *via* pH-controlled thermodynamic equilibria between four- and six-coordinated forms, that the reactivity of the tetra-coordinated square planar form was substantially higher than the hexa-coordinated form [168]. In addition, cellular ligand field (CLF) analyses have been made for several tetragonal-octahderal complexes, including the macrocyclic complexes $[NiX_2L]$ ($X = Cl^-$ or NCS^-; L = 14-, 15- or 16-membered tetraaza macrocycle). It was reported that, while most complexes satisfied Pauling's electroneutrality principle i.e. as the strength of the equatorial donation decreases, the axial donors bind more strongly to compensate, for the macrocyclic complexes the significant increase in the axial bonding parameters need not necessarily be accompanied by a marked decrease in the Ni-X bond length. This effect was explained in terms of steric interactions [169].

1.4.1 Macrocycles with nitrogen donor atoms

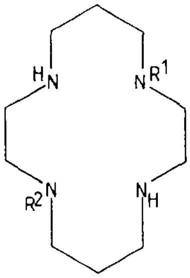
The low temperature single-crystal absorption spectrum, far-infrared spectrum and single-crystal X-ray structure determination of $[NiL_2](ClO_4)_2.H_2O$ (L = 1,4,7-triazacyclononane) have been determined. The complex cation, $[NiL_2]^{2+}$, was found to possess approximate D_{3d} symmetry, while trigonal splitting of the NiN_6 octahedral modes of vibration, as well as several macrocyclic ring-deformation modes, were observed in the far-infrared spectrum [170].

In an attempt to design ligands which impose tetrahedral coordination, a convenient synthetic route to the preparation of aminoethyl and aminopropyl pendant arm derivatives of 1,5,9-triazocyclododecane has been found. The macrocyclic ligands 1-(2-aminoethyl)-1,5,9-triazocyclododecane (L^1) and 1-(3-aminopropyl)-1,5,9-triazocyclododecane (L^2) have been prepared from 2,4-dioxo-1,5,9-triazocyclododecane, and the complex $[NiL^2(NCS)_2]$ synthesized and its crystal and molecular structure determined. The structure of $[NiL^2(NCS)_2]$ can best be described as *cis*-octahedral, with the macrocyclic ligand occupying one face of the coordination octahedron, whilst the pendant arm chelates to a fourth site. The NCS ligands occupy the remaining two coordination sites in a *cis* configuration. Relevant structural data are Ni-N = 2.179(8), 2.117(6), 2.088(12) and 2.094(6)*Å*, and Ni-NCS = 2.134(7) and 2.054(8)*Å* [171].

Turning to tetraaza macrocyclic complexes, cyclam and particularly its variously-substituted analogues dominate this category. In an ongoing study, the kinetics of complexation of Ni(II) with N_4 macrocycles of the cyclam type, in dmf, have been reported. Ligands that have been studied include 1,4,8,11-tetraazacyclotetradecane, 1-methyl-1,4,8,11-tetraazacyclotetradecane, 1,4-dimethyl-1,4,8,11-tetraazacyclotetradecane, 1,4,8-trimethyl-1,4,8,11-tetraazacyclotetradecane and 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane [172], as well as 1,4,8,11-tetraazadibenzo[*b,i*]cyclotetradecane, 1,4,8,11-tetramethyl-1,4,8,11-tetraazadibenzo[*b,i*]cyclotetradecane, *rac*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, *meso*-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane, and *meso*-5,12-dimethyl-*meso*-7,14-diphenyl-1,4,8,11-tetraazacyclotetradecane [173]. Complex formation was found to be a two step process with an initial fast second-order reaction (first order in both metal ion and ligand concentration), generating an intermediate species which is then converted, via a slow first-order process, to the product $[NiL]^{2+}$.

The crystal structure and thermal reaction of *cis*-$[Ni(isocyclam)(H_2O)_2]Cl_2.2H_2O$ (isocyclam = 1,4,7,11-tetraazacyclotetradecane) have been reported. The complex was found to have distorted octahedral geometry with two water molecules coordinated in *cis* positions and the cyclam ligand coordinated in a folded fashion. Relevant structural data are Ni-N = 2.130(6), 2.086(6), 2.133(6) and 2.101(6)Å, and Ni-O = 2.176(5) and 2.161(5)Å. Thermal treatment of *cis*-[Ni(isocyclam)-$(H_2O)_2]Cl_2.2H_2O$ resulted in deaquation-anation in the solid state, yielding the *cis*-dichloro complex *cis*-$[Ni(isocyclam)Cl_2]$. Further heating resulted in conversion of the *cis*-dichloro complex to its *trans* form, with a change in ligand configuration from folded to coplanar chelation [174].

Stereoselective synthesis of variously-1,8-disubstituted derivatives of 1,4,7,11-tetraazacyclotetradecane (**46**) has been undertaken, and the corresponding Ni(II) complexes prepared. The crystal and molecular structure of the complex cation $[NiL]^{2+}$ (L = (**46**) with $R^1 = R^2$ = Bu), isolated as its perchlorate salt, were determined, revealing a square planar coordination environment for Ni(II). Ni-N bond lengths varied from 1.939(2)Å (Ni-NH) to 1.970(2)Å (Ni-NBu) [175].



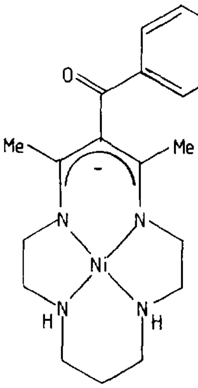
($R^1 = R^2$ = Bu; $R^1 = R^2$ = Me; R^1 = Bu, R^2 = Me)

(**46**)

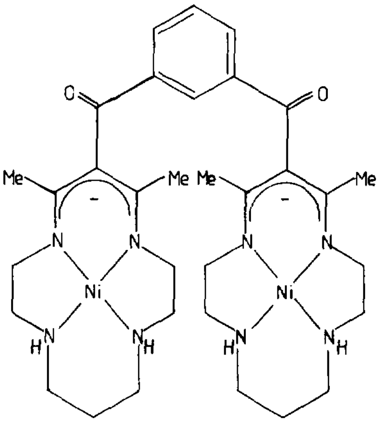
1,8-Diethyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene (L) has been synthesized as its dihydroperchlorate salt and reacted with Ni(II). The resultant complex cation, $[NiL]^{2+}$, was further reacted with $NaBH_4$ producing the complex cation $[NiH_4L]^{2+}$, where H_4L = 1,8-diethyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradecane. Both complex cations have planar geometry and contain two ethyl groups at the donor N atoms of the ligands [176].

The crystal structures of *racemic* and *meso* (5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(II) perchlorate have been reported. Both complexes are essentially square planar, the most noticeable differences being in the Ni-N bond lengths. The Ni-N(amine) and Ni-N(imine) bond lengths were found to be significantly different in the two structures, with both Ni-N(amine) and Ni-N(imine) bond lengths in the *meso* form being 0.023(4)Å longer than in the *racemic* form. These differences have been attributed to the folding of the macrocycle in the *racemic* structure [177].

5,7-Dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato)nickel(II) iodide has been reacted with benzoyl chloride and isophthaloyl chloride, producing the mononuclear and dinuclear complexes (**47**) and (**48**) respectively. Crystal structures of the two complexes have been determined, confirming square planar geometry for the Ni atom in (**47**) (Ni-N = 1.861(6), 1.932(7), 1.959(7) and 1.826(6)Å) and square planar geometry for both Ni atoms in (**48**)(Ni(1)-N = 1.81(2), 1.90(2), 1.91(2) and 1.86(2)Å; Ni(2)-N = 1.83(2), 1.93(2), 1.97(2) and 1.85(2)Å). In addition, the two coordination planes in the dinuclear complex are nearly coplanar [178].



(47)

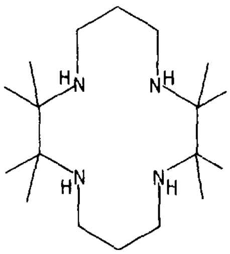


(48)

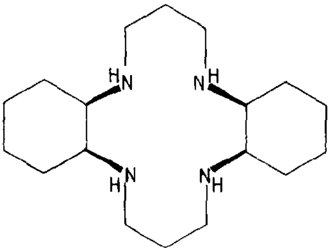
Template cyclocondensation of ethylenediamine with the reaction product of 1,2-dichloro-4,5-dinitrobenzene and salicyaldehyde, has been used to prepare the tetracoordinated macrocyclic complexes $[NiL]X_2$ (L = (*b,j*)dibenzo-*m*-(dinitrobenzo)-5,8-diaza-1,12-dioxacyclotetradeca-4,8-diene; X = Cl, SCN, BF_4, ClO_4). The complexes were characterised using elemental analysis, molar conductance, IR spectra, magnetic measurements, and electronic spectral studies [179].

The electronic structure of dibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine nickel(II) has been studied using theoretical *ab initio* and UV-photoelectron spectroscopic methods. Theoretical calculations provided a complete assignment of the photoelectron spectra, as well as information relating to the valence electron system [180].

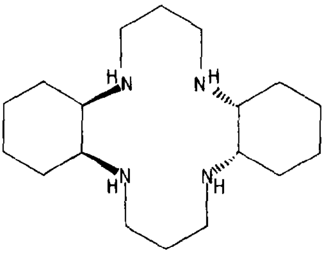
A series of sterically congested cyclam derivatives (**49**), (**50**), (**51**), (**52**), (**53**) and (**54**) have been prepared and reacted with Ni(II). It was found that the less congested complexes NiL^{2+} (L = cyclam, (**54**)) existed as high-spin complexes in the solid state, while NiL^{2+} (L = cyclam, (**53**), (**54**)) existed as mixtures of high-spin and low-spin species in solution. On the other hand, the highly sterically congested species NiL^{2+} (L = (**49**), (**50**), (**52**)) were shown to be low-spin in both the solid state and solution, while NiL^{2+} (L = (**51**)) was found to occur as a high spin complex in the solid state and a low-spin complex in solution. Structures in solution were confirmed *via* electronic spectra, while molecular structures in the solid state were determined using single-crystal X-ray techniques [181].



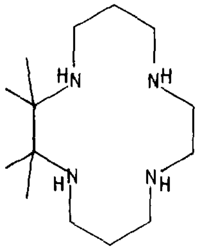
(**49**)



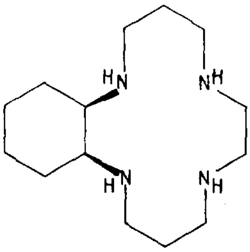
(**50**)



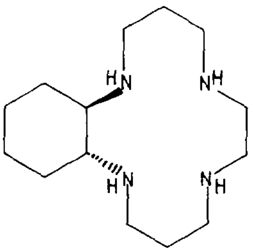
(**51**)



(**52**)



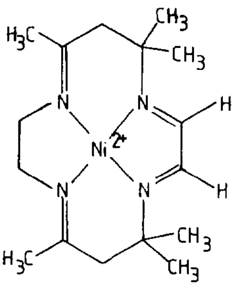
(**53**)



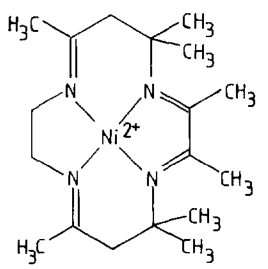
(**54**)

The synthesis, characterisation and complexation of 7,16-dinicotinoyltetraaza[14]annulene and 7,16-diisonicotinoyltetraaza[14]annulene with Ni(II) have been reported. Square planar coordination geometry was assigned to both complexes based on IR and NMR spectroscopic evidence [182].

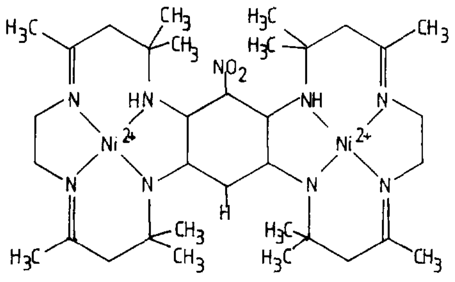
Attempts have been made to use nitromethane as a reactant to attach nitromethyl pendant arms to C-functionalised macrocyclic nickel(II) complexes. However, reaction of nitromethane, in the presence of base, with 5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-1,3,7,11-tetraene nickel(II) did not yield the expected macrocyclic complex, containing two coordinated pendant *aci*-nitromethyl groups (**55**), but rather the dimethylated complex (**56**) and the dimeric complex (**57**). The formation of (**56**) was explained in terms of nitromethane addition to the C=N double bond followed by elimination of HNO_2, while the formation of (**57**) was explained *via* the formation of a dimeric dinitro adduct followed by elimination of HNO_2 [183]. Using this as a basis for further study, the same group investigated this reaction with a series of polyalkyl-1,4,8,11-tetraazacyclotetradeca-1,4,8,11-tetraenenickel(II) diperchlorate complexes. In this case they were able to add two nitromethane molecules to the less sterically hindered C=N double bonds giving rise to novel macrocyclic ligand complexes containing two coordinated pendant *aci*-nitromethyl groups. Furthermore, reduction of the nitro groups yielded the corresponding 2,9-bis(aminomethyl)-substituted nickel(II) complexes in which the pendant amino groups were coordinated or uncoordinated, depending on the steric environment [184].



(55)



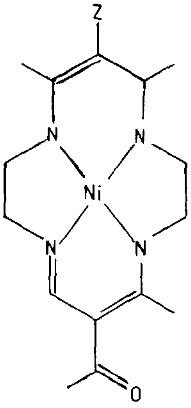
(56)



(57)

Turning to asymmetric macrocyclic complexes, the preparation and characterisation of (3,10-diacetyl-2,11-dimethyl-17-nitro-1,5,8,12-tetrazabicyclo*[13.4.0]*nonadeca-1,3,6,8,10,16,18-heptaenato)nickel(II) and (3,10-diacetyl-17-amino-2,11-dimethyl-1,5,8,12-tetrazabicyclo*[13.4.0]*nonadeca-1,3,6,8,10,16,18-heptaenato)nickel(II) have been reported. The synthesis of (3,10-diacetyl-2,11-dimethyl-17-nitro-1,5,8,12-tetrazabicyclo*[13.4.0]*nonadeca-1,3,6,8,10,16,18-heptaenato)-nickel(II) was performed *via* the template condensation of the asymmetric precursor with 1,3-propanediamine, while catalytic reduction of the nitro group in this complex gave rise to (3,10-diacetyl-17-amino-2,11-dimethyl-1,5,8,12-tetrazabicyclo*[13.4.0]*nonadeca-1,3,6,8,10,16,18-heptaenato)nickel(II). The asymmetric nature of these complexes was demonstrated by ^1H and ^{13}C NMR spectroscopy [185].

The same group have reported the synthesis and characterisation of a series of new tetraaza macrocyclic complexes of nickel(II) (**58**). These complexes were prepared *via* reaction of a nucleophilic macrocycle with an appropriate acid chloride, or *via* peripheral functionalisation of a suitable macrocycle. The asymmetry of these macrocyclic complexes was verified by their NMR spectra [186].



(Z = H, 4-ClC_6H_4CO, 4-IC_6H_4CO, 4-$NO_2C_6H_4CO$, 4-$CH_3CO_2C_6H_4CO$, 4-$BrCH_2C_6H_4CO$)
(4-$CH_3C_6H_4CO$, 4-$CH_2CHC_6H_4CO$, 4-$Br_2CHC_6H_4CO$, 4-$NH_2C_6H_4CO$, 4-$CH_3CONHC_6H_4CO$,
4-HOC_6H_4CO)

(**58**)

1,3,6,9,11,14-Hexaazatricyclo-(12,2,1,1)octadecane (L) has been complexed with a number of nickel(II) salts. The resultant complexes $[NiL]Cl_2.3H_2O$, $[NiL]Br_2.3H_2O$, $[NiL]I_2.H_2O$ and $[NiL](NO_3)_2$ were isolated and characterised as diamagnetic. The crystal and molecular structure of $[NiL]I_2.H_2O$ was determined, confirming approximately square planar coordination geometry with Ni-N ranging from 1.920(6) to 1.951(7)Å. In addition, the diamagnetic sulfate complex $[NiL](SO_4)_2$ was prepared by oxidation of $[NiL]Cl_2.3H_2O$ with $Na_2S_2O_8$ [187].

Porphyrin and variously-substituted porphyrin nickel(II) complexes continue to attract considerable interest. Studies in this area include an investigation of the kinetic trends during the formation of transition metal porphyrin complexes in a series of coordinating solvents [188], the synthesis and characterization of 2,7,12,17-tetra(benzoylthio)tetraazaporphyrin and its nickel complex [189], and the effect of tetraphenylporphyrin and its nickel complex on hydrogen ion transfer across the water/nitrobenzene interface [190].

The molecular structures of 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetramesitylporphyrin and its nickel(II) complex, as well as 2,3,7,8,12,13,17,18-octabromo-5,10,15,20-tetrakis(pentafluorophenyl)porphyrin nickel(II) have been reported. Both complexes were found to be nonplanar, displaying saddle-shaped conformations. Ni-N bond lengths were found to be 1.916(12)Å in the former complex, and ranged from 1.8849(10) to 1.906(10)Å in the latter complex [191].

The synthesis, characterization, and complexing behaviour of the potentially dinucleating porphyrin ligand, α,α-5,15-bis(*o*-nicotinoylamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrin, [H_2(DPE)]-$(py)_2$, have been reported. Reaction with nickel(II) acetate in methanol yielded the mononuclear complex [Ni(DPE)]-$(py)_2$, the crystal structure of which has been determined in its di$CHCl_3$-solvated form, [Ni(DPE)]-$(py)_2.2CHCl_3$. The Ni ion was found to be coordinated in a square planar environment with Ni-N ranging from 1.917(3) to 1.922(4)Å, while the pyridine binding site remained free. In addition, the dinuclear complexes [Ni(DPE)]-$(py)_2PdCl_2$ and [Ni(DPE)]-$(py)_2ZnCl_2$ have been isolated and characterized [192].

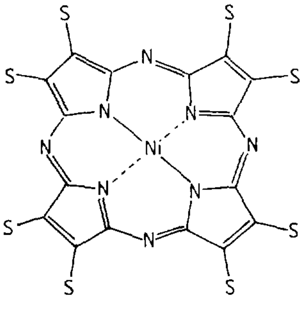
The same group have determined the structure of α,α-5,15-bis(*o*-nicotinoylamidophenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphyrinato nickel(II) monohydrate, [Ni(DPE)]-$(py)_2.H_2O$, and compared it with [Ni(DPE)]-$(py)_2.2CHCl_3$. The porphyrin skeletons in both structures were found to have similar bond lengths and angles, comparable with other crystallographically characterized Ni(II) porphyrin complexes. The most unusual difference between the two complexes was the manner in which S_4-ruffling occurred. In the monohydrate complex, the *meso*-carbons bearing the aryl groups are displaced above the porphyrin plane towards the pyridyl groups by 0.55(1) and 0.48(1)Å, while in the $CHCl_3$-solvated structure the corresponding *meso*-carbons are displaced below the porphyrin plane by -0.524(4) and -0.452(4)Å [193].

[*N*-methyltetrakis(4-sulfonatophenyl)porphyrinato]nickel(II), [Ni^{II}(*N*-Me)TSPP], has been prepared and reduced in aqueous solution. One-electron reduction was found to take place forming a transient π-radical anion, [Ni^{II}(*N*-Me)TSPP]$^{-}$, which then could undergo two competing reactions depending on the concentration of the radicals, namely (a) disproportionation and protonation to yield the two-electron reduced phlorin anion, Ni^{II}(*N*-Me)TSPPH^{-}, favoured at high radical concentrations, and (b) migration of the methyl group from the pyrrole nitrogen to the metal centre forming a Ni-C bond, and the complex MeNi^{III}TSPP. MeNi^{III}TSPP was unstable and yielded Ni^{II}TSPP and methyl radicals [194].

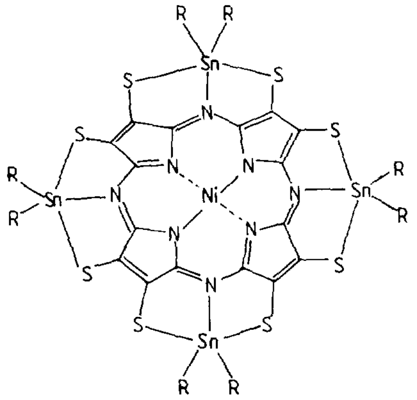
In a related study, phenyl Grignard reagent has been added to solutions of the nickel(II) monohalide complexes of *N*-methyltetraphenyl porphyrin (NCH_3TPPH) and 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin (SDPDTPH). The resultant paramagnetic (σ-phenyl)nickel(II) derivatives were characterized by means of ^1H and ^2H NMR. A homolytic cleavage of the Ni^{II}-C bond was observed for $(SDPDTP)Ni^{II}(C_6H_5)$ in toluene, with formation of the Ni^I species $(SDPDTP)Ni^I$, while decomposition of $(NCH_3TPP)Ni^{II}(C_6H_5)$ resulted in demethylation and the formation of $(TPP)Ni^{II}$ [195].

2,3,9,10,16,17,23,24-Octapropyltetrapyrazinoporphyrazine (H_2L) has been reacted with Ni(II) and the spectral and electrochemical properties of the resultant complex, [NiL], determined. Oxidation of the complex was found to be irreversible and ligand-centred, with decomposition of the complex [196].

