Coordination Chemistry Reviews, 71 (1986) 139—234
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

4. NICKEL

M. SCHRÖDER

CONTENTS

0010-8545/86/$33.60

INTRODUCTION

This review covers the coordination chemistry of nickel that appeared in the literature during 1981 and late 1980 with coverage predominantly of volumes 94 and 95 of Chemical Abstracts and is a continuation of the previous article in this series.[1] The organometallic and catalytic chemistry of nickel is not included in this review, although reference is made to such complexes when relevant to coordination chemistry. The material is organised by oxidation state of the metal centre and within each oxidation state by type of donor atoms with cross-referencing where appropriate. In the case of compounds incorporating mixed ligand donors the chemistry is described in terms of the dominant ligand.

A brief review of nickel compounds as catalysts has appeared in the literature.[2]

4.1 NICKEL(IV)

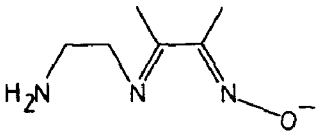
The chemistry of tetravalent nickel compounds has been reviewed.[3]

4.1.1 Halides

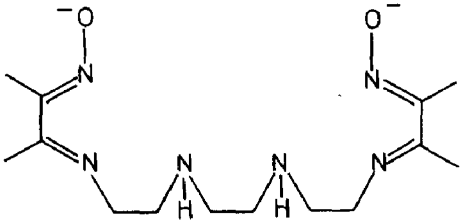
The single crystal X-ray structure of $(NF_4)_2[NiF_6]$, prepared by the method of Christie,[4] shows a tetragonal stereochemistry related to $K_2[PtCl_6]$ with Ni-F = 1.72, 1.76 Å and N-F = 1.30-1.40 Å.[5]

4.1.2 Nitrogen-donor ligands

Oxidation of the nickel(II) precursor with HNO_3 gives the corresponding nickel(IV) complex mer-$[Ni(L)_2](ClO_4)_2$ (L = 2-(2-aminoethyl)imino-3-butanoneoximate, (1)) which shows a distorted octahedral structure with Ni-N (oxime) = 1.967, Ni-N (imine) = 1.873 and Ni-N (amine) = 2.006 Å.[6] The related nickel(IV) complex $[Ni(L)]^{2+}$ (L = (2)) has been resolved with K(+)-antimonyl tartrate by elution on SP Sephadex, and the configuration of one of the optical isomers established by its circular dichroism spectrum; this isomer was found to oxidise L-(+)-cysteine at a rate >50% faster than its enantiomer.[7] The reduction of $[Ni(L)]^{2+}$ (L = (2)) by ascorbate ion shows second order kinetics with rate constant $k = 3.02 \times 10^5$ and 1.36×10^4 M^{-1} sec^{-1} for the protonated and deprotonated oxidant respectively; e.s.r. spectral data for the reduction suggest a process involving two, one electron steps via a nickel(III) intermediate.[8]



(1)



(2)

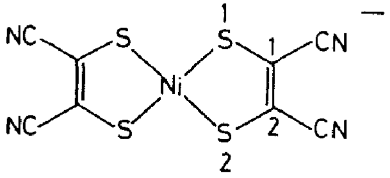
A study of high valent nickel peroxy species has been reported.[9]

4.2 NICKEL(III)

The synthesis, reactivity and characterisation of trivalent nickel compounds have been reviewed in two important articles by Nag and Chakravorty,[3] and Haines and McAuley.[10]

4.2.1 Sulphur-donor ligands

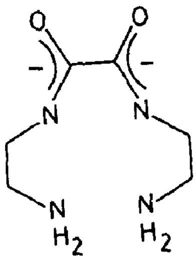
The single crystal X-ray structure of the tropylium salt of bis-(1,2-dicyanoethylenedithiolato)nickel(III) (3) shows a square planar nickel centre with Ni-S = 2.143, 2.146, C_1-C_2 = 1.368 Å and <S(1)NiS(2) = 92.42°.[11] The magnetic susceptibility of the complex is dominated by a one-dimensional, isotropic antiferromagnetic exchange coupling of $-4.4\ cm^{-1}$ and an anisotropic coupling of $0.26\ cm^{-1}$.[11] The oxidative properties of a series of mixed ligand nickel(II) complexes incorporating dithiolate, dithiocarbamate and related chalcogenolates have been assessed voltammetrically; the corresponding nickel(III) products were generated by oxidation with I_2 and characterised by e.s.r. spectroscopy.[12]



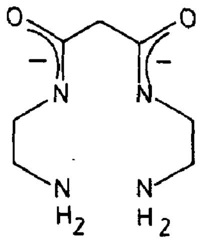
(3)

4.2.2 Nitrogen-donor ligands

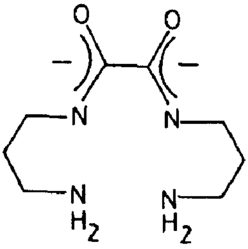
The nickel(II)/(III) redox couples of tris-chelate complexes of type $[Ni(L)_3]^{2+}$ (L = phen, bipy and substituted derivatives) were found to vary between +1.5V for the 4,4'-dimethyl-2,2'-bipyridine complex and +1.82V vs. NHE for the 5,5'-dinitro-2,2'-bipyridine derivative.[13] The nickel(III) products were generated electrochemically and characterised by e.s.r.(g_{av} = 2.1) and uv.visible spectroscopy. The complexes were found to be good one-electron oxidants.[13] A series of nickel(III) complexes incorporating the open-chain N_4 donor ligands (4)-(10) have been prepared ($E_{\frac{1}{2}}$ = +0.7 - +1.4V vs. NHE).[14] These amine and deprotonated amide nitrogen donor ligands were found to stabilise the high valent state very effectively, with the 5-5-5 chelate system being preferred by the nickel(III) centre.[14] The kinetics



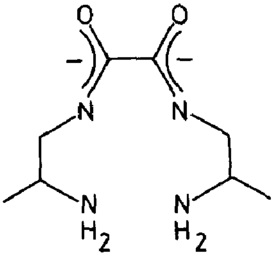
(4)



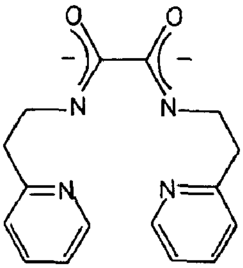
(5)



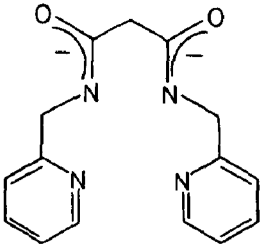
(6)



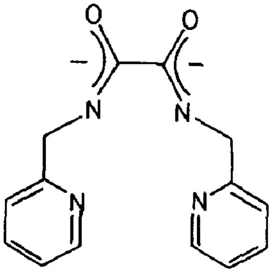
(7)



(8)



(9)



(10)

of I^- oxidation by tri(α-aminoisobutyric acid)nickel(III) occurs via two pathways involving either two, one electron transfers inhibited by $[Ni^{II}]$, or one, two electron process via a transition state incorporating two nickel and two I^- ions.[15] The overall rate of loss of $[Ni^{III}]$ was given by:

$$2(k_C + k_C^H[H^+] + \frac{k_B}{[Ni^{II}L]})[I^-]^2[Ni^{III}(L)]^2$$

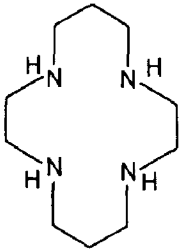
with $k_C = 3x10^{10}\ M^{-3}\ sec^{-1}$, $k_C^H = 3.8x10^{11}\ M^{-4}\ sec^{-1}$ and $k_B = 2.5x10^5\ M^{-2}\ sec^{-1}$.[15]

4.2.3 Macrocyclic ligands

The stablisation of the nickel(III) oxidation state has been achieved most successfully using macrocyclic ligands reflecting the relative thermodynamic stability and kinetic inertness of such systems.

The nickel(II)/(III) redox couples for the nickel complexes of [12]aneN_4, [13]aneN_4, sym-[14]aneN_4 (cyclam,(11)), asym-[14]aneN_4, [15]aneN_4, [16]aneN_4, [15]aneN_5, [16]aneN_5, [17]aneN_5, [18]aneN_6 (see 4.3.5.4) have been measured in acetonitrile.[16] The attainment of the nickel(III) oxidation state was found to be achieved most easily with the 14-membered ring macrocycle ($E_{\frac{1}{2}}$ = +0.702V vs. Ag/Ag^+ for $[Ni(cyclam)]^{2+}$ in CH_3CN) with the half-wave potential increasing dramatically for ring sizes greater or less than 14. The nickel(III) products were generated chemically with $NOBF_4$ or electrochemically and characterised by e.s.r. spectroscopy.[16] The kinetics of the outer-sphere oxidation $[Ni(cyclam)]^{2+}$ by cobalt(III) in $HClO_4$ has been investigated;[17] no effect on the rate of reaction was noted on addition of SO_4^{2-} although a nickel(III)-sulphate complex was obtained.[17]

$$[Ni(cyclam)]^{2+} + [Co(OH)]^{2+} \xrightarrow{k} [Ni(cyclam)]^{3+} + Co^{2+}_{(aqu)},$$
$$k = 4.7 \times 10^5 \; M^{-1} \; sec^{-1}$$



(11)