The potentially polynucleating porphyrinic ligand, 2,3,7,8,12,13,17,18-octakis(benzylthio)porphyrazine, $(pz)(S^-)_8$, has been prepared and reacted with Ni(II) yielding the complex (**59**). This complex has the capability of coordinating further metal ions either in a didentate fashion (S,S), or a tridentate fashion (S,N,S). Reaction of the sodium salt of (**59**) with R_2Sn (R = *t*- or *n*-butyl) resulted in formation of the polynuclear complexes (**60**). The crystal structure of the *t*-butyl complex, μ-[(porphyrazine-2,3,7,8,12,13,17,18-octathiolato)nickel(II)-$(S,N,S)^4$]tetrakis(di-*tert*-butyltin(IV)), has been determined revealing an essentially square planar coordination sphere about the Ni ion, with distorted square pyramidal geometry for the Sn atoms. Relevant data are Ni-N = 1.871(3), 1.871(3), 1.873(4) and 1.873(4)Å, Sn-S = 2.595(1), 2.581(1), 2.592(1) and 2.582(1)Å, Sn-N = 2.318(3) and 2.305(3)Å and Sn-C = 2.204(5), 2.199(4), 2.196(5) and 2.198(4)Å [197].



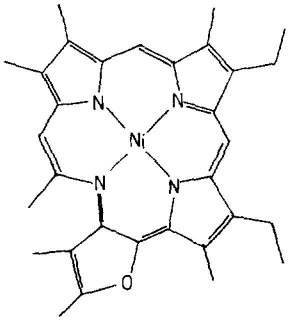
(**59**)



(R = *t*-Bu, *n*-Bu)

(60)

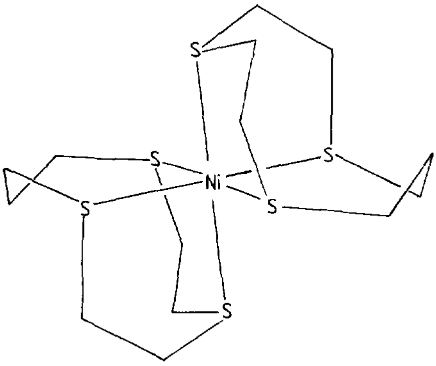
The new "furochlorophin" nickel(II) complex (**61**) has been prepared and its crystal and molecular structure determined. The nickel ion was found to be essentially coplanar with the four nitrogen donor atoms, but significant deviation from planarity was observed for the rest of the molecule, especially at the furan ring. Selected bond distances are Ni-N = 1.945, 1.902, 1.901 and 1.908Å [198].



(61)

1.4.2 Macrocycles with sulfur donor atoms

The nickel(II) complex cation of 1,4,7-trithiacyclododecane has been isolated as its perchlorate salt and characterized by single-crystal X-ray diffraction. The crystal structure revealed a distorted octahedral environment for the Ni atom which is coordinated to six S atoms, three from each ligand occupying a trigonal face (**62**). Relevant data are Ni-S = 2.403(2), 2.386(2) and 2.396(2)Å [199].

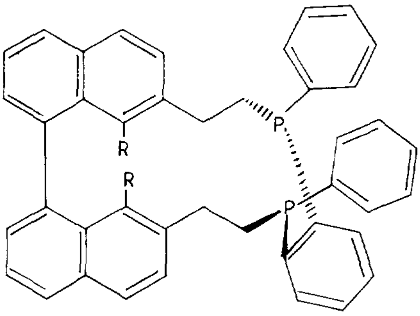


(62)

In a continuing study of nickel thioether chemistry, the synthesis of a series of nickel(II) complexes of tetra- and penta-thia macrocyclic ligands has been reported. Ligands complexed with nickel(II)tetrafluoroborate include 1,4,7,10-tetrathiacyclododecane, 1,4,7,10-tetrathiacyclotetradecane, 1,4,7,10,13-pentathiacyclopentadecane and 1,5,9,13-tetrathiacyclohexadecane. In addition, the crystal structures of $[NiL(H_2O)_2](BF_4)_2$ (L = 1,5,9,13-tetrathiacyclohexadecane) and $[NiL'](PF_6)_2$ (L′ = 1,4,7,10,13-pentathiacyclopentadecane) have been determined. $[NiL(H_2O)_2]^{2+}$ was found to have a *trans*-octahedral structure with the four S atoms of the macrocycle occupying the equatorial plane (Ni-S = 2.4290(10) and 2.4231(10)Å), with the remaining axial sites occupied by coordinated water molecules (Ni-O = 2.083(3)Å). The structure of $[NiL']^{2+}$ revealed distorted square pyramidal geometry about Ni, with the macrocycle functioning in a pentadentate S_5 donor fashion (Ni-S = 2.413(5), 2.177(6), 2.146(7), 2.169(6) and 2.198(6)Å) [200].

1.4.3 Macrocycles with phosphorus donor atoms

The diphosphacyclohexadecapentaene derivative (**63**) has been prepared and reacted with nickel(II) chloride. The crystal structure of the resultant complex, $[NiLCl_2]$, was determined, revealing a slightly distorted square planar geometry for the Ni atom (Ni-P = 2.13 and 2.14Å, Ni-Cl = 2.20 and 2.21Å). Interestingly, the NiP_2Cl_2 plane was found to be completely twisted out of the macrocycle, giving some indication of the flexibility of the complex [201].

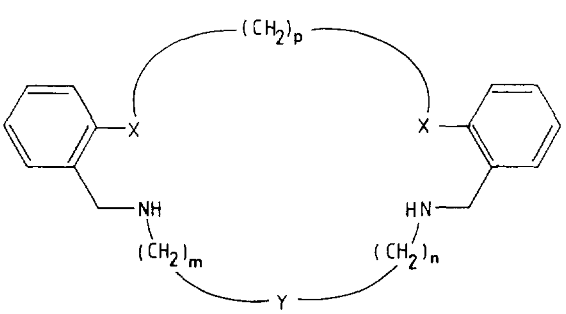


(63)

1.4.4 Macrocycles with nitrogen-oxygen donor atoms

The *N,N'*-diacetate derivatives of the 12-membered polyoxa-polyaza macrocycles, 1-oxa-4,7,10-triazacyclododecane, 1,7-dioxa-4,10-diazacyclododecane and 1,4-dioxa-7,10-diazacyclododecane, have been synthesized and complexed with a variety of transition metal ions. Stability constants were determined potentiometrically in aqueous solution. Surprisingly the Irving-Williams' order of stability was not observed in each case, with the nickel(II) complexes of 1,7-dioxa-4,10-diazacyclododecane and 1,4-dioxa-7,10-diazacyclododecane exhibiting lower stability than the corresponding Co(II) complexes [202].

In a study investigating ligand design and metal ion recognition, the interaction of Ni(II) with a variety of 16- to 19-membered mixed-donor macrocycles (**64**) has been studied. The ligands examined in this study provide an extensive array of macrocyclic structures in which the position and type of donor atom, their spacing, and the macrocyclic ring size, have all been varied in a systematic manner. Physical measurements were employed to confirm 1:1 metal:macrocycle ratio. In addition, the crystal structure of $[NiL(H_2O)](NO_3)_2$ (L = 5,6,7,8,10,11,12,13,19,20-decahydrodibenzo[*f,l*]oxadithiadiazacycloheptadecine) confirmed hexa-coordination, with distorted octahedral geometry about Ni, and the ligand functioning in a ON_2S_2 donor fashion (Ni-S = 2.413(3) and 2.370(3)Å, Ni-N = 2.086(9) and 2.078(9)Å, Ni-O = 2.063(7)Å, Ni-OH_2 = 2.113(8)Å) [203].



(X = O, NH, S; m = 2, 3; n = 2, 3, 4; p = 1, 2, 3, 4)

(64)

1.4.5 Macrocycles with nitrogen-sulfur donor atoms

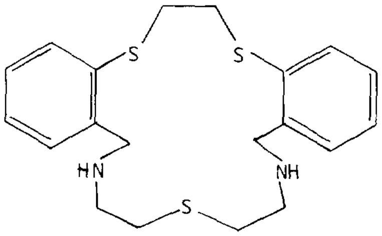
1-Thia-4,8-diazacyclodecane (L) has been prepared and complexed with nickel(II) bromide. The resultant complex, $[NiL_2]Br_2$, was found to have an essentially octahedral coordination environment, with the Ni atom coordinated in a facial manner to two N atoms and one S atom from each macrocyclic ligand. Relevant crystallographic data are Ni-N = 2.141(5) and 2.143(4)Å, Ni-S = 2.395(10Å) [204].

Complexation of the related ligands 1-thia-4,7-diazacyclononane, 1-thia-4,8-diazacyclodecane and 5-thia-2,8-diazanonane with Ni(II) has been investigated in aqueous solution. The stability constants were determined by pH potentiometry. In addition, the effect of the chelate ring size upon complex stability was investigated [205].

The synthesis, structural characterization, spectroscopic and magnetic properties of a series of complexes containing macrocyclic ligands derived from 1,5-bis(2-mercaptoethyl)-1,5-diazacyclooctane have been described. Complexes isolated include (4,8-dithia-1,11-diazabicyclo[9.3.3]heptadecane)nickel(II)bromide and (7-oxa-4,10-dithia-1,13-diazabicyclo-[11.3.3]nonadecane)iodonickel(II)X (X = iodide, tetraphenylborate). The crystal structure of (4,8-dithia-1,11-diazabicyclo[9.3.3]heptadecane)nickel(II)bromide revealed an almost ideal square planar environment for Ni(II), coordinated in three six-membered metalla rings. The chelate rings derived from the diazacyclononane portion of the ligand were found to be in chair and boat configurations, while the additional S-containing ring was in the chair configuration (Ni-N = 1.983(8) and 1.990(7)Å, Ni-S = 2.201(3) and 2.188(3)Å). However, the crystal structure of (7-oxa-4,10-dithia-1,13-diazabicyclo[11.3.3]nonadecane)iodonickel(II)(tetraphenylborate) revealed a distorted octahedral coordination environment for Ni(II), with the remaining two coordination sites being occupied by a bromide ligand and the additional ether donor atom of the macrocyclic ligand. Surprisingly, in this complex, the chelate rings derived from the diazacyclononane portion of the ligand were found to be in a chair/chair conformation (Ni-N = 2.101(5) and 2.116(5)Å, Ni-S = 2.405(2) and 2.362(2)Å, Ni-O = 2.387(5)Å, Ni-I = 2.814(1)Å) [206].

Nickel(II) perchlorate has been reacted with the 17-membered dibenzo macrocycle L (**65**). The crystal and molecular structure of the resultant complex, $[NiL(ClO_4)](ClO_4)$, was determined, revealing an octahedral coordination environment for Ni(II). The macrocycle ligand was found to function in a pentadentate N_2S_3 fashion, with the sixth coordination site occupied by an oxygen atom from the perchlorate ligand. Relevant structural data are Ni-S = 2.432(3), 2.490(4) and 2.406(3)Å, Ni-N = 2.132(10) and 2.137(9)Å, Ni-O = 2.074(8)Å) [207].

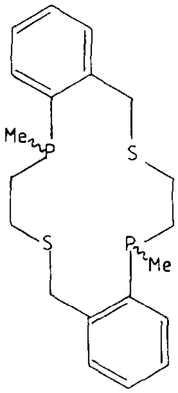
The proton NMR spectra of a series of high-spin nickel(II) monohalide complexes of tetra-21-thiaporphyrin (STPP) have been recorded and assigned using specific deuteration, methyl substitution, and line width analysis. Complexes investigated were Ni(STPP)X (X = Cl, Br, I, ClO_4). It was observed that imidazole was able to displace the halide in solution, and that the tetra-21-thiaporphyrin ligand exhited great flexibility [208].



(65)

1.4.6 Macrocycles with phosphorus-sulfur donor atoms

5,6,7,9,14,15,16,18-Octahydro-5,14-dimethyldibenzo[*e*,*l*][1,8,4,11]dithiadiphosphacyclotetradecin (**66**) has been isolated in its *R**,*R** and *R**,*S** forms. In addition, the crystal and molecular structure of the monoacetone solvate of the nickel(II) perchlorate complex of the *R**,*R** diastereomer of the macrocycle have been reported. The complex is essentially square planar with Ni-P = 2.173(2) and 2.171(2)Å and Ni-S = 2.154(2) and 2.168(2)Å [209].



(66)

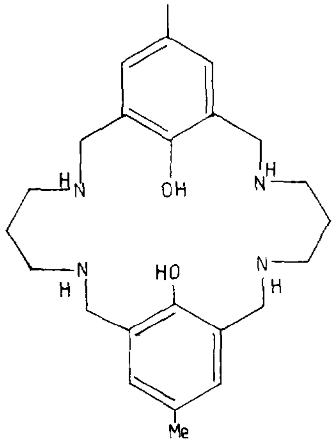
1.4.7 Polynuclear complexes containing macrocycle ligands

To conclude the section on nickel(II) macrocycle complexes and to introduce the next section which reviews polynuclear complexes, we look at polynuclear complexes which contain macrocycle ligands. There is growing interest in this area, as manifested by two reviews and a series of articles. The first review forms part of an ongoing study into the thermodynamic and structural aspects of transition metal compounds, and looks specifically at polynuclear complexes of aza-macrocycles [210]. Three modes of preparing polynuclear macrocycle complexes have been discussed. These are (a) the preparation of large macrocycles and macrobicycles able to incorporate several metal ions, (b) the preparation of bis(macrocycles), and (c) the preparation of bridged macrocyclic metal complexes. For consistency, we have generally used this classification in the discussion that follows.

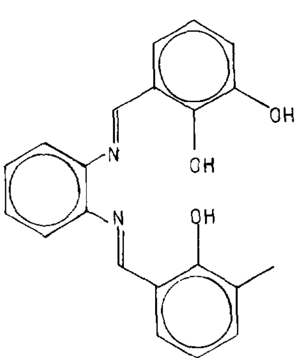
Macrocyclic Schiff base and related ligands have been used to great effect in the preparation of large macrocycles that are able to incorporate more than one metal ion. This is exemplified in an article which reviews the synthesis and application of macrocyclic and macroacyclic Schiff bases. Included in the review are aspects relating to the design and synthesis of ligands capable of organising more than two metal centres into a predetermined arrangement, in order to develop new materials [211].

The tetraazadiphenol macrocyclic ligand H_2L = (**67**) has been reacted with Ni(II) perchlorate. The resultant dinuclear complex, $[Ni_2L(MeOH)_2(ClO_4)_2].2NHEt_3HClO_4$, has been further reacted with a range of bases B = NH_3, imidazole, pyridine and pyrazine, resulting in the formation of complexes of the type $[Ni_2L(B)_2](ClO_4)_2$. With pyrazole (Hpz), the complexes $[Ni_2L(pz)(H_2O)_2]ClO_4$ and $[Ni_2L(pz)(Hpz)(H_2O)]ClO_4$, in which pz^- appears to function as a bridging ligand, were obtained. The crystal structure of $[Ni_2L(py)_2](ClO_4)_2$ was also determined, revealing two nickel(II) centres within a square-pyramidal configuration, each coordinated to a N_2O_2 donor set involving two phenoxide bridges and two *trans*-axially disposed pyridine ligands [212]. In addition, the reaction of $[Ni_2L(MeOH)_2(ClO_4)_2].2NHEt_3HClO_4$ with the amino acids glycine, β-alanine and glycylglycine has been investigated. Complexes of the type $[Ni_2L(^-O_2C\text{-}NH_3^+)\text{-}(H_2O)_2](ClO_4)_2.nH_2O$ were isolated and characterized. The crystal structure of $[Ni_2L(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2](ClO_4)_2.2H_2O$ was determined, revealing two distorted octahedral nickel(II) centres bridged by two phenoxide O atoms and two carboxylate O atoms of the zwitterionic form of glycine. The coordination sphere, NiN_2O_4, is completed by two secondary N atoms of the macrocycle ligand and a water molecule *trans*-axially disposed to the carboxylate O atom [213].

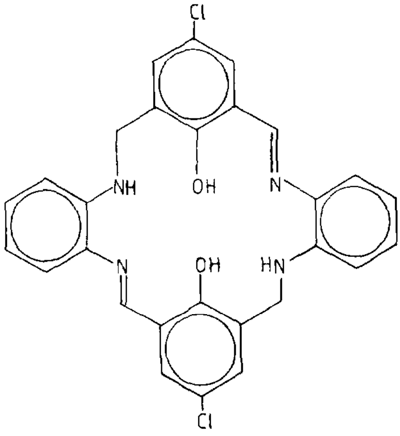
In a study investigating macrocyclic and macroacyclic compartmental Schiff bases, the synthesis, characterization and interaction with metal ions, of a number of potentially hexadentate and decadentate acyclic ligands, have been described. Ni(II) complexes that have been reported in this study include the precursor complex, $NiH_2L.1/2H_2O$ (H_4L = (**68**)), and the heterodinuclear complex, $NiCuL(Ac)_2.4H_2O$ (L = (**69**)) [214].



(67)

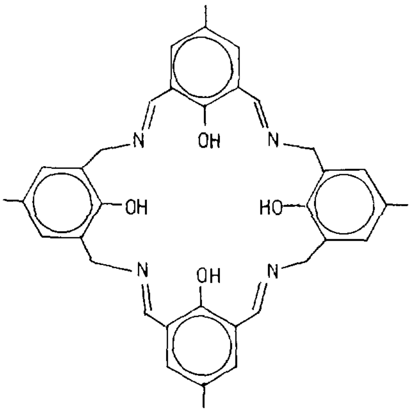


(68)



(69)

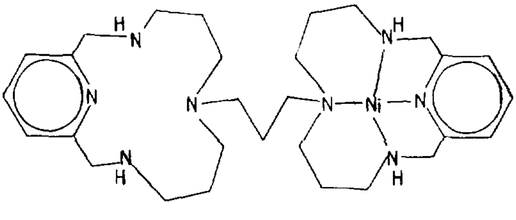
The tetranuclear complexes [$LNi_4(OH)(CH_3O.H.OCH_3)(N_3)_2(H_2O)_2$] and [$LNi_4(OH)$-($CH_3O.H.OCH_3)_3$].3.3$CH_3OH$.0.7$H_2O$ have been prepared from their parent acetato complex [$LNi_4(OH)(CH_3O.H.OCH_3)(CH_3CO_2)_2$] ($H_4L$ = (**70**)). The crystal and molecular structures were determined for both new complexes revealing an intact [$LNi_4(OH)(CH_3O.H.OCH_3)]^{2+}$ core, which was also present in the acetato complex. Similarly, both complexes contain a bowl-like [$LNi_4(OH)]^{3+}$ unit with an unusual μ_4-OH group at the bottom of the bowl, located below the centre of an approximately rectangular Ni_4 arrangement [215].



(**70**)

Turning to bis(macrocycle) complexes, the dimeric complex $[Ni_2L](ClO_4)_4$ (L = 1,1′-ene-bicyclo-3,6,10,13-tetraazatetradeca-2,13-dienylidene) has been prepared by reaction of nickel(II) cyclam with hydrogen peroxide in acidic perchlorate media. The crystal and molecular structure of the dinuclear complex cation reveal essentially square planar coordination for the nickel centres with Ni-N = 1.849(9), 1.851(8), 1.926(8) and 1.940(8)Å. The molecule as a whole can be considered as planar, with the two N_4 planes bending slightly [216].

Of particular interest is the very novel electrochemical synthesis of the "lariat" mononuclear Ni(II) complex with a bimacrocyclic ligand. The complex was prepared from the heterobinuclear complex $[CuNiL](ClO_4)_4$ (L = 7,7′-trimethylenebis[3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene]) by selective electrolytic reduction of the Cu(II) using a Hg pool. The resultant product, $[NiL](ClO_4)_2$, was isolated and characterised as the mononuclear Ni(II) complex (**71**) [217].



(**71**)

The synthesis and coordination chemistry of the potentially dinucleating ligand 1-(2′,2″-bipyridyl-5′-yl-methyl)-1,4,8,11-tetraazacyclotetradecane (L), have been reported. Reaction with *cis*-$[(bpy)_2RuCl_2]$ produced the complex cation $[Ru(bpy)_2(L)]^{2+}$ which was then further reacted with Ni(II) to produce the dinuclear complex cation $[Ru(bpy)_2(L)Ni]^{4+}$, isolated as its PF_6 salt [218]. In addition, two other groups have examined structurally related complexes. Fujita et al have examined the photophysical properties of covalently attached $Ru(bpy)_3^{2+}$ and $Nicyclam^{2+}$ complexes, including $[Ru(bpy)_2(L)Ni]^{4+}$ and a number of structurally related variously-substituted bipyridine analogues [219]. Kimura et al have prepared the 1,10-phenanthroline analogue, $[Ru(phen)_2(L)Ni]^{4+}$, isolated as its perchlorate salt. The complex was tested for photoreduction of CO_2 and appears to be an interesting hybrid molecule composed of a $Ru(phen)_3^{2+}$ subunit which acts as a photosensitizer, and a $Ni(cyclam)^{2+}$ subunit which acts as the catalytic reduction site [220].

The dinuclear complex $[\{(HL)Ni(NCS)\}_2(CO_3)](ClO_4)_2$ (L = 1-(3-dimethylaminopropyl)-1,5,9-triazacyclodecane) has been prepared and its crystal and molecular structure determined. The nickel(II) centres are octahedrally coordinated with the macrocycle binding in a facial manner. It was found that the pendent arm remains uncoordinated, with the coordination sphere being completed by an N-bonded thiocyanate and μ-bridging carbonate. Apparently this is the first example of a μ-carbonato dinickel(II) complex [221].