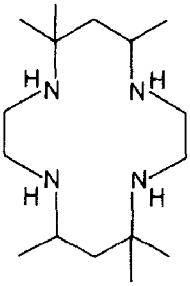
The rac- and meso-nickel(III) complexes of (12) have been shown to be five-coordinate at pH10, while the corresponding cyclam species is octahedral.[18] The kinetic stablisation of the nickel(III) meso isomer by SO_4^{2-} occurs via the formation of $[Ni(SO_4)_2(L)]^-$ and was found to be 5000 times larger than for the rac isomer; decomposition of nickel(III) by $\dot{O}H$ was shown to be first order in $[\dot{O}H]$.[18] The oxidation of cyclohexanone by meso-$[Ni(L)]^{3+}$ (L = (12)) in the presence of CF_3CO_2H, shows[19] inhibition due to $[H^+]$ with:-

$$\frac{-d[Ni(III)]}{dt} = \frac{k[Ni(III)][cyclohexanone]}{[CF_3CO_2H]}$$

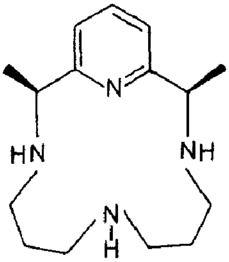
A mechanism involving deprotonation of the macrocycle, formation of a ligand radical species and abstraction of H from cyclohexanone (k_H/k_D = 3.2 for isotope effect for 2,2,6,6-tetradeuterocyclohexanone) was proposed.[18] The photo-induced oxidation and dimerisation of $[Ni(L)]^{2+}$ (L = (12)) via a nickel(III) intermediate has been described.[20]

The oxidation of $[Ni(L)]^{2+}$ (L = (13)) to nickel(III) has been achieved using Br_2^- [21]; the equilibrium constant K = 360 M^{-1} for replacement of Br^- by H_2O in $[Ni(Br)(L)(OH_2)]^{2+}$,

$$[Ni(Br)(L)(OH_2)]^{2+} + H_2O \xrightleftharpoons{K} [Ni(L)(OH_2)_2]^{3+} + Br^-$$



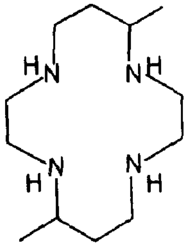
(12)



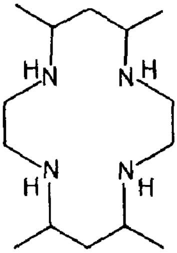
(13)

while at pH>5 displacement of Br^- was found to be first order with respect to $[^-OH]$, k = 6×10^9 $M^{-1}sec^{-1}$. The disappearance of $[Ni(OH)(L)]^{2+}$ was pH dependent suggesting amine dissociation followed by the formation of a ligand radical species leading to increased unsaturation of the macrocycle.[21] The generation of nickel(III) products incorporating dimethyl glyoxime with a series of axial ligands has been described.[22]

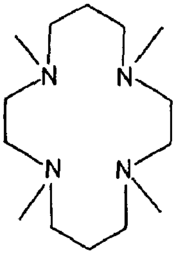
An alternative route to nickel(III) tetraaza macrocyclic products has been reported via oxidative addition of alkyl halides RX to nickel(I) precursors (see 4.4) yielding products $[Ni(R)(X)(L)]^+$ (L = (11), (12), (14)-(20)).[23] The electrochemistry, routes to decomposition and reactivity of these



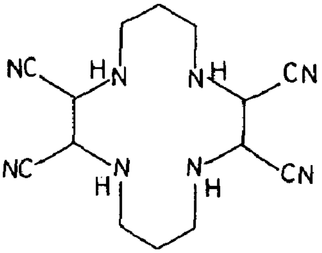
(14)



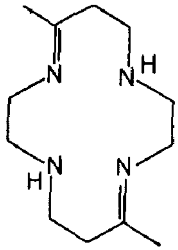
(15)



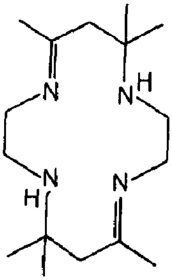
(16)



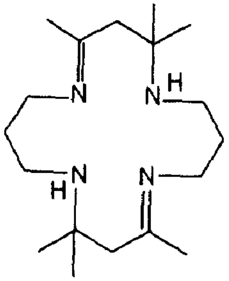
(17)



(18)

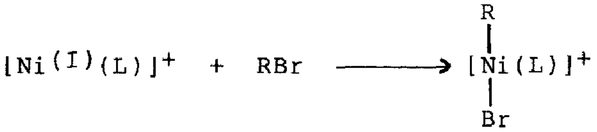


(19)

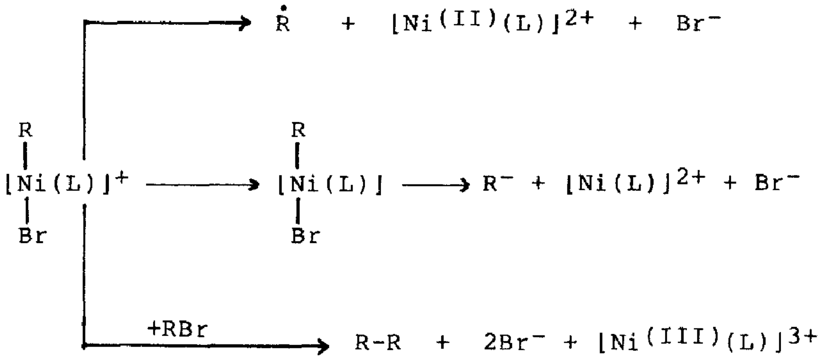


(20)

nickel(III) species has been discussed fully.[23] Interestingly related addition and elimination processes via nickel(II)/(III) intermediates have been found to be of importance in the reactivity of arylmethyl nickel(II) complexes.[24]

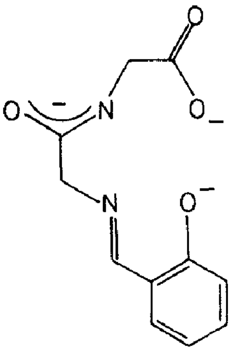


$$[\mathrm{Ni}^{(I)}(L)]^+ + RBr \longrightarrow [\overset{R}{\underset{Br}{\mathrm{Ni}}}(L)]^+$$

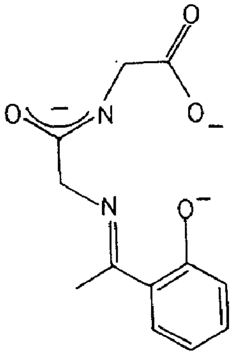


4.2.4 Mixed-donor ligands

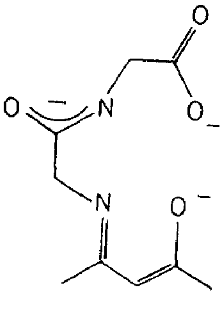
Nickel(III) complexes of tripeptide and dipeptide Schiff base ligands (21)-(25) incorporating N_2O_2 and N_3O donor sets have been studied electrochemically and related to the corresponding N_4 open chain ligands (see 4.2.2).[14] Oxidation of bis-(8-hydroxyquinolato)nickel(II) with Cl_2 or Br_2,[25] and the iminodiacetate species [Ni(L)] (L = $HN(CH_2CO_2^-)_2$) with Br_2^- [26] leads to the formation of the corresponding nickel(III) products. Interestingly, reaction of nickel(II) iminodiacetate with $\dot{O}H$ leads to attack at the ligand centre via H abstraction followed by organic radical disproportionation.[26]



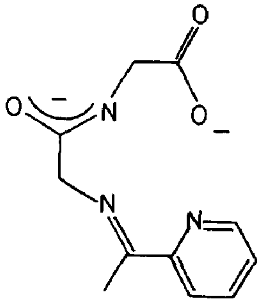
(21)



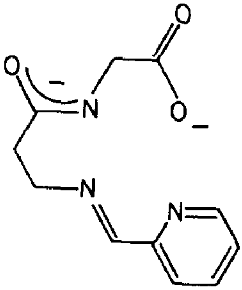
(22)



(23)



(24)



(25)

4.3 NICKEL(II)

Such a vast literature has developed around the chemistry of nickel(II) that it becomes impossible not to be selective when reviewing this work. Emphasis has been placed therefore upon the most relevant and well-characterised coordination compounds. Square planar <—> tetrahedral conversion for four coordinate complexes has been assessed using the angular overlap model.[27]

4.3.1 Hydrides

A neutron diffraction study on Mg_2NiD_4 indicates that Ni-D and Mg-D distances are 1.49 and 2.305 Å respectively.[28] The use of this and related nickel hydrides as hydrogen storage materials[29] and their structural[30-32] and electronic[33,34] properties have been of particular interest recently. These products are not strictly nickel(II) species.