The reaction between the metallorganic complexes, tetramethyldibenzo[b,i]tetraaza[14]-annulenenickel(II) and tetramethyldinaphtho[b,i]tetraaza[14]annulenenickel(II), and π-cation radicals generated by the electrochemical or chemical oxidation of pyrrole, has been investigated in acetonitrile and dichloromethane. Tetramethyldibenzo[b,i]tetraaza[14]annulenenickel(II) was found to co-polymerize upon chemical oxidation, whereas tetramethyldinaphtho[b,i]tetraaza[14]annulenenickel(II) did not [222].

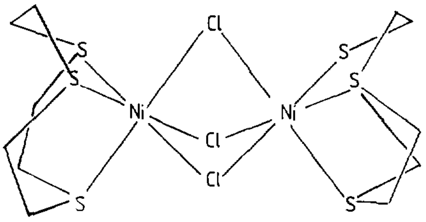
1.5 NICKEL(II) POLYNUCLEAR COMPLEXES

Polynuclear complexes constitute a growing area of interest in nickel(II) coordination chemistry. This has already been observed in the previous discussion relating to polynuclear macrocyclic complexes, and is further manifested by a review which discusses some synthetic and theoretical aspects of the chemistry of polynuclear transition-metal complexes [223]. Other aspects of polynuclear complexes that have been investigated include number of metal atoms, nature of metal atoms i.e. homonuclear and heteronuclear complexes, and the nature of bridging groups. Bridging moieties that have been used include halides, azides, sulfur- and oxo-containing ligands, polyfunctional acids and bases, and Schiff base and related ligands.

1.5.1 Homonuclear complexes

The crystal and molecular structure of tri-μ-chloro-bis(1,4,7-trithiacyclononane)dinickel(II) tetrafluoroborate acetonitrile solvate has been determined. Each nickel atoms was found to be approximately octahedrally coordinated to all three S atoms of the macrocycle and three Cl atoms. Of particular interest is the fact all three Cl atoms function as bridging groups (**72**). Ni-S bond lengths range from 2.345(3) to 2.370(3)Å, while the Ni-Cl distances range from 2.396(3) to

2.440(3)Å [224]. Similarly, an analogous triply chloride bridged complex cation, $[Ni_2(\mu\text{-}Cl)_3(thf)_6]^+$, has been isolated as its $[SnCl_5(thf)]^-$ salt. As in the previous case, the crystal structure of this cation revealed two octahedrally coordinated nickel(II) ions bridged by three Cl atoms, with the coordination sphere completed by three thf ligands. In this case Ni-O bond lengths range from 2.037(7) to 2.107(3)Å, while the Ni-Cl distances range from 2.392(3) to 2.408(3)Å [225].

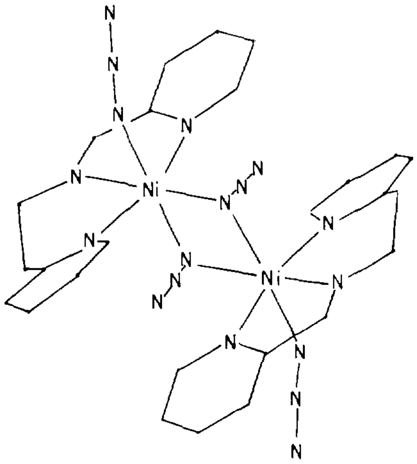


(72)

Turning to azido bridged polynuclear complexes, the crystal and molecular structure of *catena*-$[Ni_2(\mu\text{-}N_3)_3(dpt)_2](ClO_4)$ (dpt = bis(3-aminopropyl)amine) have been reported. The structure reveals what is thought to be the first nickel(II) alternating chain, with two different end-to-end azido bridges. Each Ni atom is coordinated by one dpt ligand (Ni-N = 2.076(4), 2.117(4) and 2.059(5)Å) and three azido bridging ligands in a *mer* arrangement, two of which are shared with one Ni(II) atom (Ni-N = 2.194(4) and 2.153(4)Å), with the third being shared with another Ni(II) atom (Ni-N = 2.143(4)Å) [226].

Two new octahedrally coordinated nickel(II) dimers, $[\{Ni(pepci)(N_3)_2\}_2]$ and $[\{Ni(pepci)(NCS)_2\}_2]$ (pepci = *N'*-(2-pyridin-2-ylethyl)pyridine-2-carbaldimine) have been prepared, and the crystal structure of $[\{Ni(pepci)(N_3)_2\}_2]$ determined. The structure was found to consist of isolated dimeric units in which the nickel ions are linked by two azide bridging groups in an end-on fashion. Two pepci ligands and two terminal azide groups complete the essentially octahedral coordination sphere (**73**). On the basis of this structure and spectroscopic and magnetic data, a dimeric structure involving end-to-end thiocyanate bridging groups was proposed [227].

The stepwise formation of metal(II) complexes with azide ions has been investigated in aqueous solution. Extensive polynuclear complex formation was observed with Ni(II). This behaviour was quite different from that of Zn(II), Cu(II), Cd(II) and Co(II) where only mononuclear species were observed [228].



(73)

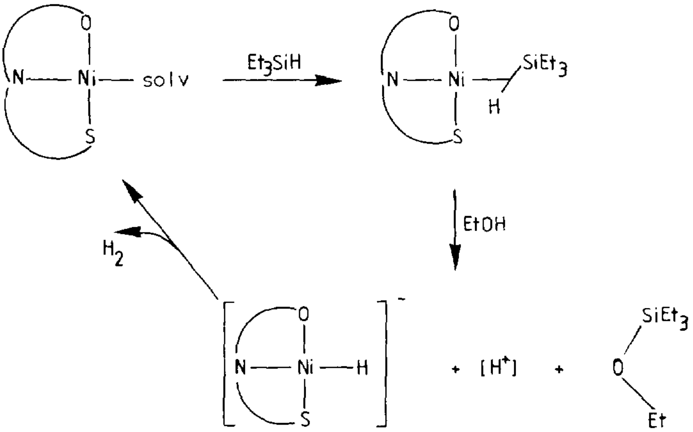
Two new complexes of Ni(II) with the tetradentate ligand *N,N'*-bis-8-quinolylethylenediamine (L) and N_3^- or NCO^- have been prepared and characterized. On the basis of spectroscopic and magnetic data, $[LNi(N_3)_2NiL](PF_6)_2$ has been assigned a dinuclear structure with two azido bridging ligands, while $[LNi(OH)(NCO)NiL](PF_6)_2.3H_2O$ has been assigned a dinuclear structure with one cyanato and one hydroxo as bridging ligands [229].

A number of complexes containing μ-hydroxo bridging ligands have been reported. The crystal and molecular structures of $[NBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)_2]$ and $[NBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)$-(μ-pyrazolato)] have been determined using single-crystal X-ray methods. The dinuclear anion $[\{Ni(C_6F_5)_2(\mu\text{-}OH)_2]^{2-}$ was found to have square planar coordination geometry about the nickel centres (Ni-O = 1.89(1) and 1.898(8)Å), whereas for $[\{Ni(C_6F_5)_2(\mu\text{-}OH)(\mu\text{-pyrazolato})]^{2-}$ the coordination geometry about the nickel centres was found to be somewhat tetrahedrally distorted from square planar (Ni(1)-O = 1.892(4)Å, Ni(1)-N = 1.916(5)Å, Ni(2)-O = 1.890(4)Å, Ni(2)-N = 1.900(5)Å) [230].

The tridentate chelating ligands 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene (L1) and 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene have been used in the preparation of the penta-coordinate complexes, $[Ni(L1)(OH)_2](ClO_4)_2$ and $[Ni(L2)(OH)_2](ClO_4)_2$, both of which contain di-μ-hydroxo bridging groups. The complexes were characterised using elemental analysis coupled with spectroscopic and magnetic measurements [231].

$[Ni(tzdt)_2]$ (tzdt = 1,3-thiazolidine-2-thionate) has been reacted with dry and wet pyridine. Reaction with dry pyridine produced the mononuclear paramagnetic complex, $[Ni(tzdt)_2(py)_2]$, which was assigned an octahedral structure. However, reaction with wet pyridine produced the tetranuclear diamagnetic complex, $[Ni_4(OH)_4(tzdt)_4(py)_4].2py$. The crystal structure of this complex was also determined, revealing a Ni_4O_4 core with four μ-hydroxo bridging groups. Each Ni atom was found to be located in a distorted octahedral environment, coordinated to three μ-hydroxo bridging O atoms (Ni-O = 2.04(1), 2.05(1) and 2.08(1)Å), one pyridine N atom (Ni-N = 2.13(1)Å), and one N and one S atom belonging to two different tzdt ligands (Ni-N = 2.11(2)*A*, Ni-S = 2.44(1)*A*) [232].

The dimeric nickel complex of salicylaldehyde thiosemicarbazone, $[Ni(tss)]_2$ (H_2tss = salicylaldehyde thiosemicarbazone), has been used as a catalyst for silane alcoholysis. $[Ni(tss)]_2$ was found to catalyze silane alcoholysis at room temperature in 50% dmso-benzene with EtOH or MeOH as substrate. The catalytic scheme proposed involves dissociation of the dimer in the presence of solvent to give a mononuclear tetracoordinate solvated complex, which then reacts *via* the mechanism shown below (**74**) to produce the silane alcohol compound [233].



(**74**)

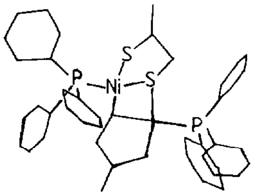
EPR studies have been carried out on the complexes $[Ni_2BPMP(O_2CC_2H_5)_2]BPh_4.CH_3COCH_3$ and $[Ni_2BPMP(O_2CCH_3)_2]ClO_4$ (HBPMP = 2,6-bis[(bis(2-pyridylmethyl)amino)methyl]-4-methylphenol). Both complexes were found to exhibit properties expected of complexes with (μ-phenoxo)bis(μ-carboxylato)dimetal cores. In addition, electronic spectra indicated an octahedral coordination environment for the two Ni ions [234].

The crystal structure of $[\{NiL(HL)\}_2](PF_6)_2.1/2MeCN.1/2Et_2O$ (HL = 6-(2-hydroxyphenyl)-2,2′-bipyridine) has been reported. The structure reveals two approximately octahedral NiL_2 units with *cis*-N_4O_2 geometries which are associated into dimers *via* strong hydrogen bonding between the phenolate O atoms of the two NiL(HL) units. Ni-N bond lengths ranged from 1.98(2) to 2.08(2)Å, while Ni-O ranged from 2.03(2) to 2.07(2)*A* [235].

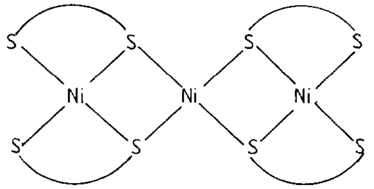
Thiolate and dithiolate ligands constitute an excellent source of S-bridging groups. The crystal and molecular structure of the nickel-thiolate dimer anion, $[(RS)Ni(\mu_2\text{-}SR)_3Ni(SR)]^-$ (R = 2,4,5-$Pr^i_3C_6H_2$), have been determined, revealing a rare face-sharing ditetrahedral geometry.

Structural data of importance are Ni-S(terminal) = 2.190(4) and 2.194(4)Å, while Ni-S(bridging) ranges from 2.267(4) to 2.324(4)Å with a mean of 2.30Å. A short Ni-Ni interaction of 2.607(3)Å was also observed [236].

In a study investigating the complexing behaviour of unsymmetrical dithiolate ligands, propane-1,2-dithiolate has been complexed with Ni(II). The crystal and molecular structure of the dimeric complex $Ni_2(PPh_3)_2(SC_3H_6S)_2$ have been reported, revealing square planar geometry for each of the Ni atoms. The coordination sphere is made up of one P atom (Ni-P = 2.193(1)Å) and three S atoms, one of which is mono-coordinated (Ni-S = 2.170(1)Å), and two of which function in a bridging fashion (Ni-S = 2.201(1) and 2.209(2)Å) (**75**) [237]. In addition, the trinuclear complex, $(Ph_4P)_2[Ni_3(SC_3H_6S)_4]$.2MeCN, has been synthesized and its crystal structure determined. In this case the anion, $[Ni_3(SC_3H_6S)_4]^{2-}$, was formed by chelation of two $[Ni_2(SC_3H_6S)_2]^{2-}$ units to a central Ni atom (**76**). The three NiS_4 planes were found to form a chair configuration with a crystallographic centre of symmetry [238].



(75)

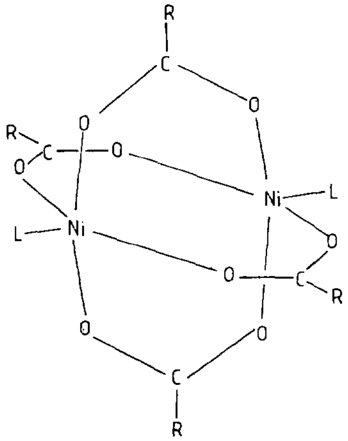


(76)

Thiolate-bridged dinuclear nickel(II) complexes, $[Ni_2(L)_2](ClO_4)_2.1/2H_2O$ and $[Ni_2(L)_2](PF_6)_2$ (HL = *N,N*-bis[2-(2-pyridyl)ethyl]-2-aminoethanethiol), have been prepared and characterized by elemental analysis, spectroscopic, and magnetic methods. In addition, the crystal structure of $[Ni_2(L)_2](ClO_4).1/2H_2O$ has also been determined, revealing a novel dinuclear structure in which one of the Ni ions is coordinated by a square planar N_2S_2 donor set (Ni-S = 2.204(3) and 2.162(3)Å, Ni-N = 1.991(8) and 1.922(8)Å), while the other has a distorted square-pyramidal N_3S_2 donor set, with the pendant pyridyl N atom at the apex (Ni-S = 2.345(3) and 2.399(3)Å, Ni-N = 2.034(7), 2.034(7) and 2.112(6)Å) [239].

The tris(thioxanthate)nickel(II) salt, $(Et_4N)[Ni(txn)_3]$, has been prepared and characterized. At ambient temperature, $[Ni(txn)_3]^-$ was found to undergo facile spontaneous decomposition, producing the dimeric complex, $Ni_2(SEt)_2(CS_3)_2^{2-}$, the structure of which was determined as its tetraethylammonium salt. It was found that each Ni centre is tetra-coordinated to two bridging thiolato S atoms (Ni-S = 2.184(4) to 2.199(4)Å) and to two S atoms of the CS_3^{2-} chelate ligand (Ni-S = 2.170(5) to 2.172(4)Å) [240].

A number of polyfunctional carboxylic acids have bee used to prepare polynuclear Ni(II) complexes. The structures of five dimeric Ni^{II} carboxylates, tetrakis(μ-2,2-dimethylpropanoato-*O,O′*)bis(2,5-lutidine)dinickel, tetrakis(μ-2,2-diphenylpropanoato-*O,O′*)-diquinolinedinickel bis-(trichloromethane), tetrakis(μ-2-methyl-2-phenylpropanoato-*O,O′*)-diquinolinedinickel, tetrakis-(μ-2,2-dimethylpropanoato-*O,O′*)-bis(2-ethylpyridine)dinickel, tetrakis(μ-2,2-dimethyl-propanoato-*O,O′*)-bis(2-picoline)dinickel and one dimeric Ni^{II} silanecarboxylate, tetrakis-(μ-methyldiphenylsilanecarboxylato-*O,O′*)-bis(triphenylphosphine)dinickel, have been determined. The complexes were all found to have a crystallographic centre of symmetry, with the coordination environment of the Ni atom being slightly distorted from square pyramidal (**77**) [241].



(L = 2,5-lutidine, R = Me_3C)
(L = quinoline, R = $MePh_2C$)
(L = quinoline, R = Me_2PhC)
(L = 2-ethylpyridine, R = Me_3C)
(L = 2-picoline, R = Me_3C)
(L = Ph_3P, R = $MePh_2Si$)
(**77**)

The synthesis and X-ray crystal structure of $[Ni_2(TPHA)(bpy))_4](ClO_4)_2$ (H_2TPHA = terephthalic acid, bpy = 2,2′-bipyridine) have been reported. The structure was found to consist of a terephthalo-bridged nickel(II) dinuclear cation, in which the terephthalato ligand is functioning in a bis didentate fashion. A distorted octahedral coordination environment was determined for each of the Ni atoms. Relevant structural data are Ni-O = 2.112(3) and 2.144(3)Å, while Ni-N ranges from 2.049(4) to 2.063(4)Å [242].

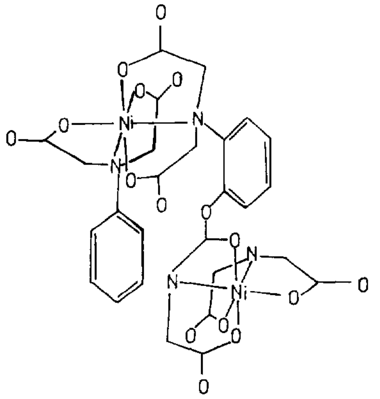
Similarly, the crystal and molecular structure of $[Ni_2(BPDTO)(\mu\text{-}C_2O_4)](NO_3)_2.2H_2O$ (BPDTO = 1,8-bis(pyridine-2-yl)-3,6-dithiaoctane) have been determined. In this case, the oxalato ligand was found to function as the bridging moiety in a bis didentate fashion. The octahderal coordination sphere is completed by the BPTDO ligands which function in a tetradentate N,S,S,N fashion [243].

The complexation of Ni(II) with oxamide-*N,N′*-diacetic acid (H_4L) has been studied by potentiometry in aqueous solution. In addition, the dinuclear complex, $[Ni_2(L)(H_2O)_6].4H_2O$, has been isolated and its crystal and molecular structure determined. Nickel ion coordination was found to be distorted octahedral with L^{4-} functioning as a bridging bis-terdentate ligand. The coordination sphere is made up of three atoms from L^{4-} and a water ligand in the equatorial plane, the two remaining axial positions being occupied by water molecules [244].

The complex $Ni_3L_2.10H_2O$ ($H_3L = (CH_2CH_2COOH)_3PO$) has been synthesized and characterized. The coordination geometry about Ni was found to be distorted octahedral [245].

The polymeric complex $[Ni(2,6\text{-DMB})_2(H_2O)_3]_n.nH_2O$ (2,6-DMB = 2,6-dimethoxybenzoate) has been reacted with a number of basic ligands, including pyridine, 4-ethylpyridine, pyrazine, 2-methylpyrazine, imidazole and 1-methylimidazole. In all cases, with the exception of pyrazine, it was found that the polymeric complex was converted to the monomeric bis-adduct complex, with the bridging water ligands being displaced by the basic ligands. In the case of pyrazine, a mono-adduct dimer was obtained in which the pyrazine ligand functions in a bridging didentate fashion [246].

The complex species formed in aqueous solution between 2,6-toluenediamine-*N,N,N′,N′*-tetraacetic acid (H_4L) and Ni(II) has been studied at 25°C. A number of species including Ni(II)(NiH_2L, $[NiHL]^-$, $[NiL]^{2-}$, $[Ni_2HL]^+$, $[Ni_2HL_2]^{3-}$ and $[Ni_2L_2]^{4-}$, have been observed, depending on the metal:ligand ratios employed. The dimer species $[Ni_2L_2]^{4-}$ has been identified for the first time in potentiometric studies and has been assigned the proposed structure (**78**) [247].

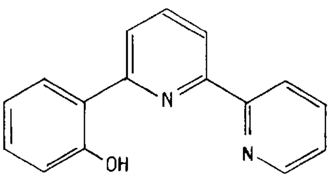


(**78**)

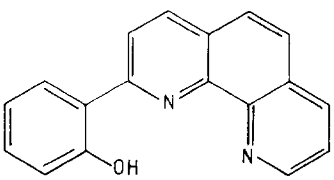
$[NiL_3](ClO_4)_2$ (L = *N,N*-dimethylethylenediamine), when dissolved in aqueous ethanol, was found to spontaneously adsorb and fix CO_2, yielding the trinuclear complex $[Ni_3L_6(CO_3)(H_2O)_4](ClO_4)_4$, the crystal structure of which has been determined. The complex cation was found to consist of three octahedral nickel(II) complexes, Λ-*cis*-(*O,O*)-$[NiL_2(CO_3)]$, and the cations Λ- and Δ-*cis*-(*O,O*)-$[NiL(H_2O)_2]^{2+}$, all joined by a novel hydrogen bonding network around the coordinating carbonate ligand. A number of analogous complexes, with variously-substituted amines including *N,N'*-dimethylethylenediamine, *N,N*-diethylethylenediamine, *N*-methylethylenediamine and, *N*-ethylethylenediamine, were tested for CO_2 uptake. The effect of the substituent was found to be fundamental to CO_2 fixation, with only the *N,N*-dimethylethylenediamine analogue being successful [248].

The crystal and molecular structure of the dimeric complex μ-dioxane-bis-[(ethanol)-bis-(hexafluoroacetylacetonato)nickel(II)] have been determined. Both nickel centres were found to possess octahedral coordination geometry, with each nickel atom bonded to two equatorial F_6acac ligands, an ethanol ligand, and a dioxane ligand which functions as the bridging moiety. Relevant structural data are Ni-O(F_6acac) = 2.019(5), 2.014(4), 2.015(5) and 2.013(4)Å, Ni-O(EtOH) = 2.032(4)Å and Ni-O(dioxane) = 2.136(4)Å [249].