Reaction of $[Ni(PCy_3)_2]$ with organo bromides in toluene produces $[Ni(Br)(H)(PCy_3)_2]$[35] while the related species $[Ni(Br)(H)(PPh_3)_3]$ can be converted to $[Ni(H)(NCCH_3)(PPh_3)_3](BF_4)$ by treatment with $TlBF_4$ in acetonitrile.[36]

4.3.2 Halides

The photoelectron spectra of NiX_2 ($X = F^-, Cl^-, Br^-$) have been reported[37,38] while the nature of $NiCl_2$ in aqueous solution has been discussed.[39]

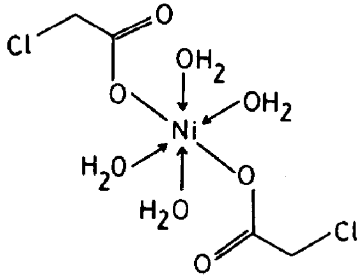
4.3.3 Oxygen-donor ligands

4.3.3.1 Aquo complexes

The single crystal X-ray structure of the octahedral $[Ni(OH_2)_6]^{2+}$ cation has been determined in the salts $Ni_3[(UO_2)_2F_7]_2.18H_2O$,[40] $Cd_2NiCl_6.12H_2O$,[41] $Cd_4NiCl_{10}.10H_2O$ [42] and $(NH_4)_2Ni(BeF_4)_2.6H_2O$ [43] with Ni-O = 2.072, 2.063, 2.027 Å for the latter complex. The symmetric Ni-O stretching vibration for $[Ni(OH_2)_6]^{2+}$ has been identified at 402 cm^{-1} and 405 cm^{-1} in the $[TiF_6]^{2-}$ and $[SiF_6]^{2-}$ salts respectively.[44] The variations in redox properties of $[Ni(OH_2)_6]^{2+}$ in the presence of alkaline earth base electrolytes has been investigated, and the polarographic characteristics and double layer parameters determined.[45] The electronic structure of nickel monoxide [46] and a structural study of $NiTe_2O_5$ (prepared by fusion of NiO with TeO_2 (1:4) at 1100K)[47] have been reported.

4.3.3.2 Carboxylate complexes

The single crystal X-ray structure of trans-[Ni(OAcCl)$_2$(OH$_2$)$_2$] (26) shows a distorted octahedral stereochemistry around nickel(II) with Ni-O(OH$_2$) = 2.025, 2.105, Ni-O(OAc) = 2.104 Å.[48] The complexes [Ni(L)$_3$][SbCl$_6$]$_2$ (L = HCO$_2$H, AcOH, EtCO$_2$H, ClCH$_2$CO$_2$H) have been prepared by reaction of NiCl$_2$ with SbCl$_5$ in MeNO$_2$ for 4h at 50-60° C to give [Ni(MeNO$_2$)$_6$][SbCl$_6$]$_2$ followed by treatment with excess of L.[49] Related complexes of benzoic acid[50] and phenoxyacetic acid derivatives[51] have been reported. For the formation of [Ni(HL)]$^+$ (H$_2$L = vanillomandellic, mandellic, thiolactic acid), rate constants of 3.64×10^3, 4.93×10^3, 7.66×10^3 M^{-1} sec^{-1} and stability constants of 33, 45 and 56 have been reported respectively.[52]

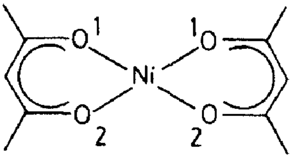


(26)

Reaction of [Ni(cod)$_2$] with RCO$_2$COR' in the presence of L, or treatment of [Ni(O$_2$CR')(R)L] with CO at -78°C yields [Ni(COR)(O$_2$CR')L] (L = (PEt$_3$)$_2$, bipy; R = Me, Et, R' = Me, Ph),[53] while treatment of [Ni(O$_2$CR')(R)(L)] with excess of CO at room temperature gave anhydrides RCO$_2$COR'.[53] Reaction of [Ni(R)$_2$L] with XH (X = $^-$OCPh, 4-cyanophenoxo, 4-phenylphenoxo, $^-$O$_2$CEt, Cl$^-$) yields the complexes [Ni(R)(X)L], while reaction with R'COX affords [Ni(R)(X)L] together with the ketones RCOR'.[54] The complexes undergo disproportionation to, for example, [$NiEt_2$(bipy)] and [$Ni(X)_2$(bipy)] (X = ^-O_2CEt, ^-O_2CPh, Cl^-).[54]

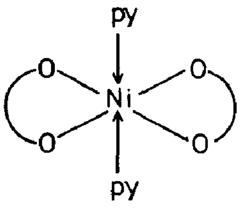
4.3.3.3 Ketonate complexes

The role of π-bonding in planar β-diketonate complexes has been assessed using the CNDO/2 method.[55] The ionisation potential of the core electrons in [$Ni(acac)_2$] has been correlated with the metal oxidation state.[38] An important electron diffraction study of [$Ni(acac)_2$] (27) has shown the complex to have a monomeric square planar structure in the gas phase with Ni-O = 1.876, C-O = 1.273, C-C(ring) = 1.401, C-C(CH_3) = 1.504 Å, <O(1)NiO(2) = 93.6°.[56] This contrasts with the octahedral trimeric structure found for this complex in the solid state.[57] The polarography of acetylacetonate and hexafluoroacetylacetonate nickel complexes in dmso has been reported and related to dimerisation and polymerisation of the complexes in solution.[58] The substitution chemistry of a range of ketonate complexes has been studied to give [$Ni(acac)_3$]$^-$,[59] [Ni(β-dik)$_2$(L)], [Ni(β-dik)(L)$_2$]$^+$, [Ni(L)$_3$]$^{2+}$ (β-dik = acac, hfacac, tfacac; L = bipy, phen, en, tmen) 60-62 and [Ni(β-dik)(L)$_4$] (β-dik = nitromalonaldehyde; L = py, H_2O).[63] The

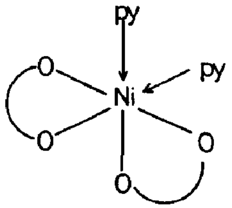


(27)

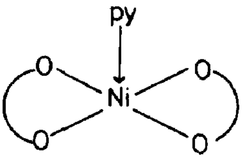
thermal decomposition of these and related complexes via dimerisation, dehydration and disproportionation has been investigated.[60,61] Rearrangement reactivity of metal diketonates has been monitored by mass spectrometry.[64] A ^{19}F n.m.r. study on py adducts of $[Ni(hfacac)_2]$ indicate the presence of four types of complexes (28)-(31). At low temperatures, exchange is slow and well resolved n.m.r. spectra are observed with cis isomers being favoured.[65]



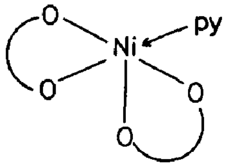
(28)



(29)

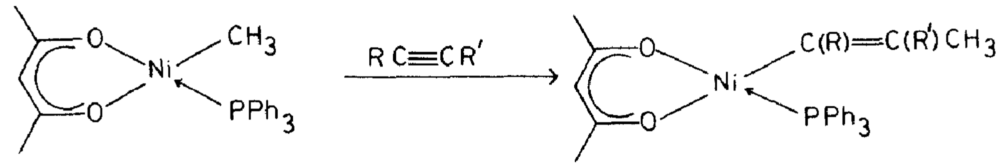


(30)



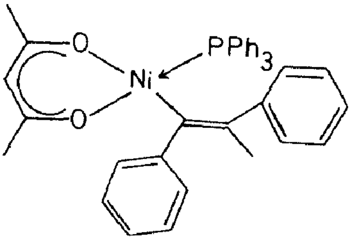
(31)

Insertion of alkynes into $[Ni(CH_3)(acac)(PPh_3)]$ (32) to give vinyl complexes $[Ni(C(R) = C(R')(CH_3))(acac)(PPh_3)]$ (33) has been described.[66] The single crystal X-ray structure of (Z)-$[Ni(C(Ph) = C(Ph)(CH_3))(acac)(PPh_3)]$ (34) shows a planar nickel(II) centre with Ni-P = 2.178, Ni-O = 1.91 and Ni-C = 1.897 Å; alkynes with dissimilar substituents added to the nickel complex to give a vinyl product with the sterically larger group nearest the metal centre. Elimination of olefinic products was achieved by addition of I_2, CH_3Li, $LiAlH_4$ or CO-MeOH.[66]

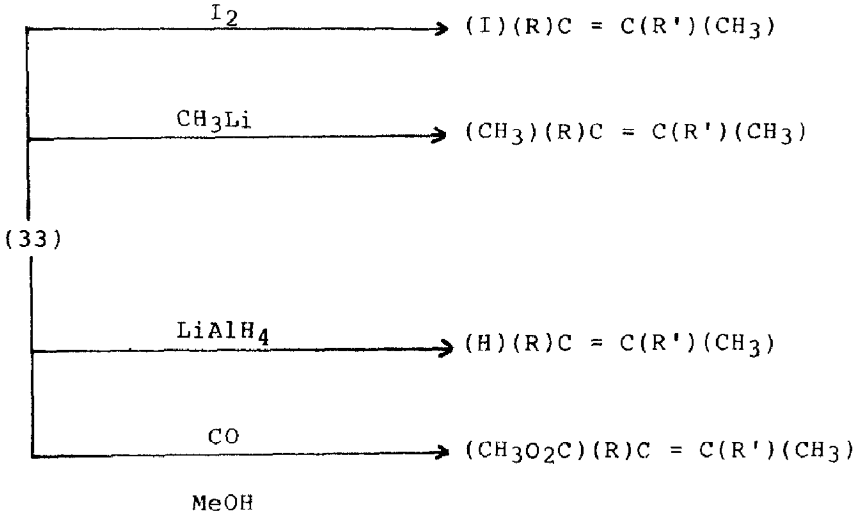


(32)

(33)

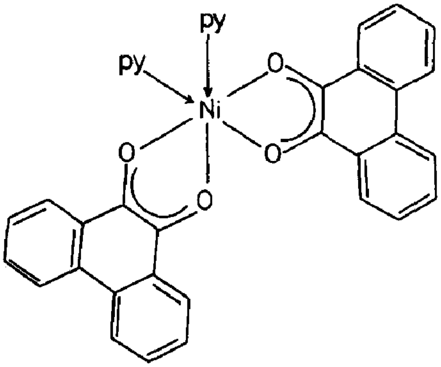


(34)



Reaction of $[Ni(R)_2L]$ with XH gives the products $[Ni(R)(X)L]$ (R = Me, Et; X = acac, benzoylacetonato; L = $(PEt_3)_2$, bipy).[54]

Studies on other diketonate systems have been reported.[67-69] The single crystal X-ray structure of cis-$[Ni(py)_2(L)]$ (35) (L = 9,10-phenanthrenesemiquinone) shows Ni-O = 2.022, 2.082 and 2.028, 2.100 Å with Ni-N = 2.069, 2.099 Å.[70] Variable temperature magnetic susceptibility measurements indicate a weak intramolecular antiferromagnetic exchange interaction between the semiquinone ligand and metal centre.[70]



(35)

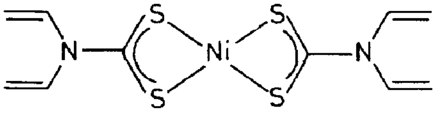
4.3.3.4 Miscellaneous complexes

A single crystal e.s.r. spectroscopic study on the centrosymmetric complex $[Ni(L)_6](BrO_3)_2$ (L = pyridine-N-oxide) reports $g_{\parallel} = 2.26$, $g_{\perp} = 2.33$ with $D/k_B = 4.55$, $zJ/k_B = -0.10$.[71] $[Ni(L)_4(OH_2)_2]^{2+}$ (L = 8-quinolinol-N-oxide) has been prepared, the N-oxide ligand being coordinated via the phenolic O-donors to give a MO_6 coordination sphere;[72] octahedral complexes $[NiCl_2(L)_2]$ and $[Ni(NO_3)_2(L)_2]$ (L = 4,4'-bipyridine-N,N'-dioxide) have been generated and characterised by magnetic measurements and uv-visible spectroscopy.[73] Triazene-1-oxide complexes of nickel have been prepared.[74] Reaction of $Ni(ClO_4)_2$ with L (L = $(PhCH_2)Ph_2PO$, Ph_3PO) in anhydrous ethanol followed by addition of HCO_2Et as a dehydrating agent yields the complex $[Ni(L)_4](ClO_4)_2$.[75] Complexation of nickel(II) with N-^{t}butylurea to form $[Ni(L)_6]^{2+}$,[76] with 1,3,5-trihydroxycyclohexane,[77] nitro-naphthol[78] and cycloserine[79] derivatives have also been described.

Reaction of $NiCl_2$ with ClO_3 yields anhydrous $Ni(ClO_4)_2$ in which the metal ion is octahedral with strongly and weakly bound ClO_4^-.[80] The photoelectron spectral data for $[Ni(NO_3)_2]$ has been compared and correlated with other simple nickel salts.[38] The binding of sulphite to nickel in $NiSO_3.xH_2O$,[78] of thiosulphate in $[Ni(L)_n(S_2O_3)]^{x+}$ (L = N-donor ligand)[82] and the mechanism of zirconium phosphate exchange with nickel(II)[83] have been investigated. A molecular orbital study of O_2 activation at a nickel penta-ammine centre has been reported.[84]

4.3.4 Sulphur and Selenium-donor ligands

The single crystal X-ray structure of bis-(diallyldithiocarbamato) nickel(II) (36) shows a square planar nickel(II) centre with Ni-S = 2.198, 2.210 Å with the S_2CNC_2 ligand nearly planar.[85] The i.r. spectrum of the diethyl derivative of (36) has been measured in an N_2 matrix and all the bands assigned and classified on the basis of their polarisation in D_{2h} symmetry.[86] The extraction of nickel(II) by dialkyldithiophosphate has been shown to occur via the formation of $[Ni(S_2P(OCH_3)_2)_2]$.[87,88]



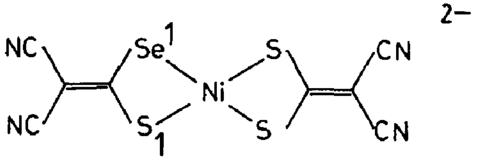
(36)

Photolysis of $[Ni(S_2C_2Ph_2)(phen)]$ in $CHCl_3$ yields an oxidised product $[Ni(S_2C_2Ph_2)(phen)]^+$ assigned as a ligand radical species (g = 2.0093). Ligand dissociation of this radical species occurs at room temperature.[89]

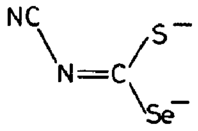
$$[Ni(S_2C_2Ph_2)(phen)] \xrightarrow{h\nu, 77K} [Ni(S_2C_2Ph_2)(phen)]^+$$

$$2[Ni(S_2C_2Ph_2)(phen)]^+ \xrightarrow{RT} [Ni(S_2C_2Ph_2)_2] + [Ni(phen)_2]^{2+}$$

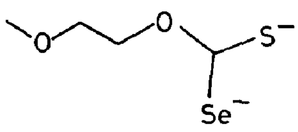
The single crystal X-ray structure of $(Bu_4N)_2[Ni(SSeC{=}C(CN)_2)_2]$ (37) shows a square planar nickel centre with Ni-Se = 2.330, Ni-S = 2.292 Å and <Se(1)NiS(1) = 82.02°.[86] *Bis* nickel(II) complexes of L (L = (38),(39)) were also prepared.[90] The diselenocarbamate complex $[Ni(Se_2CNEt_2)_2]$ reacts with $[NiCl_2(PEt_3)_2]$ in acetone to yield $[NiCl(Se_2CNEt_2)(PEt_3)]$ as a dark red product.[91]



(37)

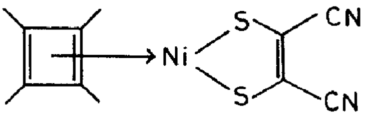


(38)

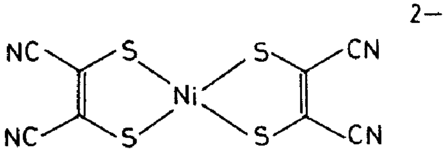


(39)

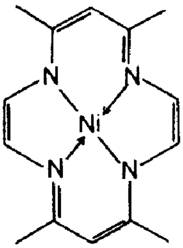
The structure of (40) has been reported and shows an average C-C distance of the cyclobutadiene ring of 1.465 Å.[92] Reaction of MeI with (41) leads to methylation of the sulphur donor atoms.[93] The rate-determining step for the methylation reaction is methylation of the first sulphur of the complex ($k=10^{-3}$ M^{-1} sec^{-1}) to give the monoanion complex. The alkylated complex decomposes to yield the metal-free alkylated dithio ligand.[93] Reaction of (**42**) with (**43**) in CH_3CN at 60°C gives a semi-conducting paramagnetic 2:1 adduct.[94]



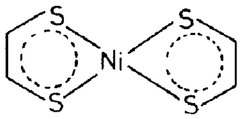
(40)



(41)

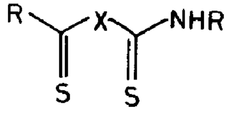


(42)



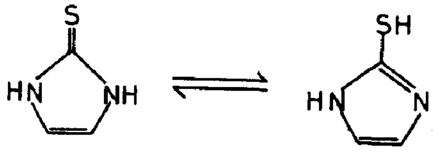
(43)

The role of π-bonding in dithio-β-diketonates has been the subject of a CNDO/2 study.[65] The binding of 1-thioacylthioureas (**44**) to nickel(II) to yield bis complexes of type $[Ni(L)_2]^{2+}$ has been reported.[95] Dissolution of $[Ni_2Br_2(tu)_8](NO_3)_2$ in acetone yields tetrahedral $[NiBr_2(tu)_2]$ and octahedral $[Ni(NO_3)(tu)_5]^+$ [96] while coordination of imidazoline-2-thione and alkylated derivatives to nickel(II) centres affords the complexes $[Ni(L)_4X_2]$ ($X = Cl^-, Br^-, I^-, NO_3^-, BF_4^-, ClO_4^-, SCN^-$; L = (**45**)) in which (L) is bound via the sulphur donor.[97,98] Related studies on S-bound tetrahydropyrimidine-2-thione,[99] hydrazodithioamide,[100] dicyano(dithionitrito)amide,[101] and thiophenol and 4-toluenethiol[102] complexes of nickel(II) have been discussed.