Dinuclear nickel(II) complexes have been obtained from the reaction of 6-(2-hydroxyphenyl)-2,2'-bipyridine, HL^1 (**79**), and 2-(2-hydroxyphenyl)-1,10-phenanthroline, HL^2 (**80**), with Ni(II) acetate. The crystal structures of the complex cations, $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2]^+$ and $[\{NiL^1(HL^1)\}_2]^{2+}$, have been determined as their PF_6^- salts. $[Ni_2L^2_2(\mu\text{-}MeCO_2)(MeCN)_2]^+$ was found to exist as a μ-acetato, diphenoloate bridged dimer. The coordination sphere about each of the essentially octahedral Ni centres consists of two N atoms and a bridging O atom from the same ligand, and a bridging phenolate O atom from a neighbouring ligand. The remaining sites are occupied by an O atom from the bridging acetate ligand and an N atom from the coordinated MeCN ligand. However, $[\{NiL^1(HL^1)\}_2]^{2+}$ was found to consist of two near octahedral NiL^1 units, each with a *cis*-N_4O_2 donor set, held adjacent to each other by two intermolecular hydrogen bonds. The complex is unusual in that it displays both π stacking and hydrogen bonding [250].



(**79**)



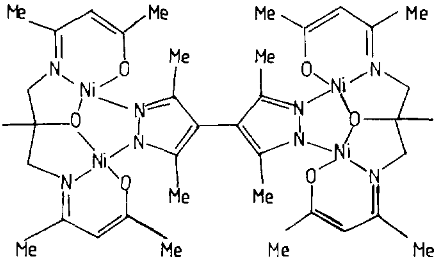
(**80**)

μ-[*N,N′,N″,N‴*-Tetrakis(2-aminoethyl)-1,1,2,2-ethanetetraamido-*N,N′:N″,N‴*]dinickel(II) has been synthesized and its structure determined by single-crystal X-ray methods. Each Ni atom was found to be coordinated by four N atoms, two amino and two amido, and exhibited square planar geometry. Relevant structural data are Ni-N = 1.912(3), 1.865(2), 1.915(3) and 1.867(2)*A* [251].

In a continuing study of the coordination chemistry sulfonyl amides, *N,N′,N″,N‴*-tetramethylsulfonyl-1,4-benzoquinonediimine-2,5-diamine (H_4L) has been prepared by the reaction of 1,2,4,5-tetraaminobenzene and methylsulfonyl chloride, and complexed with Ni(II) acetate in pyridine. The resultant complex and complex cation were assigned the molecular formulae $[Ni_2(py)_4(\mu\text{-}L)]$ and $[Ni_2(py)_4(\mu\text{-}L)]^{2+}$ respectively. The ligand functions as a tetradentate tetrabasic ligand in the former complex, and as a tetradentate dibasic ligand in the complex cation [252].

The preparation and some of the properties of the complexes of 2-methylpyrazine with metal(II) chlorides have been described. Magnetic and spectroscopic data suggest that the nickel(II) complexes have polymeric octahedral structures [253].

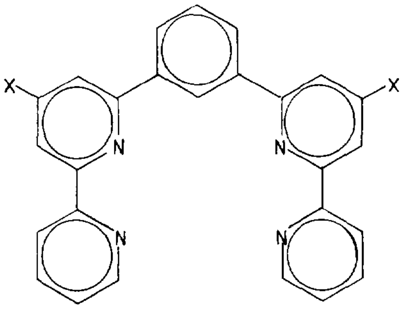
Two dinuclear Ni(II) Schiff base moieties have been linked together *via* an exogenous μ-di-3,5-dimethylpyrazolate bridge, yielding the complex $[(LNi_2)_2(mdpz)]$ (LH_3 = *N,N′*-(2-hydroxypropylene)bis(acetylacetoneimine); mdpz = 4,4′-di-3,5-dimethylpyrazole) (**81**). The crystal structure of (**81**) has also been reported confirming that the structure consists of a pair of dimers, with each Ni centre having a *trans*-square planar configuration [254].



(81)

The double helical complex $[Ni_2(spy)_2](PF_6)_4$ (spy = 2,2′:6′,2″:6″,2‴:6‴,2⁗:6⁗,2⁗′-sexipyridine) has been prepared in good yield. The synthesis involves a nickel(0)-complex templated coupling of 6-bromo-2,2′:6′,2″-terpyridine [255].

In a continuing study of molecular species which exhibit double-helical topology, the same group have prepared the new ligands, (**82**), which have been complexed with nickel(II) acetate, yielding complexes of the type $[Ni_2(OAc)_2L_2](PF_6)_2$ (L = (**82**)), after the addition of $(NH_4)PF_6$ solution. In addition, the crystal structure of $[Ni_2(OAc)_2L_2](PF_6)_2$ (L = (**82b**)) has been determined, revealing a double helical cation with each nickel(II) centre coordinated to a 2,2′-bipyridal moiety from each of two (**82b**) ligands. The coordination geometry about each Ni atom was found to be distorted octahedral with a N_4O_2 coordination sphere [256].



(**a**: X = H; **b**: X = SMe)

(**82**)

2-Pyridylcyanoxime (HL) has been prepared and complexed with Ni(II), yielding polymeric complexes with the stoichiometry NiL_2 and $NiL_2(H_2O)_2$. IR spectral data indicate that the ligand functions in a didentate fashion, with the NO group bridging *via* the O atom [257].

Similarly, a range of 8-hydroxyquinoline-5-iminoketone ligands have been complexed with nickel(II) chloride. The resultant complexes, $[NiLCl].H_2O$ (HL = 5-(2-iminocyclopentanone)-8-hydroxyquinoline, 5-(2-iminocyclohexanone)-8-hydroxyquinoline, 5-(4-imino-1-phenyl-3-methyl-5-oxo-pyrazolin)-8-hydroxyquinoline), were isolated and characterized on the basis of thermal, spectroscopic and conductiometric data. It was proposed that the ligands function in a monobasic, didentate N,O donor fashion, and that the complexes are square planar having a polymeric structure with intermolecular carbonyl bridging [258].

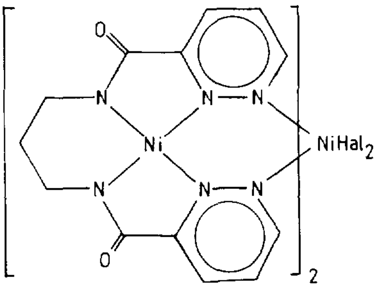
The macrocyclic thiourea ligands 1,8,10, 17-tetraazacyclo-octadecane-9,18-dithione (L), 1,10,12,21-tetraazacyclodoeicosane-11,22-dithione (L′), and imidazolidine-2-dithione (L″), have been synthesized and complexed with Ni(II). The polymeric complexes, $[Ni(L)Cl_2.H_2O]$, $[Ni(L')Cl_2.H_2O]$, and $[Ni(L'')Cl_2]$, were characterized by means of elemental analyses, a range of spectroscopic techniques, as well as magnetic and X-ray diffraction studies. In all cases a doubly-sulfur bridged structure was proposed [259].

In an ongoing study of polynuclear transition metal complexes, the reactivity of the new potentially dinucleating ligand, 2,6-diacetylpyridinebis(1′-phthalazinylhydrazone) (H_2L), towards a variety of nickel(II) salts, has been investigated. The crystal and molecular structure of the bisdeprotonated complex $[LNi]_2.dmf.H_2O$ has been reported, revealing two nickel ions at the centres of distorted octahedra. Ni-N bond distances were found to vary considerably with Ni-N(diiminic) = 1.981Å (average value) and Ni-N(heterocyclic) = 1.999Å. In addition, the adducts $\{[H_2LNi._2H_2O]$-

[2Cl]}$_2$, {[H_2LNi.$_2$dmf][2Cl]}$_2$ and {[H_2LNi.$_2$dmso][2Cl]}$_2$ were isolated, as well as the monodeprotonated species {[HLNi][Cl]}$_2$ and {[HLNi][ClO_4]}$_2$, and the undeprotonated complex [$(H_2L)_2$Ni][ClO_4]$_2$ [260].

μ-Alkoxo-μ-pyrazolato-bridged dinuclear nickel(II) complexes with 1,3-bis(salicylideneamino)-2-propanol (H_3L_a), 1,4-bis(salicylideneamino)-2-butanol (H_3L_b), and 1,5-bis(salicylideneamino)-3-pentanol (H_3L_c) have been prepared. The resultant complexes $Ni_2(L_a)$(pz), $Ni_2(L_b)$(pz) and $Ni_2(L_c)$(pz) (pz = pyrazolate anion) were isolated and characterized using a variety of analytical techniques. The crystal and molecular structures of each of the complexes were determined, revealing similar structures for all the complexes. In each case the two nickel centres are essentially square planar with bridging effected *via* an alkoxo O atom and two pyrazolate N atoms [261].

In a novel synthetic approach, the metal complexes of quadridentate bis-pyridazinecarboxamides have been used as ligands for further coordination to metal halides. Thus, the complex Ni(bpdpn)$_2$ (H_2bpdpn = *N,N'*-bis(3'-pyridazinecarboxamide-1,3-propane)) has been further complexed with $NiCl_2$, yielding the dinuclear compound {Ni(bpdpn)$_2$}$_2$$NiCl_2$, (**83**). In addition, the structurally related mixed metal complex, {Cu(bpdpn)$_2$}$_2$$NiCl_2$, was also prepared in an analogous fashion [262].

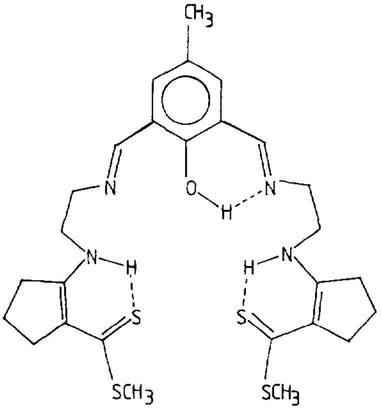


(**83**)

In a continuation of this work, the same group have prepared the dinuclear complex [Ni(bpdpn)Ni(hfacac)$_2$].CCl_4 (H_2bpdpn = *N,N'*-bis(3'-pyridazinecarboxamide-1,3-propane, Hhfacac = hexafluoroacetylacetone), the crystal structure of which has been determined. It was found that the deprotonated bis-pyridazinecarboxamide complex, Ni(bpdpn), functions as a N,N donor, complexing to the Ni(hfacac)$_2$ species *via* the 1-pyridazine N atoms, resulting in *cis*-N_2O_4 coordination to the β-diketonate species. The coordination geomtries of the Ni centres were quite different, with Ni in Ni(bpdpn) being square planar, while Ni in Ni(hfacac)$_2$ was found to be essentially octahedral [263].

Homo- and hetero-dinuclear complexes of Ni(II) with Ni(II), Cu(II) and Zn(II) have been prepared with the dinucleating Schiff base ligand (L), derived from the condensation of 2 moles of 2,6-diformyl-4-methylphenol and 1 mole of 1,3-diaminopropane. Complexes isolated include $CuNiL(ClO_4)_2.2H_2O$, $NiNiL(ClO_4)_2.3H_2O$, $NiCuL(ClO_4)_2.2H_2O$, $NiZnL(ClO_4)_2.3H_2O$, and $ZnNiL(ClO_4)_2.2H_2O$. The complexes were characterized by elemental analysis, magnetic, spectral, and electrochemical data [264]. In an extension of this work, the dinuclear Ni(II) complexes of the hexadentate Schiff base ligands derived from 2,6-diformyl-4-methylphenol, 1,3-diaminopropane, and variously-substituted anilines, have been prepared and isolated as their perchlorate salts [265].

The heptadentate ligand (**84**) (H_3L) has been synthesized by reaction of 4-methyl-2,6-diformylphenol with methyl-2-((2-aminoethyl)amino)cyclopent-1-enedithiocarboxylate. Both mono and dinuclear complexes, [NiL] and $[Ni_2L](ClO_4)$ respectively, were isolated and characterized [266].



(**84**)

A number of polymeric Ni complexes have been reported. These include the complexes of Ni(II) with poly(4-vinylpyridine) [267], poly(vinyl ketone) [268], poly(2,2′-bipyridine-5,5′-diyl) [269], 3-[2-imidazolylazo]-benzoyl-poly(ethyleneimine) [270], the homopolymer from 4-(2,2′:6′,2″-terpyridin-4′-yl)styrene, and copolymers of 4-(2,2′:6′,2″-terpyridin-4′-yl)styrene and styrene, vinyl acetate, and acrylic acid [271].

Polymer-supported Schiff base ligands have been used to complex with nickel(II). These include the Schiff base ligand prepared by reaction of chloromethylated divinylbenzene-styrene copolymer with ethylenediamine and salicylaldehyde [272], and the polystyrene-supported Schiff base derived from *o*-aminobenzyl alcohol and 3-formylsalicylic acid [273].

Finally, polymers containing β-diketonato complexes of Ni^{2+}, Cu^{2+} and Co^{3+} have been reported. The polymers were prepared from new thermotropic liquid-crystalline poly(acrylate esters) with a mesogenic didentate β-diketone in the side chain. The complexes were synthesized by reaction of the polymer with the appropriate metal chloride in the presence of base [274].

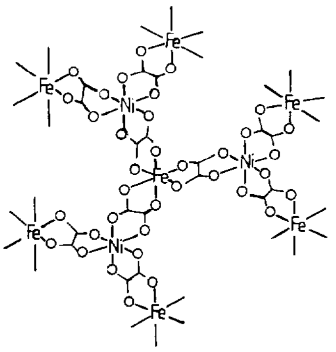
1.5.2 Heteronuclear complexes

The complexation of *N*-methyl-3-(2-ethoxymethoxy)salicylaldimine (HL) with Ni(II) has been further investigated. A number of the features of the complex NiL_2 have been examined. Previously, it was reported that the complex was able to bind Na^+ and Ni^{2+} with its flexible polyether chains, and evidence indicated a "crown-like" cage structure. However, the results of this study indicate that (a) the complex remains monomeric and square planar in acetone until only dry NaCl is added, (b) that cation binding occurs in the absence of picrate anion, and (c) that the binding constants can be determined accurately in the absence of a standard using methods usually applied to biological self-assembly [275].

A number of complexes containing Ni and Fe have been synthesized. Of particular interest are complexes which contain ferrocene as a component of the coordinating ligand. Complexes of this type that have been isolated and characterized include $NiL.nH_2O$ (H_2L = 1,1′-di(*N*-salicyloylhydrazone)ferrocene) [276], NiL (H_2L = 1,1′-bis(*N*-furoylhydrazonoethyl)ferrocene) [277], NiL_2 (HL = 1-acetylferrocene-4-phenylthiosemicabazone) [278], and NiL (H_2L = 1,1′-diacetylferrocene-bis(4-phenylthiosemicabazone)) [279]. All complexes were characterized *via* elemental analysis, IR, NMR and electronic spectra, molar conductivity, thermal analysis, and magnetic moment data.

Heterometallic nickel-containing cluster compounds with $NiFe_3Q_4$ (Q = S, Se) cores, such as $[NiFe_3Q_4(PPh_3)(SEt)_3]^{2-}$ and $[NiFe_3Q_4(SEt)_4]^{3-}$ [280], and cubane-type clusters of the type $[NiFe_3S_4]^{z+}$, including $[NiFe_3S_4(SEt)_4]^{2-}$, $[NiFe_3S_4(PPh_3)(SEt)_3]^{2-}$, and $[NiFe_3S_4(PPh_3)(Smes)_3]^{2-}$ (Smes = mesitylthiol) [281], have been prepared and their chemistry investigated. The complexes were characterized using NMR spectroscopy and single-crystal X-ray diffraction techniques.

The mixed-metal assembly $\{NBu_4[Ni(II)Fe(III)(ox)_3]\}_{3\infty}$ has been prepared and characterized. A suggested three-dimensional network structure (**85**) has been proposed on the basis of elemental analysis and magnetic susceptibility data [282].

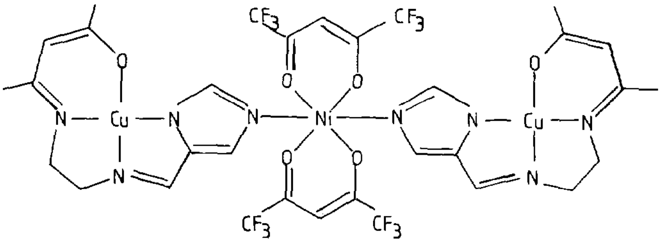


(85)

Turning to Co and Ni bimetallic complexes, the kinetics and mechanism of the reversible complex formation between (oxalato)pentaamminecobalt(III) and Ni(II) have been investigated in aqueous micellar medium, using stopped flow spectrophotometry [283]. In addition, the same reaction has been investigated in aqueous methanol (50% v/v) solution. It was postulated that the partially coordinated oxalate ligand functions as the bridging moiety [284].

The synthesis and structural characterization of the novel S-bridged complex cation $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (aet = 2-aminoethanethiolate), isolated as its chloride salt, have been reported. The complex cation was found to consist of two octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits and one nickel atom coordinated to four thiolato S atoms. The coordination sphere about Ni was revealed as markedly distorted from square planar to tetrahedral, with Ni-S = 2.208(1) and 2.199(1)Å [285].

The trinuclear imidazolate-bridged complex, $[Cu(L)Ni(hfac)_2Cu(L)]$ (H_2L = 4-(6-methyl-8-hydroxy-2,5-diazononane-1,5,7-trienyl)imidazole; Hhfac = hexafluoroacetylacetone), has been synthesized and its magnetic properties investigated. The postulated structure of $[Cu(L)Ni(hfac)_2Cu(L)]$ is shown below (**86**) [286].



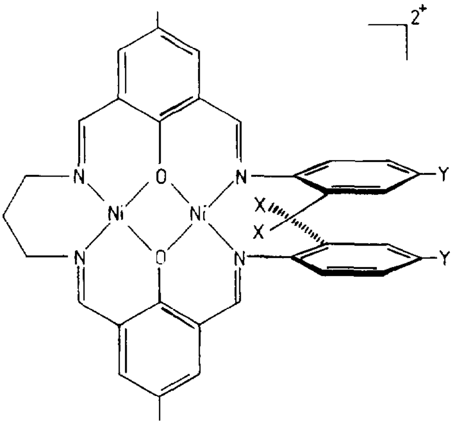
(86)

Similarly, six new [NiCuNi] heterotrinuclear complexes have been prepared and their magnetic properties examined. Complexes isolated include $\{[Ni(eth)]_2[Cu(OHpba)]\}(ClO_4)_2$, $\{[Ni(eth)]_2[Cu(Me_2pba)]\}(ClO_4)_2$, $\{[Ni(Me_3[12]N_3)]_2[Cu(OHpba)]\}(ClO_4)_2$, $\{[Ni(Me_3[12]N_3)]_2[Cu(Me_2pba)]\}(ClO_4)_2$, $\{[Ni(Me_4[12]N_3)]_2[Cu(OHpba)]\}(ClO_4)_2$ and $\{[Ni(Me_4[12]N_3)]_2[Cu(Me_2pba)]\}(ClO_4)_2$ where eth is *d,l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, $Me_3[12]N_3$ is 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene, $Me_4[12]N_3$ is 2,4,4,9-tetramethyl-1,5,9-triazacyclododec-1-ene, OHpba is 2-hydroxo-1,3-propylenebis(oxamato), and Me_2pba is 2,2′-dimethyl-1,3-propylenebis(oxamato) [287].

The crystal and molecular structure of $Cu_3[Ni(cdta)]_2(NO_3)_2.15H_2O$ (cdta = *trans*-cyclohexane-1,2-diamine-*N,N,N′,N′*-tetraacetate) have been reported. The coordination geometry about Ni was found to be distorted octahedral with the basal plane being occupied by two N atoms and two O atoms, while the axial sites are occupied by two acetate O atoms of the ligand, which functions in a hexadentate fashion. The Ni atom is bridged *via* carboxylate groups to two Cu atoms, which exhibit square planar and square pyramidal coordination spheres respectively. The remaining coordination sites of the Cu atoms are occupied by water ligands [288].

A range of $Ni^{II}Cu^{II}$ heterodinuclear complexes have been prepared and characterized. Complexes isolated in which the nickel(II) ion is octahedrally coordinated include $[Ni(cth)Cu(oxpn)](ClO_4)_2$, $[Ni(cth)Cu(2\text{-}OHoxpn)](ClO_4)_2$ and $[Ni(cth)Cu(2,2'\text{-}diMe_2oxpn)](ClO_4)_2$ (cth = *d,l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; oxpn = *N,N′*-bis-(3-aminopropyl)oxamido), while complexes in which the nickel(II) ion is pentacoordinated comprise $[Ni(L)Cu(oxpn)](ClO_4)_2$ and $[Ni(L)Cu(diMe_2oxpn)](ClO_4)_2$ where L = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene or its 9-methyl derivative [289].

The dinuclear complexes $[CuNiL](ClO_4)_2.3H_2O$, $[NiCuL](ClO_4)_2.1\text{-}3H_2O$ and $[NiZnL](ClO_4)_2.2H_2O$, where L are the dinucleating Schiff base ligands derived from the condensation of 1 mole of 2-hydroxy-5-methylbenzene-1,3-dicarbaldehyde, 1 mole of 1,3-diaminopropane, and 2 moles of *ortho*- or *para*-substituted aniline (**87**). Spectral data suggest square pyramidal coordination geometries for Ni complexes of the type $[CuNiL](ClO_4)_2.3H_2O$ and $[NiCuL](ClO_4)_2.1\text{-}3H_2O$, while octahedral geometry for Ni was suggested for the complexes $[NiZnL](ClO_4)_2.2H_2O$ [290].