X = NH,CH_2

(44)

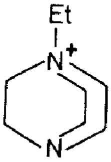


(45)

4.3.5 Nitrogen-donor ligands

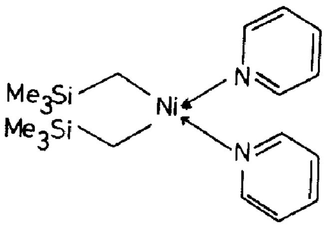
4.3.5.1 Monodentate ligands

Stability constants of pyridine and nicotine bound to nickel(II) have been determined polarographically;[103] complex formation of nickel(II) with 4-phenyl pyridine and isoquinoline in water: ^{t}butanol has been measured using stopped flow techniques.[104] The i.r. spectra of [Ni(imid)$_6$] (X = NO_3^-, ClO_4^-) and their deuterated analogues have been analysed and the internal imidazole vibrations assigned.[105] The structural and ligand field parameters for [NiX_3L] (X = Cl^-, Br^-; L = (46)) have been measured by single crystal paramagnetic susceptibility measurements (295-20K) and absorption spectroscopy (300-77K) and analysed by the angular overlap model; the angular overlap model parameters were found to fit with the coordination bond lengths with a low spin orbit coupling coefficient relative to the cobalt(II) analogues.[106]



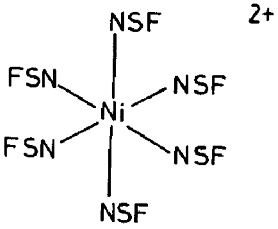
(46)

Reaction of $[Ni(C_6Cl_5)Cl(PPh_3)_2]$ with L (L = py, 3-methyl pyridine, 4-methyl pyridine, 3,5-dimethyl pyridine) in benzene in the presence of $NaClO_4$ yields $[Ni(C_6Cl_5)(L)_3](ClO_4)$; in acetone $[Ni(C_6Cl_5)py_2(PPh_3)](ClO_4)$ can be isolated.[107] By altering conditions and counter-ions a series of complexes $[NiX(C_6Cl_5)(L)_2]$ (X = Cl^-, Br^-, NO_2^-, $C_6Cl_5O^-$, NCS^-), $[Ni(C_6Cl_5)py(PR_3)_2](ClO_4)$ (R = Ph, Et), $[NiCl(C_6Cl_5)(py)(PEt_3)]$, $[Ni(C_6Cl_5)(NO_2)py(PPh_3)]$ and $[Ni(C_6Cl_5)(NCS)(py)(PPh_3)]$ were prepared and characterised.[107] Reaction of $[NiCl_2py_4]$ with $Mg(CH_2SiMe_3)Cl$ yields <u>cis</u>-$[Ni(CH_2SiMe_3)_2py_2]$ (**47**), a single crystal X-ray structure of which shows square planar nickel(II) with Ni-N = 1.957, Ni-C = 1.89 Å, <NNiN = 87.5°, <NNiC = 92.5°.[108]



(47)

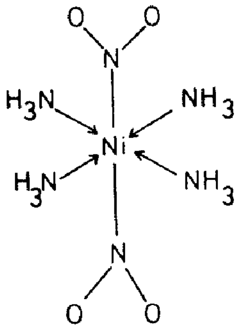
The clathrate phases of $[Ni(NCS)_2(L)_4]$ (L = 4-methyl pyridine) have been investigated in nitrotoluene[109] and in naphthalenes,[110] while the electroreduction of thiocyanates bound to nickel(II) has been reported.[111] The single crystal X-ray structure of $[Ni(NSF)_6](AsF_6)_2$ (**48**) shows octahedral nickel(II) bound to six N-donors, with Ni-N = 2.05 Å.[112]



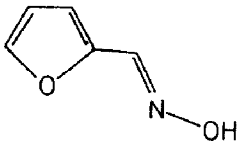
(48)

Reduction of $[Ni(NO_2)X(L)_2]$ (X = Cl^-, Br^-, I^-, NO_2^-, SCN^-; L = dppe, PPh_3, P^nPr_3, $OPPh_3$, py) with CO or PPh_3 yields the nickel(0) nitrosyl species $[Ni(NO)X(L)_2]$ which revert to the nitro complexes on oxygenation.[113,114] The single crystal X-ray structure of trans-$[Ni(NO_2)_2(NH_3)_4]$ (**49**) shows Ni-N(NO_2) = 2.14, Ni-N(NH_3) = 2.10 Å.[115] The magnetic susceptibility of the complex follows the Curie-Weiss Law ($\Theta = -5.5K$) between 10-300K, and is temperature independent below 3K; long range hydrogen bonding was noted in the structure. A ^3A_g ground state with a zero field splitting D = 15.2K (10.4 cm^{-1}) were reproduced using the angular overlap model.[115]

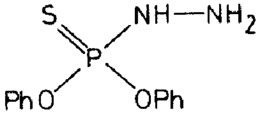
$$[Ni(NO_2)X(L)_2] \xrightarrow{CO} [Ni(NO)X(L)_2] + CO_2$$



(49)



(50)

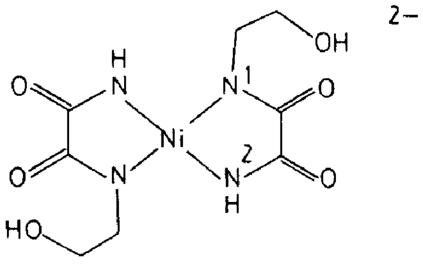


(51)

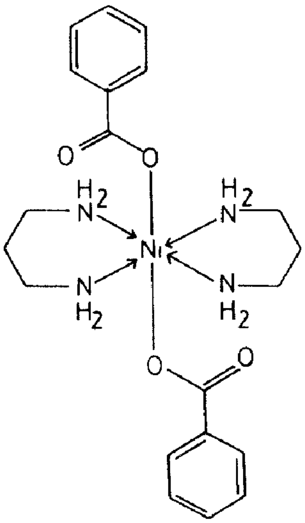
For the complexes [NiCl$_2$(L)$_4$] (L = (50),[116] (51)[117]) binding through the N(1)-donor atoms was proposed; complexes of pyrazole[118] and 5-pyrazolone[119] have been reported.

4.3.5.2 Bidentate ligands

The single crystal X-ray structure of (52) shows a square planar stereochemistry with Ni-N(1) = 1.900, Ni-N(2) = 1.857 Å,[120] while for (53) an octahedral structure was observed

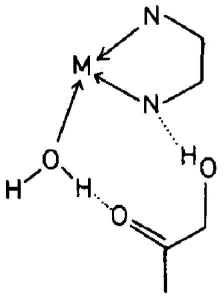


(52)

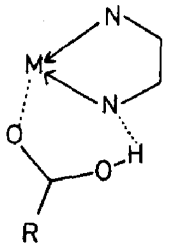


(53)

with Ni-N = 2.105, 2.121 and Ni-O = 2.128 Å.[121] The complexation of en to nickel(II) gives $[NiX_2(en)_2]$ and $[Ni(en)_3]X_2$ ($X = {}^{-}N(CN)_2$, ${}^{-}NOC(CN)_2$);[122] the apparent molar volumes of amine complexation to nickel(II) have been measured.[123] The rate of dissociation of $[Ni(en)]^{2+}$ was found to increase linearly with $[H^+]$ under aqueous conditions at pH <1.5; the dissociation of $[Ni(en)_3]^{2+}$ however exhibited no general acid catalysis under the same conditions.[124] The acid effect for $[Ni(en)]^{2+}$ was proposed to reflect the ability of the carboxylic acid to associate with the metal complex and transfer a proton within the coordination sphere, eg (54), (55). The rate constants for hydrolysis of $[Ni(en)]^{2+}$ were found to be k = 0.3 (CH_3COOH), 0.141 ($ClCH_2COOH$), 0.08 ($Cl_2CHCOOH$), 0.01 M^{-1} sec^{-1} (Cl_3CCOOH).[124]



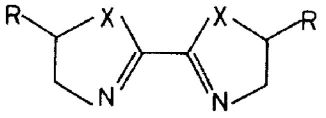
(54)



(55)

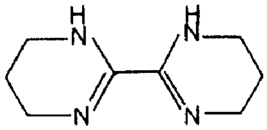
The racemisation of $[Ni(phen)_3]^{2+}$ in nitrobenzene has been investigated and association constants of the metal chelate with nitrobenzene determined and discussed.[125] Improvement in the optical purity of $[Ni(phen)_3]^{2+}$ has been achieved on colloidal clay reflecting adsorption of the racemic metal chelate onto the clay surface.[126] Related to this work, $[Ru(acac)_3]$ has been partially resolved by chromatography on a column containing

$[Ni(phen)_3]^{2+}$,[127] while stereoselective adsorption of $(+)_{510}[Fe(phen)_3]^{2+}$ has been observed on a clay surface modified by optically active $[Ni(phen)_3]^{2+}$, the iron complex being adsorbed more rapidly with $(-)_{546}[Ni(phen)_3]^{2+}$ than with the $(+)_{546}$ isomer,[128] Tris-chelate complexes of 2,2'-bi-2-imidazoline derivatives (56) and (57) have been prepared.[129] An n.m.r. study on nickel complexes of substituted bipyridine ligands has probed possible isotropic spin transfer mechanisms,[130] while complex formation with bipy and phen in water: ᵗbutanol has been monitored by stopped-flow techniques.[104]



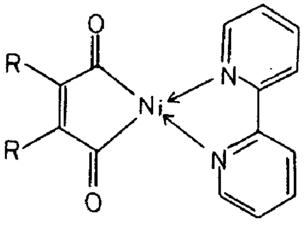
X = NH , R = H
O H
O Me

(56)



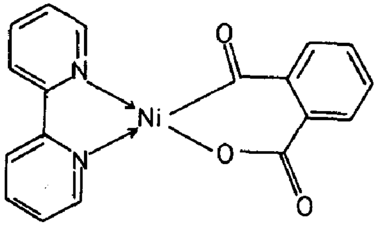
(57)