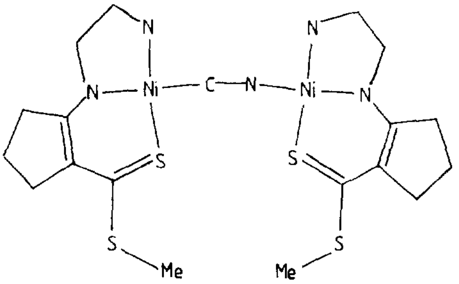
(X = H, CH_3, OCH_3, OC_2H_5, SCH_3; Y = H, OCH_3)

(**87**)

An interesting solid state reaction has been observed when [Ni(bathophen)$_3$][ZnCl$_4$].H$_2$O was heated. A colorimetric change indicated that ligand migration had occurred. This irreversible thermochromism was verified by thermal analysis and electronic spectroscopy [291].

N,N'-bis(mercaptoethyl)-1,5-diazacyclooctane (L) has been used in the preparation of a number of bimetallic complexes. The preparation and crystal structure of the pentanuclear complex, {[LNi]$_3$[ZnCl]$_2$}(BF$_4$)$_2$, have been reported. The crystal structure of this complex revealed a Ni$_3$Zn$_2$ core which contains three square planar Ni atoms and two Zn atoms in a tetrahedral configuration. Relevant data are: Ni-N = 2.01(1) and 2.01(1)Å, Ni-S = 2.183(5) and 2.189(5)Å, Zn-S = 2.361(5) and 2.348(5)Å, Zn-Cl = 2.268(8) and 2.270(9)Å [292].

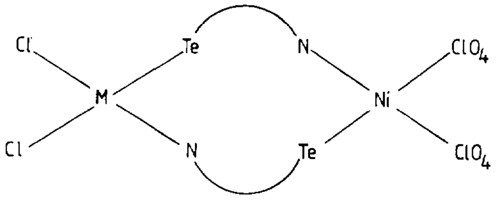
The homodinuclear complex, [Ni$_2$L$_2\mu$(CN)](ClO$_4$), and the heterodinuclear complexes, [LPd-CN-NiL](ClO$_4$) and [LNi-CN-PdL](ClO$_4$), have been prepared using the tridentate ligand methyl-2-[(2'-aminoethyl)aminocyclopent-1-enedithiocarboxylate (HL). The crystal structure of the complex cation, [LPd-CN-NiL]$^+$, was also determined as its perchlorate salt, revealing square planar geometry for both Ni and Pd. Both metals are coordinated to L *via* its N$_2$S donor set, with the remaining coordination site being occupied by the bridging cyanide group (**88**). However, the metals, as well as the C and N atoms of the cyanide group, could not be distinguished because of disorder [293].

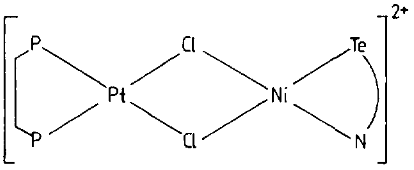


(**88**)

Tetra(4-methylpyridine-2-thiol)platinum(II)chloride, [Pt(4-mpyH)$_4$]Cl$_2$, has been reacted with nickel(II)acetate in the presence of potassium hydrogen carbonate. The resultant dinuclear complex, [PtNi(4-mpyH)$_4$(MeCN)], obtained after purification in acetonitrile, was characterized by single-crystal X-ray methods. A lantern-type structure was found with square planar PtS$_4$ coordination geometry for Pt and square pyramidal NiN$_5$ geometry for Ni. Deprotonated 4-methylpyridine-2-thiol ligands function as bridging groups with coordination to Pt *via* their S atoms (Pt-S ranges from 2.22(1) to 2.41(1)Å), and coordination to Ni *via* their N atoms (Ni-N ranges from 1.98(2) to 2.30(2)Å). The apical coordination site on Ni is occupied by a coordinated acetonitrile ligand (Ni-N = 2.13(2)Å) [294].

The compounds $[(N,Te)M(ClO_4)_2]$ (M = Pt, Pd; (N,Te) = 1-(NMe_2)-2-(TeC_6H_4OEt)-4-Me-C_6H_3) have been prepared and complexed with a number of Ni compounds. Reaction with $Ni(ClO_4)_2$ yielded the heterodinuclear complexes $[Cl_2M(\mu\text{-}N,Te)_2Ni(ClO_4)_2]$ (**89**). However, reaction of $[(N,Te)Pt(ClO_4)_2]$ with $Ni(dppe)Cl_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) yielded the heterobimetallic complex $[(dppe)Pt(\mu\text{-}Cl)_2Ni(N,Te)](ClO_4)_2$ (**90**) [295].



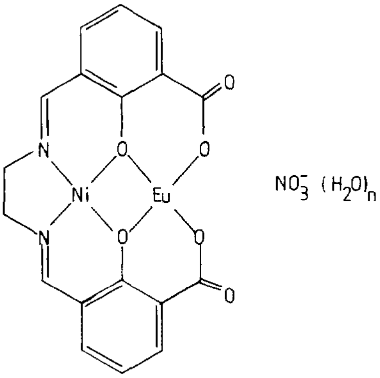


(89) **(90)**

The ability of *catena*-[(1,2-diaminopropane)cadmium(II)tetra-μ-cyanonickelate(II)] to accommodate aliphatic guest molecules has been studied. It was found that the framework of *catena*-[(1,2-diaminopropane)cadmium(II)tetra-μ-cyanonickelate(II)] forms a snake-like channel for straight chain aliphatic guest molecules such as pentane, hexane, heptane and diethylether, but changes to a nodal channel for branched aliphatic guest molecules such as tetrachloroethane, 2-chlorobutane, 1,2-dichloropropane and isopropanol [296].

The crystal structure of the novel compound $K_6Na[Ni_3(H_2O)_3PW_{10}O_{39}H_2O].12H_2O$ has been determined. The cluster anion adopts an unusual structure with an equilateral triangular Ni^{II}_3 unit, formed by three edge-sharing NiO_6 octahedra coordinated to the ligand $PW_9O_{39}^{9-}$, and a WO_6 octahedron. In addition, the tungsten atom of WO_6 was found to form a distorted $[Ni_3WO_4]$ cubane-type core with this triangular Ni^{II}_3 unit [297].

The europium(III) complex of *N,N'*-bis(3-carboxysalicylidene)ethylenediamine (H_4L), $Eu(H_2L)(NO_3).5H_2O$, has been prepared and its fluorescent spectra determined. Reaction of this compound with Ni(II) produced the dinuclear complex $NiEu(L)(NO_3).6H_2O$, the fluorescent spectra of which were also determined. The presence of the Ni(II) ion was shown to exhibit significant fluorescence quenching of Eu(III). This effect was attributed to the formation of the mixed Ni-Eu complex (**91**), in which the O atoms of the ligand function as the bridging moieties [298].



(91)

1.6 NICKEL(II) COMPLEXES WITH BIOLOGICAL LIGANDS

A substantial number of ligands with biological importance have been complexed with Ni(II). These range from simple amino acids to complex enzymes and include amino acid derivatives, peptides, coenzymes, purine bases and nucleotides. By way of introduction two articles of general interest have been published. The first reports the antifungal and antitumor activity of more than seventy five heterocyclic thiosemicarbazone ligands and a number of their metal complexes [299], while a second investigates the antibacterial activity of thiosemicarbazone derivatives and their transition metal complexes [300]. In addition, the use of nickel coordination complexes as anion-sensitive substances for anion determination in liquid samples, including blood, has been reported [301].

The complexation of a range of amino acid and amino acid derivatives with Ni(II) has been investigated. The stability constants of nickel glycinate complexes have been determined using pH titration [302], while the kinetics and thermodynamic parameters of complex formation, ligand exchange, and proton transfer of a variety of nickel(II)-amino acid complexes (amino acid = glycine, α-alanine, valine, proline, 4-hydroxyproline, histidine) have been investigated by NMR, pH titration, and spectrophotometric methods [303]. In addition, the standard molar enthalpies of formation of a series of crystalline nickel(II) amino acid complexes have been determined at 298.15K by solution-reaction calorimetry [304].

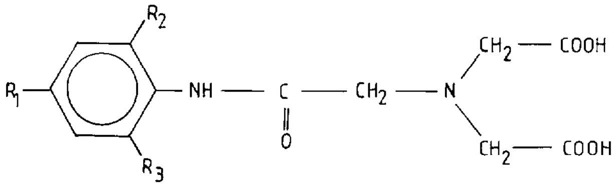
An article has appeared in which the structures and stabilities of metal(II), including Ni(II), complexes of N-protected amino acids have been reviewed. Systems discussed include binary systems in solution, ternary systems in solution, and solid state behaviour [305].

The acidity constants of protonated *N,N*-bis(2-hydroxyethyl)glycine (H_2L^+) have been measured and the interaction of the Bicenate ion, L^-, with Ni^{2+} has been studied using spectrophotometry. The stability constant of the binary complex was determined and compared with the corresponding values of the parent ligand, glycinate, and other amino acid ligands. In addition, the ternary complex containing the bicenate ion as well as adenosine 5′-triphosphate was also studied [306].

Circular Dichroism has been used to study the stereoselective formation of the complexes $[Ni(his)_2]$ (Hhis = histidine) and $[Ni(PhEt\text{-}sal)_2]$ (HPhEt-sal = *N*-(1-phenylethyl)salicylaldimine). Results indicated that a 21% excess of the mixed species of $[Ni(his)_2]$ formed, relative to the statistical amount, while a small excess was found for the complex $[Ni(PhEt\text{-}sal)_2]$ [307].

A review of hydroxamic and aminohydroxamic acids and their complexes with metal ions has been undertaken. Topics discussed include the hydroxamic group and its metal binding sites, monohydroxamic acid ligands and their metal complexes, including Ni(II), aminohydroxamic acid ligands and their metal complexes, including Ni(II), and ternary complexes of aminohydroxamic acid ligands, including Ni(II) [308]. Similarly, the Ni(II) complexes of cysteine dihydroxamic acid have been studied using pH-metric and spectrophotometric methods. The nickel complex formed in the pH range *ca* 5.5-8.5 has been assigned planar geometry with N_4 coordination [309].

The protonation and metal complex formation equilibria of *N*-(2,6-dimethylphenylcarbamoylmethyl)iminodiacetic acid and its variously-substituted analogues, (**92**), have been studied pH-metrically and compared with similar data obtained for *N*-(diethylcarbamoylmethyl)iminodiacetic acid, iminodiacetic acid and methyliminodiacetic acid. In the case of *N*-(2,6-dimethylphenylcarbamoylmethyl)iminodiacetic acid, complexes of the type NiL, $NiLH_{-1}$, NiL_2 and $NiLH_{-2}$ were observed in solution. In addition, the complexes NiL and NiH_2L_2 were isolated in the solid state [310].



($R_1 = H, R_2 = R_3 = CH_3$)

(**92**)

Electronic absorption spectra of the Ni(II) derivatives of Met121X (X = Leu, Gly, Asp, Glu) azurin mutants have been determined. LF and LMCT band shifts in the Met121 Glu proteins indicate that coordination to the metal ion occurs *via* the carboxylate functional group [311].

N-acetyldehydrophenylalanyl-*S*-proline has been reacted with Ni(II) in 95% methanol. pK values and NMR data confirmed the fact that strong coordination was occurring *via* the proline CO_2H group, while a weak interaction was observed between the metal and the amide CON groups [312].

The zinc finger peptide, CP-1, which has the sequence ProTyrLys*Cys*ProGlu*Cys*GlyLysSer PheSerGlnLysSerAspLeuValLys*His*GlnArgThr*His*ThrGly, has been complexed with Ni(II). For comparison the sequence variant CP-1(H24C)-ProTyrLys*Cys*ProGlu*Cys*GlyLysSerPheSerGlnLys SerAspLeuValLys*His*GlnArgThr*Cys*ThrGly was also studied. Spectral results obtained in the study suggest distorted Ni^{2+} complexes, consistent with Ni(imidazole)$_{2,1}$(thiolate)$_{2,3}$, rather than Ni(thiolate)$_4$ chromophores [313].

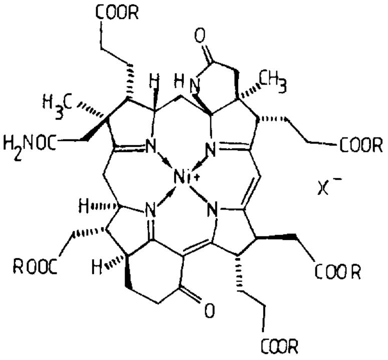
In a continuing study of metal-serum albumin structures, the structures of the nickel(II) centre in human serum albumin (HSA) and bovine serum albumin (BSA), near the isoionic point, have been investigated by UV spectroscopy. In the pH range 4.0 to 5.3 the configuration for Ni(II) was observed as square planar, with binding occurring at the *N*-terminal sequence of HSA and BSA *via* the NH_2, imidazolyl and two peptide N atoms [314].

Metalloenzymes and, in particular, Ni-containing metallo enzymes, have attracted considerable interest. This is manifested by an article which describes model studies of metalloenzymes involving metal ions as Lewis acid catalysts [315].

Factor 430, the nickel tetrahydrocorphinoid cofactor used with the enzyme methyl-coenzyme M reductase, found in many of the methanogenic bacteria which produce methane, has been the subject of a number of studies. Generally work has concentrated on synthesizing models of F430 such as, (a) nickel(I) octaethylisobacteriochlorin anion, which has been used in a mechanistic investigation of the reduction, coupling, and dehydrogenation of alkyl halides [316,317], (b) the factor F_{430}-like complex [NiL] (L = dianion of 6,8,15,17-tetramethyldibenzo[*b,i*][1,4,8,11]tetraazacyclotetradecine), which has been used to catalyze the reduction of alkyl halides by $NaBH_4$ [318], and (c) the F_{430} pentamethyl ester (**93**), which has been utilized to catalyze the reductive cleavage of sulfonium ions [319].

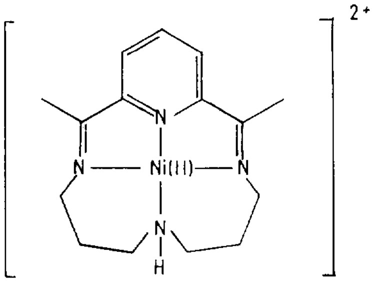
Considerable work has been published concerning the nickel coordination site in hydrogenase enzymes. Mascharak and co-workers have concentrated on complexes that model the active site(s) in [FeNi] hydrogenases. In their search for a model of the active site in [FeNiSe] hydrogenase they have prepared and characterized the complexes $[Ni(terpy)(2,4,6\text{-}(Me)_3C_6H_2Se)_2]$ (terpy = 2,2′,2″-tripyridine), $[Ni(terpy)(PhSe)_2]_2.CH_3CN$, $[Ni(dmp)(2,4,6\text{-}(Me)_3C_6H_2Se)_2]$ (dmp = 2,9-dimethyl-1,10-phenanthroline), and $[Ni(dmp)(PhSe)_2]_2.CH_3CN$. They report that the Ni-Se bond distances varied only slightly in these complexes, with the average Ni-Se distances of 2.440(3) and 2.436(1)Å being very close to the Ni-Se distance reported for *D. baculatus* hydrogenase [320].

Similarly, they have prepared a set of complex analogues of composition [Ni(terpy)(SR)$_2$] (R = C_6F_5, 2,4,6-(*i*-Pr)$_3C_6H_2$, 2,6-(Me)$_2C_6H_3$), that contain a trigonal bipyramidal NiN_3S_2 chromophore. X-ray absorption spectroscopic data for these analogues were found to match well with those reported for the nickel site in the [FeNi] hydrogenase from *Thiocapsa roseopersicina* [321]. In addition, the complex [Ni(DAPA)(SPh)$_2$] (DAPA = 2,6-bis[(1-phenylimino)ethyl]pyridine), which contains a trigonal bipyramidal NiN_3S_2 chromophore, has been prepared, characterized and its redox behaviour investigated. Both oxidation and reduction of this model compound were found to proceed readily with biologically relevant oxidants and reductants [322].



(93)

In an attempt to develop a functional model of hydrogenase, the electrocatalytic reduction of protons to dihydrogen, using the nickel macrocyclic complex (94), has been investigated. In a discussion of the mechanism of reduction and its biological relevance, a five-coordinate Ni^{III}-H species was proposed as the active form in the redox cycle [323].



(94)

Turning to dehydrogenases, in an on-going study of transition metal complexes with sulfur ligands, and, in particular, CH_3 complexes with [NiS] fragments as models for CO dehydrogenase, the synthesis and properties of $[NiL_2]$ and $[Ni(CH_3)L_2]^-$ (L^- = *o*-(methylthio)thiophenolate(1-)) have been reported. The crystal and molecular structures of these complexes were determined revealing a planar $[NiS_4]$ core for $[NiL_2]$ and a planar $[NiS_3C]$ core for $(NMe_4)[Ni(CH_3)L_2]$.MeOH, with one thioether group uncoordinated. Reaction of CO with $[NiL_2]$ was unsuccessful, while $[Ni(CH_3)L_2]^-$ was found to undergo immediate reaction with CO [324].

An article has appeared in which the discovery of a labile Ni ion, required for CO/Acetyl-CoA exchange activity in the NiFe complex of carbon monoxide dehydrogenase from *Clostridium. thermoaceticum*, has been reported. It was found that the Ni ion in the NiFe complex could be removed and replaced reversibly, and that the loss of Ni does not significantly change the protein structure [325].

Two-dimensional ^1H NMR studies of the paramagnetic metalloenzyme, copper-nickel superoxide dismutase (Cu_2Ni_2SOD), have been undertaken. These studies confirm the proposed structure of the active site in bovine Cu_2Ni_2SOD, which is thought to consist of a Cu ion bound to four histidine groups, one of which functions as the bridging moiety to a Ni ion, and a water molecule. The Ni ion is in turn bound to the bridging histidine ligand, two other histidine groups, and one aspartine residue [326].

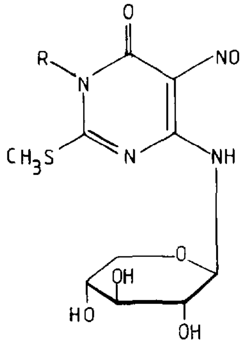
The binding of acetazolamide, *p*-fluorobenzenesulfonamide, *p*-toluenesulfonamide, and sulfanilamide to nickel(II)-substituted carbonic anhydrase has been studied using ^1H NMR and electronic absorption spectroscopy. These inhibitors were found to bind to the metal ion, forming 1:1 complexes, verified by NMR data showing a number of isotropically shifted signals corresponding to the histidine ligands [327].

Moratal and co-workers have investigated various aspects of nickel(II) carboxypeptidase, including a spectroscopic characterization of nickel-substituted carboxypeptidase using electronic and ^1H NMR spectroscopy, and comparing it with available X-ray data. The interaction with D-phenylalanine and azide has been investigated. It was found that D-phenylalanine binds first at a non-metallic site and then to the metal, while azide binds directly at the metal in the presence of the amino acid [328]. In addition, they have investigated the interaction between nickel-substituted carboxypeptidase A and a number of inhibitors, including phosphate and pyrophosphate [329], and a number of carboxylates [330]. Phosphate and pyrophosphate were found to bind directly to the metal under rapid-exchange conditions, whereas binding of the carboxylate was dependent on the particular carboxylate used. β-Phenylpropionate was found to bind at a non-metallic site, whereas phenylacetate and acetate bound directly to the metal.

Nickel peroxide has been used to cleave *N*-benzoylamino acid methyl esters to give benzamide, with high selectivity for reaction of the glycine derivative. This process is analogous to that catalyzed by peptidylglycine α-amidating monooxygenase [331].

Turning to purine base and related ligands, 6-hydroxypurine has been complexed with Ni(II). Both 1:1 cationic and 1:2 neutral complex species were observed and their stabilities determined using electrochromatography [332].

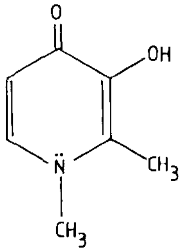
Metal complexes of 1,6-dihydro-2-methylthio-5-nitroso-6-oxo-4-xyloylaminopyrimidine (**95a**) and 1,6-dihydro-1-methyl-2-methylthio-5-nitroso-6-oxo-4-xyloylaminopyrimidine (**95b**) have been prepared and characterized using a variety of spectroscopic, magnetic and thermal techniques. In the nickel complexes $[Ni(L)_2(NO_3)_2].4H_2O$ (L = (**95a**) and (**95b**)), the ligands were found to coordinate in a chelating fashion *via* the O atom situated at C6 and the N atom of the NO group situated at C5 of the pyrimidine rings [333].



(**a**: R = H; **b**: R = CH_3)

(**95**)

The stepwise stability constants of the 1:1, 2:1, and 3:1 complexes of the didentate ligand 1,2-dimethyl-3-hydroxy-4-pyridinone (DMHP = (**96**)) with divalent and trivalent metal ions have been determined in KCl supporting electrolyte. Ni(II) was found to form stable 1:1 and 1:2 complexes with DMHP [334].



(**96**)

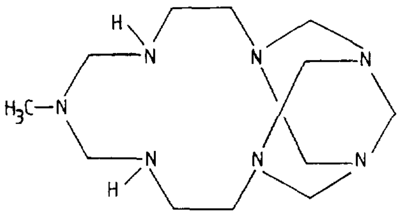
Nickel(II) macrocyclic complexes have been used to promote DNA oxidation. Oxidation of accessible guanine residues in deoxyoligonucleotides, using $KHSO_5$ as oxidant, was found to be highly dependent upon the macrocycle ligand employed. Factors that were of particular importance were ring size, degree of unsaturation, steric bulk, redox potential, in-plane ligand field strength, and conformational flexibility [335].

Similarly, the cleavage of plasmid DNA by a variety of square planar nickel complexes, in the presence of either magnesium monoperoxyphthalic acid (MPPA) or iodosylbenzene, has been reported. Ni(salen) (salen = bis(salicylaldehyde)ethylenediimine) or $Ni(CR)^{2+}$ (CR = 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene) promoted complete conversion of the coiled plasmid to the nicked circular form in 5 minutes with MPPA or iodosylbenzene as oxidant. These complexes are being investigated further as possible DNA cleavage agents [336].

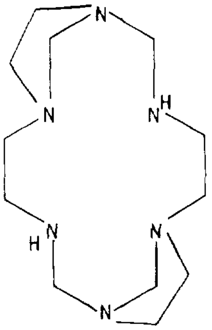
1.7 NICKEL(I)

Phosphines and macrocyclic ligands have been used extensively in the stabilization of Ni in the +1 oxidation state. The influence of steric bulk on the relative stability and interchangeability of the various oxidation states for nickel complexed to 1,2-bis(dialkylphophino)benzene (alkyl = Me, Et, *i*-Pr, *n*-Pr) has been investigated. The reduction potentials and electrochemical reversibilities of these complexes were found to be highly sensitive to the steric bulk of the substituents, with potentials for electrooxidation being shifted to more positive potentials as the bulk of the alkyl substituent was increased [337].

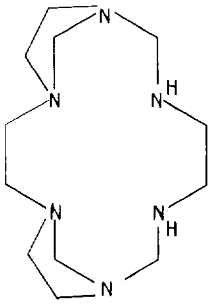
Square planar Ni(I) complexes of the saturated polyaza macrotricyclic ligands (**97**)-(**103**) have been prepared by reduction of the Ni(II) complexes with Na(Hg) in acetonitrile. The crystal and molecular structures of $[Ni(L)]ClO_4$ (L = (**97**), (**99**)) were determined. Both complexes were found to have essentially square planar coordination geometry, although $[Ni(L)]ClO_4.CH_3CN$ (L = (**97**)) did reveal some square pyramidal distortion, while $[Ni(L)]ClO_4$ (L = (**99**)) revealed partial tetrahedral distortion [338].



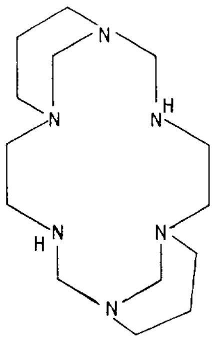
(**97**)



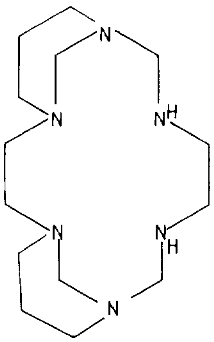
(**98**)



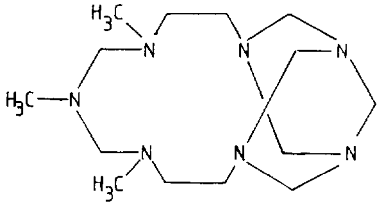
(99)



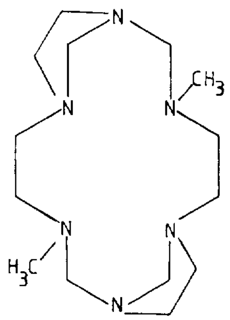
(100)



(101)



(102)



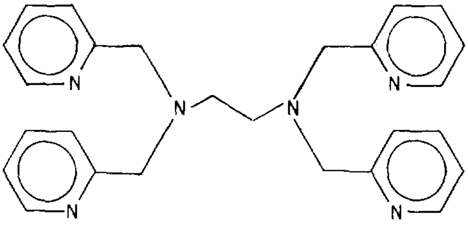
(103)

The relationship between half-wave potential, the site of electron transfer, and the catalytic activity of a given $[(P)Ni]^-$ complex ((P) = porphyrin) towards CH_3I reduction has been investigated for seven nickel(II) porphyrin complexes. Five of the seven electrogenerated complexes, $[(P)Ni]^-$, reacted catalytically with CH_3I, under an applied potential, suggesting the presence of Ni(I) in the singly reduced $[(P)Ni]^-$ derivatives [339].

Ni(I) macrocycle complexes have been used as electron transfer catalysts in the radical cyclization of halogeno ethers. The Ni(I) macrocycle complexes were generated electrochemically from their corresponding Ni(II) complexes, which resulted in enhanced catalytic activity relative to those generated by reduction with Zn or Mn metal [340].

Ab initio MO/SD-CI calculations of several Ni^I- and Ni^{II}-CO_2 complexes have been performed, and the results indicate that CO_2 should be able to coordinate to $Ni^IF(NH_3)_4$, yielding a stable η^1-CO_2 complex, but not to $[Ni^{II}F(NH_3)_4]^+$, $[Ni^I(NH_3)_4]^+$ or $[Ni^I(NH_3)_5]_+$. In addition, the coordinated CO_2 in $Ni^IF(NH_3)_4(\eta^1$-$CO_2)$ is activated to electrophilic attack and should undergo facile protonation, followed by OH^- dissociation and eventually dissociation of CO. It is noted that these results support Sauvage's reaction mechanism of electrocatalytic reduction of CO_2 by $NiCl_2$(cyclam) [341].

Potentially hexadentate *N,N,N′,N′*-tetrakis(2-pyridylmethyl)ethylenediamine (tpen) (**104**) has been reacted with Ni(II), yielding the complex, $[Ni(tpen)](ClO_4)_2.2/3H_2O$, the crystal structure of which has been determined. This complex has been further reduced to the Ni(I) complex [342].



(104)

The synthesis, structure, and fluxionality, of the dinickel(I) complex, $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ (dppm = $Ph_2PCH_2PPh_2$), have been described. $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ was prepared by reaction of the Ni(0) complex, $[Ni_2(CO)_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$, with the Ni(II) complex, $[NiCl_2(dppm)_2]$. The crystal and molecular structure of $[Ni_2Cl_2(\mu\text{-}CO)(\mu\text{-}dppm)_2]$ have been determined, revealing two different Ni centres, one essentially square planar, and the other roughly trigonal bipyramidal. In addition, a Ni-Ni interaction of 2.617(1)Å was observed [343].

1.8 NICKEL(0)

Phosphine and related ligands continue to be used in the stabilization of nickel in the zerovalent oxidation state.

The synthesis and characterization of the new Ni(0) complexes, Ni(L), $Ni(L)C_7H_8$ (L = 1,2-bis(dicyclohexylphosphino)ethane (dcpe); 1,3-bis(dicyclohexylphosphino)propane (dcpp); 1,4-bis(dicyclohexylphosphino)butane (dcpe)), $Ni_2(dcpe)_3$, $Ni_2(dcpb)_3$, $Ni(dcpe)_2$, and $Ni(depe)_2$ (depe = 1,2-bis(diethylphosphino)ethane), have been described. The electronic spectra of these complexes have also been discussed [344]. Work on these complexes has been extended by a further study which looks at the reaction of the Ni(0) complexes with carbon dioxide. In addition, the reactions of $Ni(dcpp)CO_2$ and $Ni(dcpb)CO_2$ with dioxygen have also been described [345].

^{31}P and ^{13}C NMR in solid state and solution have been used to determine a direct correlation of the modes of bonding of CO_2 in $Ni(PCy_3)_2CO_2$. It was found that, in solution at 173K, CO_2 is η^2-CO bonded to nickel, and that the ^{31}P and ^{13}C chemical shifts were almost identical to the values found in the solid state. However, a dynamic process averages, in solution, the two P atoms at room temperature *via* an intramolecular motion [346].

Pseudopotential *ab initio* calculations have been carried out on the complexes L_3NiSO_2 (L = phosphine) to investigate the influence of coligands on the η^1-coordination mode of SO_2. It was shown that the mode of coordination is very sensitive to the electronic and steric influences of the phosphine ligands [347].

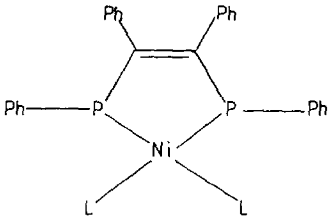
Ab initio restricted Hartree-Fock and configuration calculations have been carried out on the system, $Ni(PH_3)_2 + CH_4$, with a view to studying the energetics and mechanism of the oxidative addition reaction of CH_4, and to model the activation of the C-H bond by zerovalent, coordinatively unsaturated transition-metal complexes. Results showed that the oxidative addition of methane to $Ni(PH_3)_2$ is endothermic by 7.0 kcal/mol, and that the planar *trans* product is the most stable, being lower in energy than the *cis* isomer by 3.4 kcal/mol [348].

Similarly, force constant calculations have been carried out for $Ni(PBr_3)_4$ using simple valence force field with interaction constants. Force constant values were compared for the coordinated and free ligand, and also with *k*(Ni-P) stretching in the series of molecules $Ni(PX_3)_4$ (X = F, Cl, Me). It was found that the *k*(Ni-P) stretching force constant was lowest for $Ni(PBr_3)_4$ in the series [349].

The zerovalent complex $[Ni\{P(CH_2OH)_3\}_4]$ has been prepared by the reaction of $P(CH_2OH)_3$ with $[Ni(cod)_2]$ in toluene. $[Ni\{P(CH_2OH)_3\}_4]$ was characterized as tetrahedral, using elemental analysis and NMR spectroscopy, as well as the crystal structure of its analogous Pd complex. The complex is similar to its PMe_3 and PEt_3 analogues in many respects, with the main differences being enhanced water solubility, increased stability of the low oxidation state, and high coordination number [350].

A number of nickel(0) complexes with 2-methoxyphenyl phosphite ligands have been prepared and characterized. These include $[Ni(\eta^2\text{-}C_2H_4)\{P(OC_6H_4OMe\text{-}2)_3\}_2]$, $[Ni\{P(OC_6H_4OMe\text{-}2)_3\}_3]$, and $[Ni\{P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2\}_4]$. In addition, the catalytic activity of $[Ni\{P(OC_6H_4OMe\text{-}2)_3\}_3]$ and $[Ni\{P(OC_6H_4OMe\text{-}2)(OC_6H_4Me\text{-}4)_2\}_4]$ for the monohydrocyanation of buta-1,3-diene have been discussed [351].

The insertion of NiL_2 (L = phosphine) into the P-P bond of 1,2,3,4-tetraphenyl-1,2-dihydro-1,2-diphosphate has been achieved using two methods. The first involves cleavage of the P-P bond, after which the derivatized dianion was allowed to react with $[NiCl_2L_2]$. This yielded a nickeladiphospholene complex, (**105**), with a distorted square planar geometry at the metal centre, in which the chelating ligand acts as a two electron donor, and the metal is formally in the +2 oxidation state. The second method involves direct insertion of a NiL_2 fragment into the P-P bond at low temperature. In this case, results indicated the formation of a 1,4-diphosphadiene complex of Ni(0), in which the ligand functions as a four electron donor, and the geometry of the metal is tetrahedral [352].



(105)

$(CF_3P)_4$ and $(CF_3P)_5$ have been reacted with a number of zerovalent tertiary phosphine nickel complexes. Generally η^2-CF_3PPCF_3 complexes of the formula $L_2Ni(CF_3PPCF_3)$ were obtained. Complexes were characterized using NMR spectroscopy and single-crystal X-ray methods [353].

Ni(dppe)(edt) (dppe = $Ph_2PCH_2CH_2PPh_2$, edt = ethanedithiolate) has been reacted with Cp_2ZrH_2. Spectroscopic evidence suggests that the nickel(0) complex $Cp_2Zr(edt)(dppe)$ had formed, with concomitant evolution of hydrogen. However, attempts to crystallize this complex were unsuccessful [354].

The synthesis and structures of $[Ni(Pt\text{-}Bu)_6]$ and $[Ni_5(Pt\text{-}Bu)_6(CO)_6]$ have been reported. Diamagnetic $[Ni(Pt\text{-}Bu)_6]$ was prepared simply by reaction of $NiCl_2$ with $P(SiMe_3)_3$ and $P(t\text{-}Bu)_3$, while $[Ni_5(Pt\text{-}Bu)_6(CO)_6]$ was prepared by reaction of $P(t\text{-}Bu)_3$ with $[Ni(CO)_4]$. The crystal and molecular structures of both complexes have also been determined [355]. Also of interest is an article entitled "$[Ni(Pt\text{-}Bu)_6]$ - a strain on the 18 electron rule", in which the electronic structure of this complex has been discussed [356].

REFERENCES

1 G.A. Foulds, A.M.A. Bennett, D.A. Thornton, S.J. Brown, L.M. Clutterbuck, C Hinton, G.B. Humphreys and A.F. Masters, *Polyhedron*, 11 (1992) 1285.

2 A.J. Seen, K.J. Cavell, A.M. Hodges and A.W.-H. Mau, *J. Chem. Soc., Dalton Trans.*, (1992) 1381.

3 J.P. Cornelissen, E. Muller, P.H.S. Vaassens, J.G. Haasnoot, J. Reedijk and P. Cassoux, *Inorg. Chem.*, 31 (1992) 2241.

4 J.M. McConnachie, M.A. Ansari and J.A. Ibers, *Inorg. Chim. Acta*, 198-200 (1992) 85.

5 M.B. Davies, *Polyhedron*, 11 (1992) 285.

6 J.B. Chlistunoff and A.J. Bard, *Inorg. Chem.*, 31 (1992) 4582.

7 S.J. Dunne, R.C. Burns and G.A. Lawrance, *Aust. J. Chem.*, 45 (1992) 1943.

8 H. Straatemeier, M.A. Hitchman, D.L. Kepert, B.W. Skelton, K.E. Sugars and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1992) 3035.

9 A.M. De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, P. Pallavicini and A. Poggi, *NATO ASI Ser.*, (1992) 87; *Chem. Abstr.* 118 (1992) 2859q.

10 J. Evans, W. Levason and R.J. Perry, *J. Chem. Soc., Dalton Trans.*, (1992) 1497.

11 R.I. Haines and S.J. Northcott, *Can. J. Chem.*, 70 (1992) 2785.

12 A. Meshulam, H. Cohen, R. Van Eldik and D. Meyerstein, *Inorg. Chem.*, 31 (1992) 2151.

13 R. Sarala and D.M. Stanbury, *Inorg. Chem.*, 31 (1992) 2771.

14 B. Sonnberger, P. Huhn, A. Wasserburger and F. Wasgestian, *Inorg. Chim. Acta*, 196 (1992) 65.

15 P.J. Lukes, A.C. McGregor, T. Clifford and J.A. Crayston, *Inorg. Chem.*, 31 (1992) 4697.

16 G.A. Zvereva and G.M. Larin, *Zh. Neorg. Khim.*, 37 (1992) 147.

17 J.D. Franolic, W.Y. Wang and M. Millar, *J. Am. Chem. Soc.*, 114 (1992) 6587.

18 T. Krueger, B. Krebs and G. Henkel, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 54.

19 A.J. Blake, R.O. Gould, M.A. Halcrow, A.J. Holder, T.I Hyde and M. Schroeder, *J. Chem. Soc., Dalton Trans.*, (1992) 3427.

20 J.P. Cornelissen, J.G. Haasnoot, J. Reedijk, C. Faulmann, J.-P. Legros, P. Cassoux and P.S. Nigrey, *Inorg. Chim. Acta*, 202 (1992) 131.

21 S.B. Choudhury, D. Ray and A. Chakravorty, *J. Chem. Soc., Dalton Trans.*, (1992) 107.

22 S.E. Schadler, C. Sharp and A.G. Lappin, *Inorg. Chem.*, 31 (1992) 51.

23 S. Chandrasekhar and A. McAuley, *Inorg. Chem.*, 31 (1992) 2234.

24 E. Jona, J. Kozisek, M. Koman and R. Boca, *Polyhedron*, 11 (1992) 573.

25 M.C. Chakravorti and G.V.B. Subrahmanyam, *Can. J. Chem.*, 70 (1992) 836.

26 R.E. Bachman, K.H. Whitmire, S. Mandal and P.K. Sharadwaj, *Acta Cryst.*, C48 (1992) 1836.

27 L. Lavelle, *J. Chem. Soc., Dalton Trans.*, (1992) 3511.

28 L. Jaeger, A.Kolbe, K. Polborn, W. Beck, M. Hvastijova, *Z. Anorg. Allg. Chem.*, 617 (1992) 117.

29 W.L. Darby, R.J. Butcher and L.M. Vallarino, *Inorg. Chim. Acta*, 194 (1992) 113.

30 G. Alzuet, S. Ferrer, J. Borras, A. Castineiras, X. Solans and M. Font-Bardia, *Polyhedron*, 11 (1992) 2849.

31 M. Koman, E. Jona and E. Durcanska, *Acta Cryst.*, C48 (1992) 1652.

32 F. Mani, *Coord. Chem. Rev.*, 120 (1992) 325.

33 T.B. Rauchfuss, S. Dev, and S.R. Wilson, *Inorg. Chem.*, 31 (1992) 154.

34 E. Gutierrez, S.A. Hudson, A. Monge, M.C. Nicasio, M. Paneque and E. Carmona, *J. Chem. Soc., Dalton Trans*, (1992) 2651.

35 S. Soyama, M. Ishii, S. Funahashi and M. Tanaka, *Inorg. Chem.*, 31 (1992) 536.

36 J. Maslowska and J. Szmich, *Collect. Czech. Chem. Commun.*, 57 (1992) 263.

37 W. Linert, A. Taha and R.F. Jameson, *J. Coord. Chem.*, 25 (1992) 29.

38 D.A. Thornton and G.M. Watkins, *J. Coord. Chem.*, 25 (1992) 299.

39 N.K. Labhsetwar and O.P. Shrivastava, *Can. J. Chem.*, 70 (1992) 1927.

40 A. Decinti, M. Contreras, E. Moraga and G. Larrazabal, *Polyhedron*, 11 (1992) 1235.

41 K. Riggle, T. Lynde-Kernell and E. O. Schlemper, *J. Coord. Chem.*, 25 (1992) 117.

42 N.N. Gerasimchuk, V.V. Skopenko, K.V. Domasevich and O. Zhmurko, *Ukr. Khim. Zh.*, 58 (1992) 935; *Chem. Abstr.*, 118 (1992) 246238d.

43 J.P. Cornelissen, J.H. van Diemen, L.R. Groeneveld, J.G. Haasnoot, A.L. Spek and J. Reedijk, *Inorg. Chem.*, 31 (1992) 198.

44 N. Saha, A Saha, S. Chaudhuri, T.C.W. Mak, T. Banerjee and P. Roychoudhury, *Polyhedron*, 11 (1992) 2341.

45 A. Mahamadou, J.-P. Barbier and R.P. Hugel, *Polyhedron*, 11 (1992) 2697.

46 N. Yasuda, H. Kokusen, Y. Sohrin, S. Kihara and M. Matsui, *Bull. Chem. Soc. Jpn*, 65 (1992) 781.

47 S. Trofimenko, J.C. Calabrese, and J.S. Thompson, *Inorg. Chem.*, 31 (1992) 974.

48 J.C. Calabrese and S. Trofimenko, *Inorg. Chem.*, 31 (1992) 4810.

49 S. Trofimenko, J.C. Calabrese, J.K. Kochi, S. Wolowiec, F.B. Hulsbergen and J. Reedijk, *Inorg. Chem.* 31 (1992) 3943.

50 Y. Couturier and C. Petitfaux, *Bull. Soc. Chim. Fr.*, 129 (1992) 335.

51 C. Arana, S. Yan, M. Keshavarz-K, K.T. Potts and H.D. Abruna, *Inorg. Chem.*, 31 (1992) 3680.

52 T. Hirose, K. Hiratani, K. Kasuga, K. Saito, T. Koike, E. Kimura, Y,. Nagawa and H. Nakanishi, *J. Chem. Soc., Dalton Trans.* (1992) 2679.

53 B. Song, Q.-Y. Zhang, Y.-T. Chen and R.K. Murmann, *Inorg. Chem.*, 31 (1992) 2314.

54 S.-S. Chen, R.S. Woosley, E.G. Vassian, and R.K. Murmann, *Inorg. Chim. Acta*, 191 (1992) 91.

55 B. Chase and P.J. Fagan, *J. Am. Chem. Soc.*, 114 (1992) 2252.

56 P.J. Fagan, J.C. Calabrese and B. Malone, *Acc. Chem. Res.*, 25 (1992) 134.

57 T. Belderrain, D.A. Knight, D.J. Irvine, M. Paneque, M.L. Poveda and E. Carmona, *J. Chem. Soc., Dalton Trans.*, (1992) 1491.

58 J. Campora, E. Gutierrez, M.L. Poveda, C. Ruiz and E. Carmona, *J. Chem. Soc., Dalton Trans.*, (1992) 1769.

59 A. Becalska, R.J. Batchelor, F.W.B. Einstein, R.H. Hill and B.J. Palmer, *Inorg. Chem.*, 31 (1992) 3118.

60 E.M. Georgiev, H. tom Dieck, G. Fendesak, G. Hahn, G. Petrov and M. Kirilov, *J. Chem. Soc., Dalton Trans.*, (1992) 1311.