Reaction of [Ni(Et)(Cl)(bipy)] with alkenes having electron-withdrawing substituents gives $[NiCl_2(bipy)]$ and the organometallic complex $[Ni(alkene)_2(bipy)]$.[54] The metallocyclic complex (58) (R = Ph, Me) has been prepared by cyclisation of $[Ni(CO)_2(bipy)]$ with RC CR, by reaction of $[Ni(PhC\equiv CPh)(bipy)]$

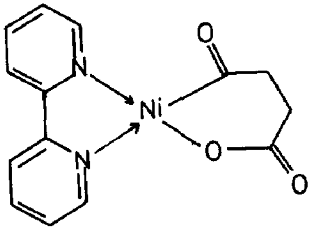


(58)

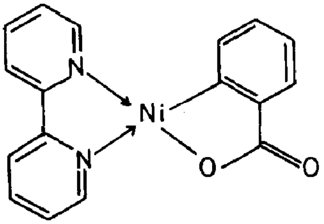
with CO, or by cyclisation of [Ni(cod)(bipy)] with PhC≡CPh and CO.[131] Reaction of phthalic and succinic anhydrides with [Ni(cod)(bipy)] give (59) and (60) which can be decarbonylated to (61) and (62) at elevated temperatures.[132] Thermal decomposition of (63) in hexane at 174° gives (64) which yields (65) (R = R' = I) on treatment with ICl and (65) (R = R' = H) with HCl.[133] Treatment of (65) (R = CO_2H, R' = H) with BuLi led to esterification of the carboxyl group; the resulting ligand reacted with [$NiCl_2$(bipy)] to give (66).[133]



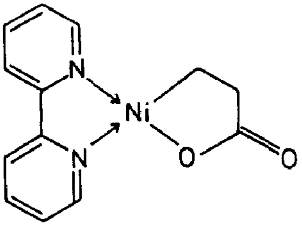
(59)



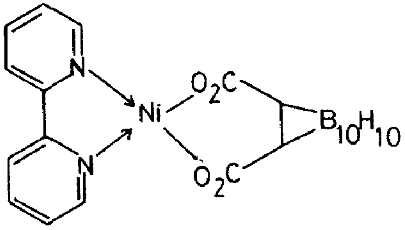
(60)



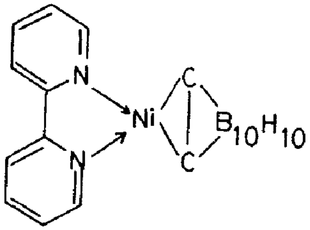
(61)



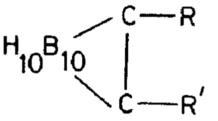
(62)



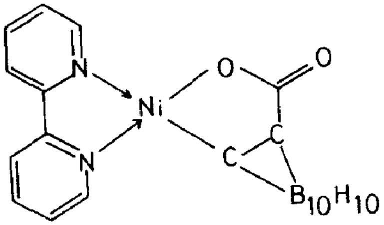
(63)



(64)

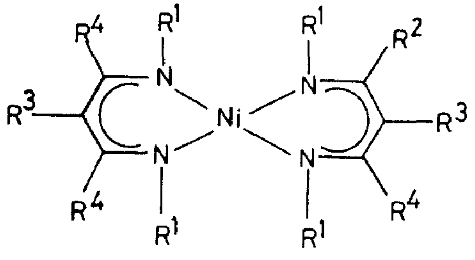


(65)

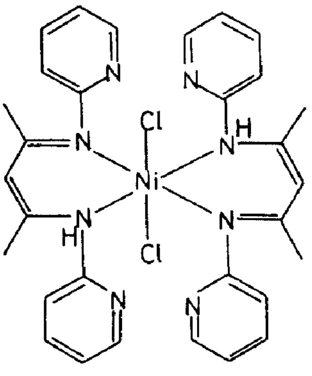


(66)

Paramagnetic ^{1}H n.m.r. shifts for the tetrahedral 1,3-diimine complex (67) have been recorded (+130 to -375 ppm).[134] A value of ΔG = 17.3 Kcal.mole^{-1} was estimated for the energy of enantiomerisation for the chiral complex ($R^1 = CH_3$, $R^2 = CH_3$, R^3 = Et, R^4 = H).[134] Condensation of 2-amino pyridine with acetyl acetone in the presence of $NiCl_2$ gave (68),[135] while reaction of $[Ni(R)_2L]$ (R = Me, Et; L = $(PEt_3)_2$, bipy) with XH (X = acetophenone oximate) affords [Ni(R)(X)L].[54] Related



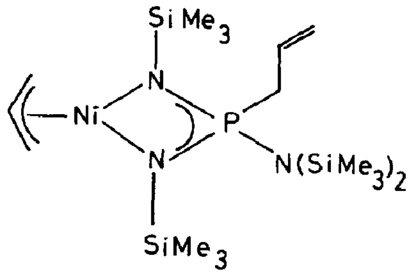
(67)



(68)

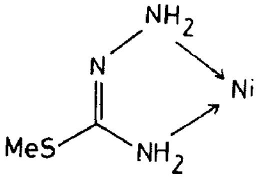
dioxime complexes have been investigated,[136] with particular emphasis being placed on their protonation-deprotonation reactivity.[137] The single crystal X-ray structure of $[Ni(L)_3]^{2+}$ (L = 1,2-cyclohexanedione dioxime) has been reported.[138]

Treatment of bis-(allyl)nickel(II) with $(Me_3SiN)_2PN(SiMe_3)_2$ yields the imino-phosphorane complex (69); the crystal structure of the palladium(II) analogue was reported.[139] Reaction of $[Ni(R)_2(L)]$ (R = Me, Et; L = $(PEt_3)_2$, bipy, $Ph_2PCH_2CH_2PPh_2$) with a series of amines (XH) affords the corresponding imido and amido species [Ni(R)(X)(L)] (X = succinimido, phthalimido, diacetamido, pyromellitimido and imidazolato);[140] alkylation of these products was described.[140]



(69)

The kinetics of reaction of nickel(II) with PADA (pyridyl-2-azo-4-dimethylaniline) were investigated in micellar solutions using stopped flow techniques;[141] increased rates of complexation were observed with micelles (alkyl sulphonates), this enhancement decreasing with decreasing alkyl chain length of the micelle.[141] A series of complexes $[Ni(L)_2]X_2$ (diamagnetic, red-brown), $[Ni(X)_2(L)_2]$ and $[Ni(L)_2(py)_2]^{2+}$ (paramagnetic, blue)



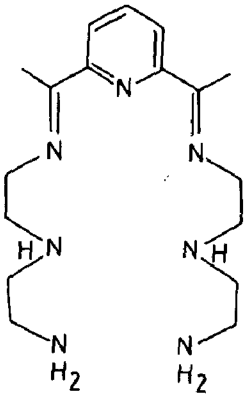
(70)

(X = halide, L = S-methylthiosemicarbazide (**70**)) have been prepared, L being bound through nitrogen donors.[142] A linear, oligomeric structure has been proposed for $[NiCl_2(L)]$ (L = purine) in which paramagnetic octahedral nickel centres are bridged by purine ligands.[143] The coordination properties of 2-alkylamino pyridines have been investigated.[144,145] The formation constant for 2-(aminomethyl)pyridine with nickel(II) is found to be larger than for 2-(aminoethyl)pyridine reflecting the increased chelate effect for the five-membered ring system.[145] Several other papers have concentrated on the complexation of nickel(II) by bidentate ligands.[146-151]

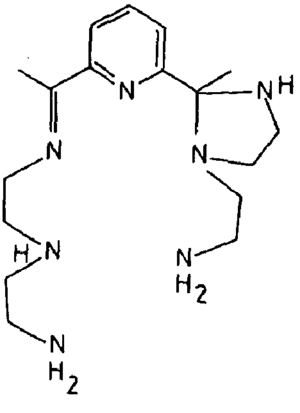
4.3.5.3 Polydentate ligands

The binding of 2,2',6',2"-terpyridine to nickel(II) in water: ^{t}butanol has been studied;[104] studies on the exchange of tetraethylenepentamine by aminocarboxylates under aqueous conditions indicate that the rate determining step is loss of water molecule followed by coordination of the first N-donor of the aminocarboxylate.[152] Circular dichroism spectra of the trigonal bipyramidal species $[NiX(L)]^{2+}$ (L = (S)-2,4,8-trimethyl-5-(3-methylazabutyl)-2,5,8-triazanonane) have been interpreted assuming C_{3v} symmetry.[153]

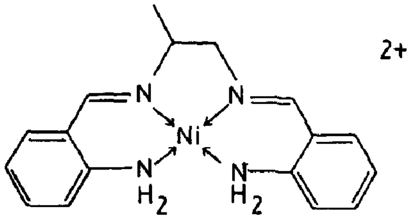
A series of four and six coordinate nickel(II) complexes incorporating hydrazino-1,10-phenanthroline derivatives (L) $[NiCl_2(L)]$, $[Ni(L)_2]^{2+}$, $[Ni(NCS)_2(L)]$, have been reported,[154,155] the field strength of 2-hydrazino-1,10-phenanthroline itself being near the crossover region for iron(II).[155] The synthesis of a pentagonal bipyramidal nickel complex of (71) has been achieved by metal exchange with the alkaline earth product; the nickel complex was found by X-ray powder diffraction to be isostructural with the corresponding copper(II) species.[156] Isomerisation of the heptadentate ligand (71) to a hexadentate species (72) has been observed, complexation of nickel(II) by (72) yielding a distorted octahedral product.[157] The single crystal X-ray structure of (73) shows Ni-N distances of 1.86,



(71)



(72)



(73)

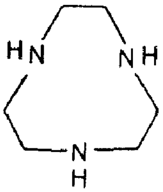
1.88, 1.86 and 1.87 Å, with the nickel ion 0.003 Å out of the plane of the donor set.[158] A series of related complexes incorporating tetradentate Schiff base polydentate ligands have been synthesised and their chemical properties assessed.[159-163]

The chemistry of nickel complexes of polydentate ligands remains a most popular and voluminous area of research, the electronic magnetic, spectroscopic and stereochemical properties of these species being of particular interest.[164-194]

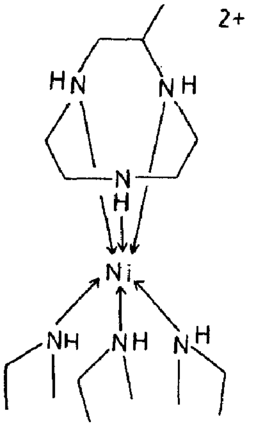
4.3.5.4 Macrocyclic ligands

Thermodynamic aspects of the formation of nickel(II) polyazamacrocycles have been reviewed.[195]

The electronic spectrum of $[Ni(L)_2]^{2+}$ (L = 1,4,7-triazacyclononane, (**74**)) has been interpreted on the basis of a trigonally distorted octahedral structure to give D_q = 1140 and B = 980 cm^{-1}.[196] The half-sandwich complex $[Ni(L)X_3](ClO_4)_2$ (**75**)



(74)

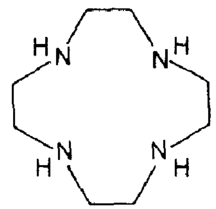


(75)

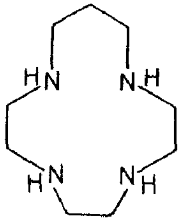
(L = 2-methyl-1,4,7-triazacyclononane, X = (aminomethyl)ethane) has been synthesized.[197]

A range of nickel(II) complexes of polyaza macrocycles ((**11**), (**76**)-(**84**)) have been synthesised and their redox, electronic and magnetic properties investigated.[16,198-200] The heats of formation of their respective nickel(II) complexes were found to increase in the order (**81**)<(**83**)<(**82**); no positive macrocyclic ethalpy effect was observed for these complexes.[198] ^{1}H n.m.r. studies on [Ni(L)]Cl$_2$ (L = (**80**)) in CDCl$_3$ and D$_2$O indicate that the coordinated ligand adopts a chair conformation in the chelate rings.[195] The kinetics of complex formation of tetraaza open chain ligands were compared with their cyclic analogues.[201,202] The bimolecular rate constants for complex formation were found to decrease in the order (**85**)$\gg$(**11**)>(**16**);[201] for (**85**) and (**11**) the rate-determining step is dissociation of the first solvent molecule with incorporation of the metal ion into the macrocycle.[201,202] A second step involving isomerisation-rearrangement of the coordinated ligand,[201,202] followed by equilibration between four, five and six coordinate metal complexes was observed in solution.[202] Complexation of nickel(II) by tetramethyl cyclam (**16**) was inhibited due to steric effects,[201] while incorporation of nickel(II) into cyclam (**11**) was found to be slower in hydrogen-bonding solvents due to protonation of the macrocycle.[202] For the aquation of [Ni(L)]$^{2+}$ (L = (**16**)), values for ΔH, ΔS and ΔV of -39.7 KJ mole^{-1},

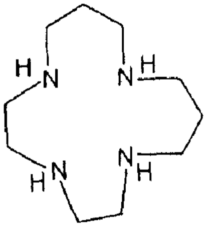
$$\underset{\text{(diamagnetic)}}{[\mathrm{Ni(L)}]^{2+}} \quad + \quad n\mathrm{H_2O} \longrightarrow \underset{\text{(paramagnetic)}}{[\mathrm{Ni(L)(OH_2)}_n]^{2+}}$$



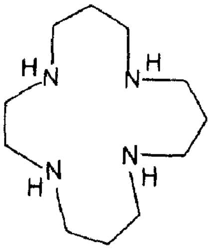
(76)



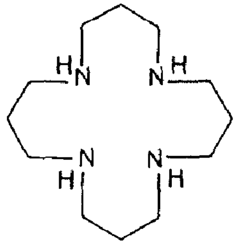
(77)



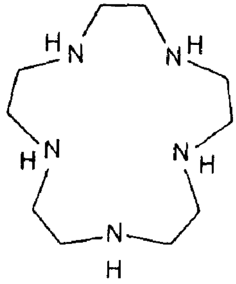
(78)



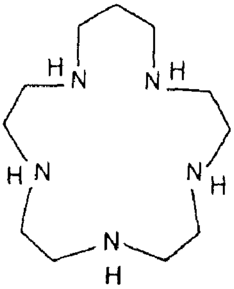
(79)



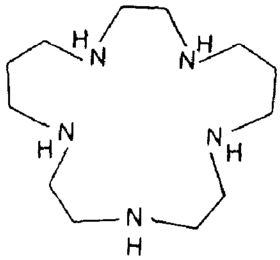
(80)



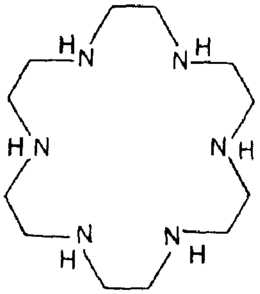
(81)



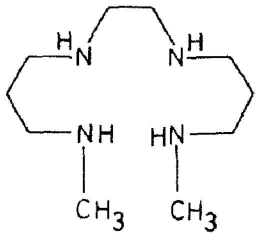
(82)



(83)



(84)



(85)

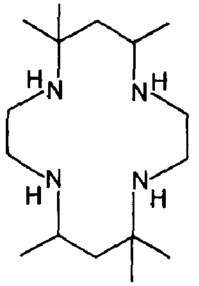
-1.33J K^{-1} $mole^{-1}$ and -10 cm^3 $mole^{-1}$ respectively were determined by n.m.r. studies.[203] An ^{17}O n.m.r. study of the four to six coordinate equilibrium in $[Ni(L)]^{2+}$ (L = [12]aneN_4, (**76**)) has

$$K_{equ} = \frac{[[Ni([12]aneN_4)]^{2+}]}{[[Ni([12]aneN_4)(H_2O)_2]^{2+}]} = 490 \times 10^{-4}$$

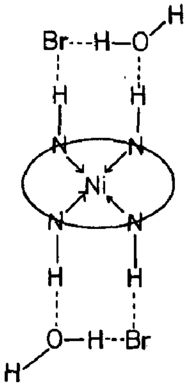
been reported,[204] while reaction $[Ni(L)](ClO_4)_2$ (L = cyclam, (**11**)) with en gives <u>cis</u>-$[Ni(L)(en)](ClO_4)_2$ which affords <u>cis</u>-$[NiBr_2(L)]$ on treatment with HBr, and <u>cis</u>-$[Ni(L)(OH_2)_2]^{2+}$ with H_3O^+.[205]

$$\begin{tikzcd}
 & & \text{cis-}[NiBr_2(L)] \\
{[Ni(L)]^{2+}} \arrow[r, "en"] & \text{cis-}[Ni(L)en]^{2+} \arrow[ur, "HBr"] \arrow[dr, "H_3O^+"'] & \\
 & & \text{cis-}[Ni(L)(OH_2)_2]^{2+}
\end{tikzcd}$$

The single crystal X-ray structure of <u>trans</u>-$[NiF_2(L)].5H_2O$ (L = <u>meso</u>-Me_6[14]aneN_4, (**12**)) shows an octahedral stereochemistry around nickel(II) with average Ni-F = 2.087 and average Ni-N = 2.090 Å.[206] The single crystal structures of the orange,

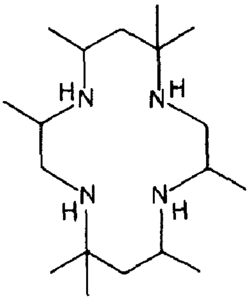


(12)

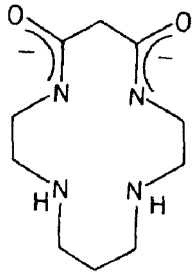


(86)

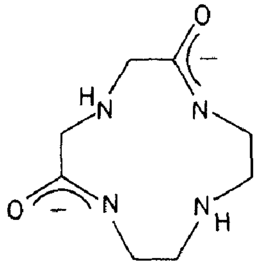
diamagnetic complex [Ni(L)]Cl_2.$2H_2O$ shows a square planar structure with average Ni-N = 1.959 Å, while the violet, paramagnetic species trans-[NiCl_2(L)].$2CHCl_3$ is octahedral with Ni-N = 2.060, 2.102 and Ni-Cl = 2.562 Å.[207,208] Spin state equilibria of nickel(II) tetraaza macrocycles have been assessed in aqueous conditions.[209] The X-ray structure of [Ni(L)]Br_2.$2H_2O$ (**86**) (Ni-N = 1.961, 1.947 Å for $P\bar{1}$ form and 1.949, 1.957 Å for Pcab form) shows the water molecules of crystallisation and Br^- ions located above the protons of the NH functions of the macrocycle via hydrogen bonds.[210] The complexes [Ni(L)]$(ClO_4)_2$ (L = (**87**), Ni-N = 1.926, 1.931 Å [211]; L = diisopropyl derivative of (**12**)[212]) have been characterised crystallographically.