61 J.-O. Malm, V. Alfredsson, G. Svensson and J. Albertsson, *Acta Cryst.*, C48 (1992) 406.

62 F. Bachechi and L. Zambonelli, *Acta Cryst.*, C48 (1992) 788.

63 M. Fourmigue and P. Batail, *Bull. Soc. Chim. Fr.*, 129 (1992) 29.

64 A. Knierzinger and P. Schonholzer, *Helv. Chim. Acta*, 75 (1992) 1211.

65 M. Di Vaira and P. Stoppioni, *Coord. Chem. Rev.*, 120 (1992) 259.

66 A.J. Downard, L.R. Hanton and R.L. Paul, *J. Chem. Soc., Chem. Commun.*, (1992) 235.

67 M. Barraho and C. R'Kha, *Acta Cryst.*, C48 (1992) 1350.

68 K. Waizumi, H. Ohtaki, H. Masuda, N. Fukushima and Y. Watanabe, *Chem. Lett.*, (1992) 1489.

69 J.L. Atwood, G.W. Orr, F. Hamada, R.L. Vincent, S.G. Bott and K.D. Robinson, *J. Inclusion Phenom. Mol. Recognit. Chem.*, 14(1) (1992) 37.

70 A. Sequeira, H. Rajagopal, M.P. Gupta, F. Vanhouteghem, A.T.H. Lenstra and H.J. Geise, *Acta Cryst.*, C48 (1992) 1192.

71 T. Glowiak, H. Kozlowski, L.S. Erre, B. Gulinati, G. Micera, A. Pozzi and S. Bruni, *J. Coord. Chem.*, 25 (1992) 75.

72 W.L. Driessen, J. Reedijk, K.R. Dunbar and L.E. Pence, *Inorg. Synth.*, 29 (1992) 111.

73 R. Larsson, *Inorg. Chim. Acta*, 191 (1992) 179.

74 T.G. Cherkasova, E.S. Tatarinova and B.G. Tryasunov, *Zh. Neorg. Khim.*, 37 (1992) 2037.

75 R.R. Romero, F. Cervantes-Lee and L.C. Porter, *Acta Cryst.*, C48 (1992) 993.

76 J. R. Polam and L.C. Porter, *Acta Cryst.*, C48 (1992) 1761.

77 D. Luneau, P. Rey, J. Laugier, E. Belorizky and A. Cogne, *Inorg. Chem.*, 31 (1992) 3578.

78 A. Al-Alousy and J. Burgess, *Polyhedron*, 11 (1992) 531.

79 N. Sato and Y. Fukuda, *Chem. Lett.*, (1992) 399.

80 Y. Nishida, T. Fujimoto and N. Tanaka, *Chem. Lett.*, (1992) 1291.

81 S. A. Samath, N. Raman, K. Jeyasubramanian and S.K. Ramalingam, *Polyhedron*, 11 (1992) 33.

82 C.V.R. Reddy, S.G. Seshikala and M.G.R. Reddy, *Orient. J. Chem.*, 8 (1992) 314; *Chem. Abstr.* 118 (1992) 133204w.

83 I. Karadjova, S. Arpadjan and I. Shiskova, *Polyhedron*, 11 (1992) 2525.

84 K.G. Mallikarjun and R.S. Naidu, *Asian J. Chem.*, 4 (1992) 135; *Chem. Abstr.*, 118 (1992) 114482c.

85 S.S. Yun, J.B. Doh and K.Y. Choi, *Bull. Korean Chem. Soc.*, 13 (1992) 659; *Chem. Abstr.*, 118 (1992) 67738v.

86 S. Cocks, P.W. Linder and A. Voye, *J. Coord. Chem.*, 25 (1992) 211.

87 M.M. El-fass, E.A. Moussa, K.M.M. Salem, A.A.H. El-Byaa and A.A.R. El-Mariah, *Sci. Phys. Sci.*, 4 (1992) 163.

88 A. Dei and D. Gatteschi, *Inorg. Chim. Acta*, 198-200 (1992) 813.

89 R.-M. Olk, B. Olk, W. Dietzsch, R. Kirmse and E. Hoyer, *Coord. Chem. Rev.*, 117 (1992) 99.

90 A. Miyazaki, A. Izuoka and T. Sugawara, *Bull. Chem. Soc. Jpn*, 65 (1992) 2528.

91 J.P. Cornelissen, R. Le Loux, J. Jansen, J.G. Haasnoot, J. Reedijk, E. Horn, A.L. Spek, B. Pomarede, J.-P. Legros and D. Reefman, *J. Chem. Soc., Dalton Trans.* (1992) 2911.

92 T. Yamamura and H. Arai, *Bull. Chem. Soc. Jpn*, 65 (1992)1799.

93 M. Ohtani, S. Ohkoshi, M. Kajitani, T. Akiyama, A. Sugimori, S. Yamauchi, Y. Ohba and M. Iwaizumi, *Inorg. Chem.*, 31 (1992) 3873.

94 C. Zhang, H.K. Reddy, R.K. Chadha and G.N. Schrauzer, *J. Coord. Chem.*, 26 (1992) 117.

95 D.K. Kamysbaev, R.N. Utegulov and Kh.K. Ospanov, *Koord. Khim.*, 18 (1992) 156.

96 F. Bonomi, S. Pagani, F. Cariati, A. Pozzi, G. Crisponi, F. Cristiani, A. Diaz and R. Zanoni, *Inorg. Chim. Acta*, 192 (1992) 237.

97 R. Cao, X. Lei, Z. Huang, M. Hong and H. Liu, *J. Coord. Chem.*, 25 (1992) 165.

98 W. Dietzsch, P. Strauch and E. Hoyer, *Coord. Chem. Rev.*, 121 (1992) 43.

99 P. Roman, A. Luque, J.I. Beitia and C. Guzman-Miralles, *Polyhedron*, 11 (1992) 1883.

100 P. Roman, A. Luque, J.M. Gutierrez-Zorilla, J.I. Beitia, and M. Martinez-Ripoll, *Zeit. Kristallogr.*, 198 (1992) 213.

101 P. Espinet, M.A. Esteruelas, L.A. Oro, J.L. Serrano and E. Sola, *Coord. Chem. Rev.*, 117 (1992) 215.

102 T. Chivers, M. Cowie, M. Edwards and R.W. Hilts, *Inorg. Chem.*, 31 (1992) 3349

103 G.R. Frauenhoff, F. Takusagawa and D.H. Busch, *Inorg. Chem.*, 31 (1992) 4002.

104 G. Matsubayashi, S. Tanaka and A. Yokozawa, *J. Chem. Soc., Dalton Trans.*, (1992) 1827.

105 C.A. Marganian, N. Baidya, M.M. Olmstead and P.K. Mascharak, *Inorg. Chem.*, 31 (1992) 2992.

106 J. Costamagna, J. Vargas, R. Latorre, A. Alvarado and G. Mena, *Coord. Chem. Rev.*, 119 (1992) 67.

107 B. Erk, Y. Baran and T. Uyar, *Kim. Kim. Muhandisligi Semp.*, 8 (1992) 21; *Chem. Abstr.*, 119 (1992) 845515h.

108 X. Cui, D. Liu, H. Sun, X. Li and S. Li, *Chem. Res. Chin. Univ.*, 8 (1992) 309; *Chem. Abstr.*, 119 (1992) 19237e.

109 D. Jia and X. Xin, *Yingyong Huaxue*, 9 (1992) 1; *Chem. Abstr.*, 118 (1992) 159830x.

110 A. El-Shakeil and A.Z. El-Sonbati, *Makromol. Chem., Macromol. Symp.*, 59 (1992) 319.

111 F.S.M. Hassan, A.A.E. Mohamed, A.A. Gabr and A.A. Gad, *Orient. J. Chem.*, 8 (1992) 25; *Chem. Abstr.*, 117 (1992) 102863k.

112 A.A.T. Ramadan, *Thermochim. Acta*, 206 (1992) 327; *Chem. Abstr.*, 117 (1992).

113 L. Carbonaro, A. Giacomelli, M. Isola and L. Senatore, *J. Chem. Soc., Dalton Trans.*, (1992) 37.

114 L. Carbonaro, A. Giacomelli, M. Isola and L. Senatore, *J. Chem. Soc., Dalton Trans.*, (1992) 41.

115 P. Gill, M.S. Palacios, M.G. Martin-Reyes, P. Martin-Zarza, C. Ruiz-Perez, F.V. Rodriguez-Romero and F.V. Lahoz, *Polyhedron*, 11 (1992) 2171.

116 C. Natarajan, P. Tharmaraj and R. Murugesan, *J. Coord. Chem.*, 26 (1992) 205.

117 Y. Elerman, H. Fuess and H. Paulus, *Acta Cryst.*, C48 (1992) 40.

118 M. Kwiatkowski and G. Bandoli, *J. Chem. Soc., Dalton Trans.*, (1992) 379.

119 A. Boettcher, H. Elias, L. Mueller and H. Paulus, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 623.

120 G.S. Garg, V. Kumar and S. Walia, *Proc. - Indian Acad. Sci., Chem. Sci.*, 104 (1992) 543; *Chem Abstr.*, 117 (1992) 259315f.

121 A.A. Ramadan, M.S. Abdel-Moez, H.S. Sleem and B.A. El-Shetary, *Acta Chim. Hung.*, 129 (1992) 619.

122 L. Battaglia, P.G. Berzolla, A.B. Corradi, C. Pelizzi, G. Pelosi and C. Solinas, *J. Chem. Soc., Dalton Trans.*, (1992) 308.

123 L. Zheng, W. Zhang and X. Xin, *Gaodeng Xuexiao Huaxue Xuebao*, 13 (1992) 1205; *Chem. Abstr.*, 118 (1992) 138654c.

124 I.M. El-Nahhal, G.S. Heaton and A.M. Jelan, *Inorg. Chim. Acta*, 197 (1992) 193.

125 V.F. Shul'gin, O.V. Konnik and A.K. Pankratov, *Ukr. Khim. Zh. (Russ. Ed.)*, 58 (1992) 855; *Chem. Abstr.*, 118 (1992) 246236b.

126 K.C. Joshi, R. Bohra and B.S. Joshi, *Inorg. Chem.*, 31 (1992) 598.

127 M. Basato, U. Casellato, R. Graziani and A.C. Veronese, *J. Chem. Soc., Dalton Trans.*, (1992) 1193.

128 M. Basato, B. Corain and G. Zanotti, *J. Chem. Soc., Dalton Trans.*, (1992) 3003.

129 P. Piu, V. Leoni, A.M. Zoroddu, G. Manca, S. Deiana and C. Gessa, *Transition Met. Chem. (London)*, 17 (1992) 283.

130 H. Lin, Z. Liu and R. Chen, *Wuji Huaxue Xuebao*, 8 (1992) 339; *Chem. Abstr.*, 119 (1992) 35006j.

131 S.F. Ledenov, E.V. Kozlovskii, V.P. Vasil'ev and G.V. Chistyakova, *Zh. Neorg. Khim.*, 37 (1992) 2303.

132 D. Jaju, U. Bharadwaj, R.K. Soni, A. Sharma, L. Jain and R.K. Mehta, *Asian J. Chem.*, 4 (1992) 798; *Chem. Abstr.*, 117 (1992) 162868a.

133 T. Gajda, N. Buzas, L. Nagy and K. Burger, *Polyhedron*, 11 (1992) 2237.

134 P. Djurdjevic, D.J. Radanovic, M. Cvijovic, M. Dimitrijevic and D. Veselinovic, *Polyhedron*, 11 (1992) 197.

135 M.V. Artemenko, V.A. Litenko, E.G. Lampeka and N.I. Zakharenko, *Ukr. Khim. Zh. (Russ. Ed.)*, 58 (1992) 285; *Chem. Abstr.*, 117 (1992) 82348r.

136 C. Schmidt, K. Polborn and W. Beck, *Chem. Ber.*, 125 (1992) 61.

137 P.K. Sahu, N.R. Bannerjee and S. Sengupta, *J. Indian Chem. Soc.*, 69 (1992) 184.

138 T. Froemmel, W. Peters, H. Wunderlich and W. Kuchen, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 612.

139 J.C. Jeffery, E. Schatz and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 1921.

140 G. Balraj, S. Raj and M.G.R. Reddy, *Orient. J. Chem.*, 8 (1992) 153; *Chem. Abstr.*, 117 (1992) 179296k.

141 S. Tagashira, K. Onoue, Y. Murakami and Y. Sasaki, *Bull. Chem. Soc. Jpn*, 65 (1992) 286.

142 S. Tagashira, K. Onoue, Y. Murakami and Y. Sasaki, *Anal. Sci.*, 8 (1992) 307.

143 A. Yuchi, H. Murakami, M. Shiro, H. Wada and G. Nakagawa, *Bull. Chem. Soc. Jpn*, 65 (1992) 3362.

144 K. Haraguchi, T. Ogata and K. Nakagawa, *Mikrochim. Acta*, 106 (1992) 75; *Chem. Abstr.*, 116 (1992) 137046c.

145 D. Carrillo, *Coord. Chem. Rev.*, 119 (1992) 137.

146 T. Kawamoto and Y. Kushi, *Chem. Lett.*, (1992) 893.

147 E. M. Martin, R.D. Bereman and J. Reibenspies, *Inorg. Chim. Acta*, 191 (1992) 171.

148 A. la Cour, B. Adhikhari, H. Toftlund and A. Hazell, *Inorg. Chim. Acta*, 202 (1992) 145.

149 C.T. Supuran, F. Cimpoesu, G. Manole and M. Brezeanu, *Rev. Roum. Chim.*, 37 (1992) 959.

150 P.P. Hankare, R.S. Rampure, A.H. Manikshetl, L.P. Deshmukh and C.K. Bhaskare, *J. Indian Chem. Soc.*, 69 (1992) 220.

151 P. Farmer, T. Solouki, D.K. Mills, T. Soma, D.H. Russell, J.H. Reibenspies and M.Y. Darensbourg, *J. Am. Chem. Soc.*, 114 (1992) 4601.

152 K.G. Ragunathan and P.K. Bharadwaj, *J. Chem. Soc., Dalton Trans.*, (1992) 2417.

153 J.A. Boyko, W.F. Furey Jr and R.A. Lalancette, *Acta Cryst.*, C48 (1992) 1606.

154 J. Maslowska and J. Szmich, *Collect. Czech. Chem. Commun.*, 57 (1992) 263.

155 S. Sahadev, K. Rakesh and S.K. Sindhwani, *Thermochim. Acta*, 202 (1992) 291.

156 J. Rodriguez and R. Cao, *Rev. Cubana Quim.*, 6 (1992) 17; *Chem. Abstr.*, 119 (1992) 194324c.

157 R. Bastida, A. de Blas, D.E. Fenton and T. Rodriguez, *Polyhedron*, 11 (1992) 2739.

158 C. Mealli, C.A. Ghilardi and A. Orlandini, *Coord. Chem. Rev.*, 120 (1992) 361.

159 S.B. Sembiring, S.B. Colbran and L.R. Hanton, *Inorg. Chim. Acta*, 202 (1992) 67.

160 M. Kita, T. Yamamoto, K. Kashiwabara and J. Fujita, *Bull. Chem. Soc. Jpn*, 65 (1992) 2272.

161 M.K. Cooper, J.M. Downes, P.A. Duckworth and E.R.T. Tiekink, *Aust. J. Chem.*, 45 (1992) 595.

162 H. Suzuki and S. Ishiguro, *Inorg. Chem.*, 31 (1992) 4178.

163 H. Cai and G.C. Farrington, *J. Electrochem. Soc.*, 139 (1992) 744.

164 H. Ohtaki, *J. Indian Chem. Soc.*, 69 (1992) 442.

165 K. Waizumi, H. Masuda and H. Ohtaki, *Inorg. Chim. Acta*, 192 (1992) 173.

166 G. De Santis, L. Fabbrizzi, M. Licchelli and P. Pallavicini, *Coord. Chem. Rev.*, 120 (1992) 237.

167 W.K. Musker, *Coord. Chem. Rev.*, 117 (1992) 133.

168 S.V. Rosokha and Y.D. Lampeka, *Teor. Esp. Khim.*, 28 (1992) 442; *Chem. Abstr.*, 119 (1992) 257273h.

169 R.J. Deeth and C.M. Kemp, *J. Chem. Soc., Dalton Trans.*, (1992) 2013.

170 R. Stranger, S.C. Wallis, L.R. Gahan, C.H.L. Kennard and K.A. Byriel, *J. Chem. Soc., Dalton Trans.*, (1992) 2971.

171 S.C. Rawle, A.J. Clarke, P. Moore and N.W. Alcock, *J. Chem. Soc., Dalton Trans.*, (1992) 2755.

172 J.R. Roeper and H. Elias, *Inorg. Chem.*, 31 (1992) 1202.

173 J.R. Roeper and H. Elias, *Inorg. Chem.*, 31 (1992) 1210.

174 Y. Satake, Y. Ihara, H. Senda, M. Suzuki and A. Uehara, *Inorg. Chem.*, 31 (1992) 3248.

175 J. Chapman, G. Ferguson, J.F. Gallagher, M.C. Jennings and D. Parker, *J. Chem. Soc., Dalton Trans.*, (1992) 345.

176 S.G. Kang and J.K. Kweon, *Bull. Korean Chem. Soc.*, 13 (1992) 256; *Chem. Abstr.*, 117 (1992) 123408f.

177 D.J. Szalda and E. Fujita, *Acta Cryst.*, C48 (1992) 1767.

178 N. Matsumoto, M. Koikawa, N. Baba and H. Okawa, *Bull. Chem. Soc. Jpn*, 65 (1992) 258.

179 S. Srivastava, N. Ahmad and P.R. Shukla, *Asian J. Chem.*, 4 (1992) 184; *Chem. Abstr.*, 116 (1992) 119727w.

180 M. Casarin, E. Ciliberto, S. Di Bella, A. Gulino, I. Fragala and T.J. Marks, *Inorg. Chem.*, 31 (1992) 2835.

181 K. Kobiro, A. Nakayama, T. Hiro, M. Suwa and Y. Tobe, *Inorg. Chem.*, 31 (1992) 676.

182 K. Sakata and M. Itoh, *J. Heterocycl. Chem.*, 29 (1992) 921.

183 B. Korybut-Daskiewicz, *J. Coord. Chem.*, 27 (1992) 219.

184 B. Korybut-Daskiewicz, *J. Chem. Soc., Dalton Trans.*, (1992) 1673.

185 J.H. Cameron, H.B. Harvey and I. Soutar, *Inorg. Chim. Acta*, 192 (1992) 253.

186 J.H. Cameron, H.B. Harvey and I. Soutar, *J. Chem. Soc., Dalton Trans.*, (1992) 597.

187 F. Brezina, M. Subcikova, J. Kamenicek, J. Lasovsky, Z. Sindelar, R. Pastorek and J. Ondracek, *Collect. Czech. Chem. Commun.*, 57 (1992) 74.

188 B.D. Berezin, D.D. Daniyarov, K.A. Askarov and M.B. Berezin, *Zh. Fiz. Khim.*, 66 (1992) 1632.

189 Y. Tang, Z. Peng and Z. Qin, *Gaodeng Xuexiao Huaxue Xuebao*, 13 (1992) 22; *Chem. Abstr.*, 117 (1992) 102962s.

190 X.H. Xia, W.D. Su and S.M. Zhou, *J. Electroanal. Chem.*, 324 (1992) 59.

191 D. Mandon, P. Ochsenbein, J. Fischer, R. Weiss, K. Jayaraj, R.N. Austin, A. Gold, P.S. White, O. Brigaud, P. Battioni and D. Mansuy, *Inorg. Chem.*, 31 (1992) 2044.

192 L.K. Woo, M.R. Maurya, R.A. Jacobson, S. Yang and S.L. Ringrose, *Inorg. Chem.*, 31 (1992) 913.

193 L.K. Woo, M.R. Maurya, R.A. Jacobson, S. Yang and S.L. Ringrose, *Inorg. Chim. Acta*, 193 (1992) 143.

194 D.M. Guldi, P. Neta, P. Hambright and R. Rahimi, *Inorg. Chem.*, 31 (1992) 4849.

195 P.J. Chmielewski and L. Latos-Grazynski, *Inorg. Chem.*, 31 (1992) 5231.

196 K. Takahashi, Y. Aoki, T. Sugitani, F. Moriyama, Y. Tomita, M. Handa, K. Kasuga and K. Sogabe, *Inorg. Chim. Acta*, 201 (1992) 247.

197 C.S. Velazquez, G.A. Fox, W.E. Broderick, K.A. Andersen, O.P. Anderson, A.G.M. Barrett and B.M. Hoffman, *J. Am. Chem. Soc.*, 114 (1992) 7416.

198 C. K. Chang, W.Wu, S.-S. Chern and S.-M. Peng, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 70.

199 S. Chandrasekhar and A. McAuley, *Inorg. Chem.*, 31 (1992) 480.

200 A.J. Blake, M.A. Halcrow and M. Schroeder, *J. Chem. Soc., Dalton Trans.*, (1992) 2803.

201 M. Widhalm and C. Kratky, *Chem. Ber.*, 125 (1992) 679.

202 M.T.S. Amorim, R. Delgado and J.J.R.F. Da Silva, *Polyhedron*, 11 (1992) 1891.

203 K.R. Adam, M. Antolovich, D.S. Baldwin, L.G. Brigden, P.A. Duckworth, L.F. Lindoy, A. Bashall, M. McPartlin and P.A. Tasker, *J. Chem. Soc., Dalton Trans.*, (1992) 1869.

204 S. Chandrasekhar and A. McAuley, *J. Chem. Soc., Dalton Trans.*, (1992) 2967.

205 D.M. Wambeke, W. Lippens, G.G. Herman, A.M. Goeminne and G.P. van der Kelen, *Polyhedron*, 11 (1992) 2989.

206 M.Y. Darensbourg, I. Font, D.K. Mills, M. Pala and J.H. Reibenspies, *Inorg. Chem.*, 31 (1992) 4965.

207 U. Kallert and R. Mattes, *Polyhedron*, 11 (1992) 617.

208 J. Lisowski, L. Latos-Grazynski and L. Szterenberg, *Inorg. Chem.*, 31 (1992) 1933.

209 T. L. Jones, A.C. Willis and S.B. Wild, *Inorg. Chem.*, 31 (1992) 1411.

210 A. Bencini, A. Bianchi and P. Paoletti, *Coord. Chem. Rev.*, 120 (1992) 51.

211 P. Guerriero, P.A. Vigato, D.E. Fenton and P.C. Hellier, *Acta Chem. Scand.*, 46 (1992) 1025.

212 K.K. Nanda, R. Das, M.J. Newlands, R. Hynes, E.J. Gabe and K. Nag, *J. Chem. Soc., Dalton Trans.*, (1992) 897.

213 R. Das, K.K. Nanda, K. Venkatsubramanian, P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, (1992) 1253.

214 A. Aguiari, E. Bullita, U. Casellato, P. Guerriero, S. Tamburini and P.A. Vigato, *Inorg. Chim. Acta*, 202 (1992) 157.

215 A. Edwards, B.F. Hoskins, E.H. Kachab, A. Markiewicz, K.S. Murray and R. Robson, *Inorg. Chem.*, 31 (1992) 3585.

216 A. McAuley and C. Xu, *Inorg. Chem.*, 31 (1992) 5549.

217 K. Mochizuki, M. Tsutsumi and Y. Yamaji, *Inorg. Chim. Acta*, 191 (1992) 35.

218 S.C. Rawle, P. Moore and N.W. Alcock, *J. Chem. Soc., Chem. Commun.*, (1992) 684.

219 E. Fujita, S.J. Milder and B.S. Brunschwig, *Inorg. Chem.*, 31 (1992) 2079.

220 E. Kimura, X. Bu, M. Shionoya, S. Wada and S. Maruyama, *Inorg. Chem.*, 31 (1992) 4543.

221 S.C. Rawle, C.J. Harding, P. Moore and N.W. Alcock, *J. Chem. Soc. Chem. Commun.*, (1992) 1701.

222 G. Ricciardi and F. Lelj, *Polyhedron*, 11 (1992) 2089.

223 A. Bencini and S. Midollini, *Coord Chem. Rev.*, 120 (1992) 87.

224 A.J. Blake, M.A. Halcrow and M.Schroeder, *Acta Cryst.*, C48 (1992) 1844.

225 Z. Janas, T. Lis and P. Sobota, *Polyhedron*, 11 (1992) 3019.

226 R. Vicente, A. Escuer, J. Ribas and X. Solans, *Inorg. Chem.*, 31 (1992) 1726.

227 R. Cortes, J.I. R. de Larramendi, L. Lezama, T. Rojo, K. Urtiaga and M. I. Arriortua, *J. Chem. Soc., Dalton Trans.*, (1992) 2723.

228 M.E.V. Suarez Iha and E.F. de Almeida Neves, *Polyhedron*, 11 (1992) 759.

229 C. Diaz and J. Ribas, *Polyhedron*, 11 (1992) 85.

230 G. Lopez, G. Garcia, G. Sanchez, J. Garcia, J. Ruiz, J.A. Hermoso, A. Vegas and M. Martinez-Ripoll, *Inorg. Chem.*, 31 (1992) 1518.

231 A. Escuer, R. Vicente and J. Ribas, *Polyhedron*, 11 (1992) 453.

232 L. Ballester, E. Coronado, A. Gutierrez, A. Monge, M.F. Perpinan, E. Pinilla and T. Rico, *Inorg. Chem.*, 31 (1992) 2053.

233 D.E. Barber, Z. Lu, T. Richardson and R.H. Crabtree, *Inorg. Chem.*, 31 (1992) 4709.

234 L. M. Sayre, K.V. Reddy, A.R. Jacobson and W. Tang, *Inorg. Chem.*, 31 (1992) 937.

235 J.C. Jeffery and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 2119.

236 M.V. Baldovi, A. Corma, V. Fornes, H. Garcia, A. Martinez and J. Primo, *J. Chem. Soc., Chem. Commun.*, (1992) 949.

237 R. Cao, Z. Huang, X. Lei, B. Kang, M. Hong and H. Liu, *Acta Cryst.*, C48 (1992) 1654.

238 X. Chen, B. Kang, L. Weng, L. Huang, H. Liu, D. Wu, X. Lei, M. Hong and J. Lu, *Transition Met. Chem. (London)*, 17 (1992) 509.

239 M. Mikuriya, M. Handa, S. Shigematsu, S. Funaki, F. Adachi and H. Okawa, *Bull. Chem. Soc. Jpn*, 65 (1992) 512.

240 S.B. Choudhury and A. Chakravorty, *Inorg. Chem.*, 31 (1992) 1055.

241 M. Morooka and S. Ohba, *Acta Cryst.*, C48 (1992) 1888.

242 Z.-L. Deng, J. Shi, Z.-H. Jiang, D.-Z. Liao, S.-P. Yan, G.-L. Wang, H.-G. Wang and R.-H. Wang, *Polyhedron*, 11 (1992) 885.

243 E. Bermejo, A. Castineiras, R. Dominguez, W. Hiller and J. Strähle, , Fourteenth European Crystallographic Meeting ECM-14, University of Twente, Enschede, the Netherlands, August 2 - 7, 1992, *Zeitschrift fur Kristallographie,* Abstracts 135.

244 F. Lloret, J. Sletten, R. Ruiz, M. Julve, J. Faus and M. Verdaguer, *Inorg. Chem.*, 31 (1992) 778.

245 F. Brezina, M. Subcikova, Z. Sindelar and R. Pastorek, *Acta Univ. Palacki. Olomuc., Fac. Rerum Nat.*, 108 (1992) 7; *Chem. Abstr.*, 118 (1992) 265392r.

246 L.S. Erre, G. Micera, B. Gulinati and F. Cariati, *Polyhedron*, 11 (1992) 101.

247 S. Dominguez, A. Rancel, J.V. Herrera, A. Mederos and F. Brito, *J. Coord. Chem.*, 25 (1992) 271.

248 T. Tanase, S. Nitta, S. Yoshikawa, K. Kobayashi, T. Sakurai and S. Yano, *Inorg. Chem.*, 31 (1992) 1058.

249 R. R. Romero, F. Cervantes-Lee and L.C. Porter, *Acta Cryst.*, C48 (1992) 1764.

250 B.M. Holligan, J.C. Jeffery and M.D. Ward, *J. Chem. Soc., Dalton Trans.*, (1992) 3337.

251 Z. Shourong, L. Qinhui, S. Mengchang and H. Liangren, *Acta Cryst.*, C48 (1992) 1926.

252 H.Y. Cheng, G.H. Lee and S.M. Peng, *Inorg. Chim. Acta*, 191 (1992) 25.

253 J.R. Allan, A.D. Paton and K. Turvey, *Thermochim. Acta*, 195 (1992) 343.

254 P.E. Kruger, G.D. Fallon, B. Moubaraki and K.S. Murray, *J. Chem. Soc., Chem. Commun.*, (1992) 1726.

255 E.C. Constable and R. Chotalia, *J. Chem. Soc., Chem. Commun.*, (1992) 64.

256 E.C. Constable, M.J. Hannon and D.A. Tocher, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 230.

257 N.N. Gerasimchuk, L. Nagy, Kh. G. Shmidt and H. Rojeski, *Zh. Neorg. Khim.*, 37 (1992) 818.

258 S.A. Ibrahim, *Polyhedron*, 11 (1992) 1349.

259 L. Mishra and A.K. Pandey, *Polyhedron*, 11 (1992) 423.

260 G. Paolucci, S. Stelluto, S. Sitran, D. Ajo, F. Benetollo, A. Polo and G. Bombieri, *Inorg. Chim. Acta*, 193 (1992) 57.

261 M. Mikuriya, T. Sasaki, A. Anjiki, S. Ikenoue and T. Tokii, *Bull. Chem. Soc. Jpn*, 65 (1992) 334.

262 G. C. Chiumia, M.A.A. Miah and D.J. Phillips, *Inorg. Chim. Acta*, 191 (1992) 19.

263 M.A.A. Miah, D.J. Phillips and A.D. Rae, *Inorg. Chim. Acta*, 201 (1992) 191.

264 B. Srinivas, N. Arulsamy and P.S. Zacharias, *Polyhedron*, 11 (1992) 211.

265 B. Srinivas and P.S. Zacharias, *Polyhedron*, 11 (1992) 1949.

266 B. Adhikary, K.K. Nanda, R. Das, S.K. Mandal and K. Nag, *Polyhedron*, 11 (1992) 347.

267 L.A. Belfiore, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, 33 (1992) 925.

268 R.M. Hassan, M.A. El-Gahami, M.A. Abd-Alla, *J. Mater. Chem.*, 2 (1992) 613.

269 T. Yamamoto, Y. Yoneda and T. Maruyama, *J. Chem. Soc., Chem. Commun.*, (1992) 1652.

270 J. Suh and M.J. Kim, *Bioorg. Chem*, 20 (1992) 366.

271 K. Hanabusa, A. Nakamura, T. Koyama and H. Shirai, *Makromol. Chem.*, 193 (1992) 1309.

272 X. Wang and L. Lu, *Yingyong Huaxue*, 9 (1992) 85; *Chem. Abstr.*, 116 (1992) 175339h.

273 A. Syamal and M.M. Singh, *J. Polym. Mater.*, 9 (1992) 105.

274 K. Hanabusa, T. Suzuki, T. Koyama and H. Shirai, *Makromol. Chem.*, 193 (1992) 2149.

275 M.W. Jones, N. Gupta, A. Schepartz and H. H. Thorp, *Inorg. Chem.*, 31 (1992) 1308.

276 H. Zhang, D. Chen, P. Chen, D. Che and S. Wang, *Huaxue Xuebao*, 50 (1992) 995; *Chem. Abstr.*, 118 (1992) 124721k.

277 H. Zhang, D. Chen, P. Chen, D. Che, G. Cheng and H. Zhang, *Polyhedron*, 11 (1992) 2313.

278 X. Zhou, Y. Liang, F. Nan and Y. Ma, *Polyhedron*, 11 (1992) 447.

279 G. Huang, Y. Liang and Y. Ma, *J. Coord. Chem.*, 26 (1992) 237.

280 S. Ciurli, P.K. Ross, M.J. Scott, S.-B. Yu and R.H. Holm, *J. Am. Chem. Soc.*, 114 (1992) 5415.

281 J. Zhou, M.J. Scott, Z. Hu, G. Peng, E. Muenck and R.H. Holm, *J. Am. Chem. Soc.*, 114 (1992) 10843.

282 H. Tamaki, M. Mitsumi, K. Nakamura, N. Matsumoto, S. Kida, H. Okawa and S. Iijima, *Chem. Lett.*, (1992) 1975.

283 A.C. Dash and S.S. Mohammed, *Indian J. Chem., Sect. A: Inorg., Bio-inorg., Phys., Theor. Anal. Chem.*, 31A (1992) 166.

284 A.C. Dash and J. Pradhan, *Int. J. Chem. Kinet.*, 24 (1992) 155.

285 T. Konno, K. Okamoto and J. Hidaka, *Inorg. Chem.*, 31 (1992) 161.

286 N. Matsumoto, K. Inoue, M. Ohba, H. Okawa and S. Kida, *Bull. Chem. Soc. Jpn*, 65 (1992) 2283.

287 R. Vicente, A. Escuer and J. Ribas, *Polyhedron*, 11 (1992) 857.

288 F. Sapina, E. Escriva, J.V. Folgado, A. Beltran, D. Beltran, A. Fuertes and M. Drillon, *Inorg. Chem.*, 31 (1992) 3851.

289 A. Escuer, R. Vicente, J. Ribas, R. Costa and X. Solans, *Inorg. Chem.*, 31 (1992) 2627.

290 B. Srinivas and P.S. Zacharias, *Can. J. Chem.*, 70 (1992) 2906.

291 N. Dragoe, E. Cristurean and M. Andruh, *Rev. Roum. Chim.*, 37 (1992) 181.

292 T. Tuntulani, J.H. Reibenspies, P.J. Farmer and M.Y. Darensbourg, *Inorg. Chem.*, 31 (1992) 3497.

293 P. Paul, R. Das, K. Nag, E.J. Gabe and J.-P. Charland, *Can. J. Chem.*, 70 (1992) 2461.

294 T. Nishioka, I. Kinoshita, K. Kitano and S. Ooi, *Chem. Lett.*, (1992) 883.

295 B.L. Khandelwal and K. Uppal, *Polyhedron*, 11 (1992) 1755.

296 K.-M. Park and T. Iwamoto, *J. Chem. Soc., Chem. Commun.*, (1992) 73.

297 C.J. Gomez-Garcia, E. Coronado and L. Ouahab, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 648.

298 M. Sakamoto, M. Hashimura, Y. Nakayama, A. Matsumoto and H. Okawa, *Bull. Chem. Soc. Jpn*, 65 (1992) 1162.

299 A.E. Liberta and D.X. West, *BioMetals*, 5 (1992) 121.

300 P. Liu, Z. Li, Y. Li, X. Wang and L. Xu, *Shandong Yike Daxue Xuebao*, 30 (1992) 340; *Chem. Abstr.*, 119 (1992) 24472g.

301 T. Sato and Y. Fukuda, *Jpn. Kokai Tokkyo Koho*, (1992); *Chem. Abstr.*, 117 (1992) 146750a.

302 Z. Li, *Daxue Huaxue*, 7 (1992) 41; *Chem. Abstr.*, 117 (1992) 179238t.

303 Y.E. Zil'berman, V.G. Shtyrlin, A.V. Zakharov and A.Z. Saprykova, *Zh. Neorg. Khim*, 37 (1992) 388.

304 M.A.V. Ribeiro da Silva, M.D.M.C. Ribeiro da Silva, J.A.B.A. Tuna and L.M.N.B.F. Santos, *Thermochim. Acta*, 205 (1992) 115.

305 A. Bonamartini Corradi, *Coord. Chem. Rev.*, 117 (1992) 45.

306 N. A. Corfu, B. Song and L. Ji, *Inorg. Chim. Acta*, 192 (1992) 243.

307 K. Bernauer, S. Bourqui, D. Hugi-Cleary and R. Warmuth, *Helv. Chim. Acta*, 75 (1992) 1288.

308 B. Kurzak, H. Kozlowski and E. Farkas, *Coord. Chem. Rev.*, 114 (1992) 169.

309 E. Farkas, E. Kozma and T.E. Gunda, *Polyhedron*, 11 (1992) 3069.

310 F. Gaizer, J. Lazar, J.T. Kiss and E. Poczik, *Polyhedron*, 11 (1992) 257.

311 A.J. Di Bilio, T.K. Chang, B.G. Malmstroem, H.B. Gray, B.G. Karlsson, M. Nordling, T. Pascher and L.G. Lundberg, *Inorg. Chim. Acta*, 198-200 (1992) 145.

312 I.N. Lisichkina, A.I. Vinogradova, N.B. Sukhorukova, M.B. Saporovskaya and V.M. Belikov, *Izv. Akad. Nauk, Ser. Khim.*, 7 (1992) 1667; *Chem. Abstr.*, 119 (1992) 9127e.

313 B.A. Krizek and J.M. Berg, *Inorg. Chem.*, 31 (1992) 2984.

314 Y. Zhou, H. Liang, Y. Hao and P. Shen, *Wuji Huaxue Xuebao*, 8 (1992) 382; *Chem. Abstr.*, 120 (1992) 156913g.

315 J. Suh, *Accounts of Chemical Research*, 25 (1992) 275.

316 G.K. Lahiri, L.J. Schussel and A.M. Stolzenberg, *Inorg. Chem.*, 31 (1992) 4991.

317 M.C. Helvenston and C.E. Castro, *J. Am. Chem. Soc.*, 114 (1992) 8490.

318 T. Arai, H. Kondo and S. Sakaki, *J. Chem. Soc., Dalton Trans.*, (1992) 2753.

319 S.-K. Lin and B. Jaun, *Helv. Chem. Acta*, 75 (1992) 1478.

320 N. Baidya, B.C. Noll, M.M. Olmstead and P.K. Mascharak, *Inorg. Chem.*, 31 (1992) 2999.

321 N. Baidya, M.M. Olmstead, J.P. Whitehead, C. Bagyinka, M.J. Maroney and P.K. Mascharak, *Inorg. Chem.*, 31 (1992) 3612.

322 N. Baidya, M.M. Olmstead and P.K. Mascharak, *J. Am. Chem. Soc.*, 114 (1992) 9666.

323 L.L. Efros, H.H. Thorp, G.W. Brudvig and R.H. Crabtree, *Inorg. Chem.*, 31 (1992) 1722.

324 D. Sellmann, H. Schillinger, F. Knoch and M. Moll, *Inorg. Chim. Acta*, 198-200 (1992) 351.

325 W. Shin and P.A. Lindahl, *J. Am. Chem. Soc.*, 114 (1992) 9718.

326 I. Bertini, C. Luchinat, L.-J. Ming, M. Piccioli, M. Sola and J.S. Valentine, *Inorg. Chem.*, 31 (1992) 4433.

327 J.M. Moratal, M.J. Martinez-Ferrer, H.R. Jimenez, A. Donaire, J. Castells and J. Salgado, *J. Inorg. Biochem.*, 45 (1992) 231.

328 I. Bertini, A. Donaire, R. Monnanni, J.-M. Moratal and J. Salgado, *J. Chem. Soc., Dalton Trans.*, (1992) 1443.

329 J.M. Moratal, A. Donaire, J. Castells, H.R. Jimenez, J. Salgado and F. Hillerns, *J. Chem. Soc., Dalton Trans.*, (1992) 713.

330 J.-M. Moratal, J. Castells, A. Donaire, J. Salgado and H.R. Jimenez, *J. Chem. Soc., Dalton Trans.*, (1992) 3317.

331 C.J. Easton, S.K. Eichinger and M.J. Pitt, *J. Chem. Soc., Chem. Commun.*, (1992) 1295.

332 A.P. Mishra, *Natl. Acad. Sci. Lett. (India)*, 15 (1992) 303; *Chem. Abstr.*, 119 (1992) 81292x.

333 R. Lopez-Garzon, M. Gutierrez-Valero, M. Melguizo-Guijarro, M. Nogueras-Montiel, A. Sanchez-Rodrigo and M. Godino Salido, *J. Coord. Chem.*, 26 (1992) 83.

334 E. T. Clarke and A.E. Martell, *Inorg. Chim. Acta*, 191 (1992) 57.

335 J.G. Muller, X. Chen, A.C. Dadiz, S.E. Rokita and C.J. Burrows, *J. Am. Chem. Soc.*, 114 (1992) 6407.

336 J.R. Morrow and K.A. Kolasa, *Inorg. Chim. Acta*, 195 (1992) 245.

337 M.A. Fox, D.A. Chandler and E.P. Kyba, *J. Coord. Chem.*, 25 (1992) 1.

338 M. P. Suh, H.K. Kim, M.J. Kim and K.Y. Oh, *Inorg. Chem.*, 31 (1992) 3620.

339 K.M. Kadish, M.M. Franzen, B.C. Han, C. Araullo-McAdams and D. Sazou, *Inorg. Chem.*, 31 (1992) 4399.

340 S. Ozaki, H. Matsushita and H. Ohmori, *J. Chem. Soc., Chem. Commun.*, (1992) 1120.

341 S. Sakaki, *J. Am. Chem. Soc.*, 114 (1992) 2055.

342 D. Da Luz, C.V. Franco, I. Vencato, A. Neves and Y.P. Mascarenhas, *J. Coord. Chem.*, 26 (1992) 269.

343 L. Manojlovic-Muir, K.W. Muir, W.M. Davis, H.A. Mirza and R.J. Puddephatt, *Inorg. Chem.*, 31 (1992) 904.

344 P. Mastrorilli, G. Moro, C.F. Nobile and M. Latronico, *Inorg. Chim. Acta*, 192 (1992) 183.

345 P. Mastrorilli, G. Moro, C.F. Nobile and M. Latronico, *Inorg. Chim. Acta*, 192 (1992) 189.

346 M. Aresta, R. Gobetto, E. Quaranta and I. Tommasi, *Inorg. Chem.*, 31 (1992) 4286.

347 J. Reinhold, M. Schueler, T. Hoffmann and E. Wenschuh, *Inorg. Chem.*, 31 (1992) 559.

348 N. Re, M. Rosi, A. Sgamellotti, C. Floriani and M.F. Guest, *J. Chem. Soc., Dalton Trans.*, (1992) 1821.

349 H.G.M. Edwards and V. Fawcett, *Inorg. Chim. Acta*, 197 (1992) 89.

350 J.W. Ellis, K.N. Harrison, P.A.T. Hoye, A.G. Orpen, P.G. Pringle and M.B. Smith, *Inorg. Chem.*, 31 (1992) 3026.

351 M.J. Baker, K.N. Harrison, A.G. Orpen, P.G. Pringle and G. Shaw, *J. Chem. Soc., Dalton Trans.*, (1992) 2607.

352 G. Sillett, L. Ricard, C. Patois and F. Mathey, *J. Am. Chem. Soc.*, 114 (1992) 9453.

353 I.G. Phillips, R.G. Ball and R.G. Cavell, *Inorg. Chem.*, 31 (1992) 1633.

354 P.M. Boorman, G.K.W. Freeman and M. Parvez, *Polyhedron*, 11 (1992) 765.

355 R. Ahlrichs, D. Fenske, H. Oesen and U. Schneider, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 323.

356 K. Dehnicke, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 424.