(87)



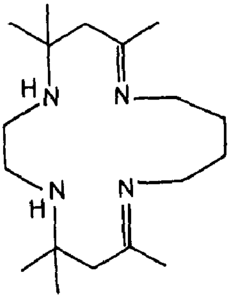
(88)



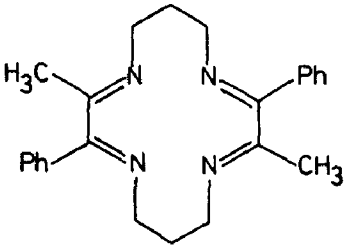
(89)

The alkylation of [Ni(L)] (L = (**88**)) with MeI and KOH in dmso affords N- and C-methylated products,[213] while the related dioxo macrocycle (**89**) shows efficient complexation of nickel(II) ion to yield a planar, low spin product.[214] The electrocatalytic reduction of CO_2 by a range of nickel tetaaza macrocycles (E =-1.3 → -1.6V vs SCE) has been reported.[215]

The Schiff-base template synthesis and reduction of $[Ni(L)]^{2+}$ (L = (**90**)) have been reported,[216] while transmetallation of $[Zn(L)]^{2+}$ (L = (**91**)) with Ni^{2+} in acidic methanol affords the corresponding nickel(II) complex.[217] The single crystal X-ray structure of [NiI(cyclops)] shows a square pyramidal stereochemistry with Ni-N = 1.886(imine), 1.863 Å(oxime) and Ni-I = 2.834 Å.[218] The out of plane and in plane modes of $[Ni(dmg)_2]$ have been identified in a far i.r. (20-600 cm^{-1}) spectroscopic study,[219] while reaction of $[Ni(dmg)_2]$ with bidentate N-donor bases yields cis-complexes and binuclear bridging products (see 4.6).[220] Reaction of $[Ni(dmg)_2]$ with trimethoxyboroxine or pentaborate affords the products (**92**) and (**93**), while with boric acid (**94**) is produced.[221] Treatment of $[Ni(dmg)_2]$ with Me_3SiCl

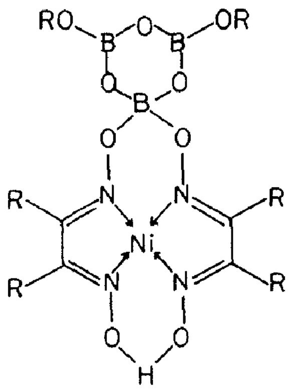


(90)

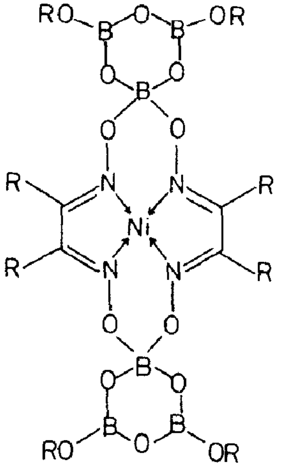


(91)

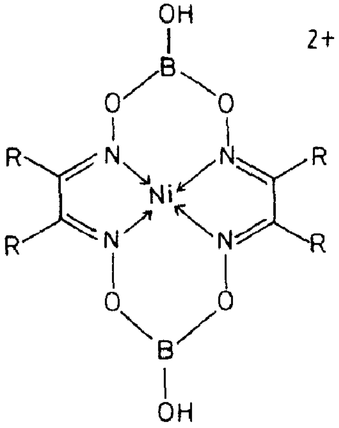
yields silanized dmg ligand.[222] The stacking of the [Ni(dmg)$_2$] planes in the solid state has been related to the different colours that these species exhibit.[137]



(92)

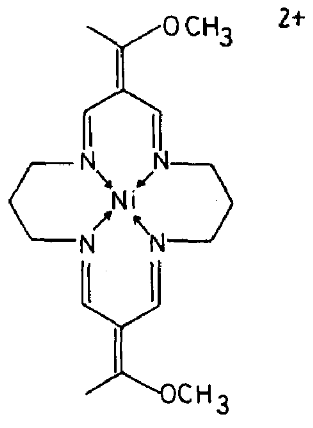


(93)

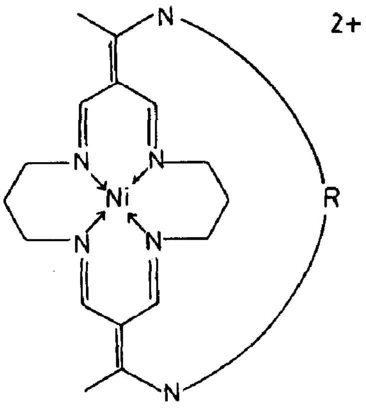


(94)

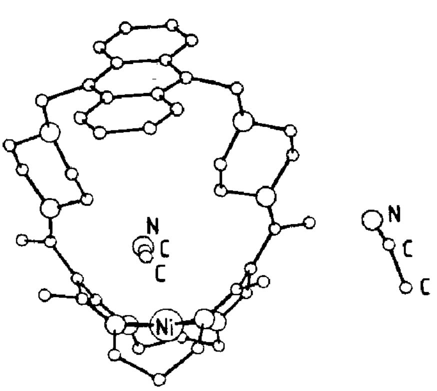
The synthesis of the lacunar complexes of general type (**96**) from the precursor (**95**) has been reported.[223,224] Treatment of (**96**) (R = $(CH_2)_n$, n = 4-8) with HCl yields the metal metal-free macrocycle.[223] The nickel(II)/(III) redox couples for these complexes have been measured.[223,224] The single crystal X-ray structure of the anthracene capped cation (**97**) shows a CH_3CN molecule in the cavity of the complex, together with another CH_3CN molecule of crystallisation; the durene derivative was found to complex n-butyl alcohol.[225]



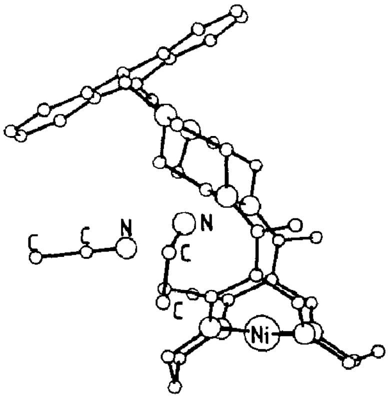
(95)



(96)



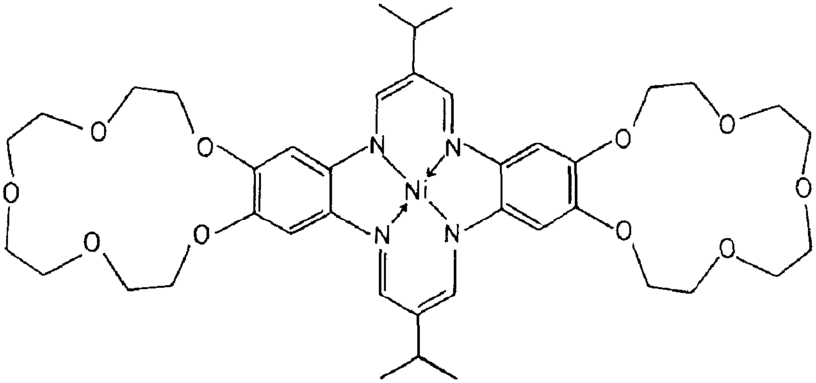
(97)



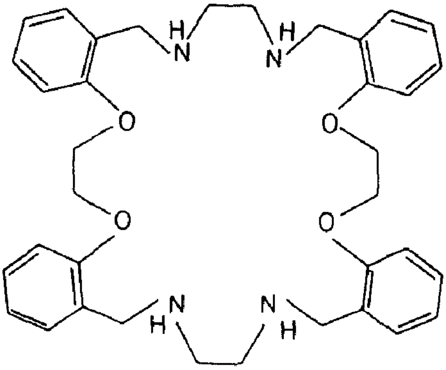
(97)

2:1 complexes of **(42)** with **(43)** and TCNQ have been prepared.[94] Nickel(II) complexes of tetraazaannulenes,[226] the 2-aminobenzaldehyde tetramer[227] and of the condensation product of 2,6-diaminopyridine and acac[228] have been reported. The ligand bonding parameters of pentagonal bipyramidal nickel complexes has been assessed by the angular overlap model.[229]

The complex (**98**) incorporating a double ionophone system has been found to be capable of binding Ni^{2+} and Co^{2+} in the N_4 donor set, and K^+ and Na^+ by the polyether arrays,[230] while the X-ray structure of cis-$[Ni(NCS)_2(L)]$ (L = (**99**)) incorporating an N_4O_4 donor set, shows octahedral nickel(II) coordinated to four nitrogen-donors of the macrocycle (Ni-N = 2.140, 2.157 Å) and two NCS^- ligands (Ni-N = 2.058 Å).[231] The binding and kinetics of



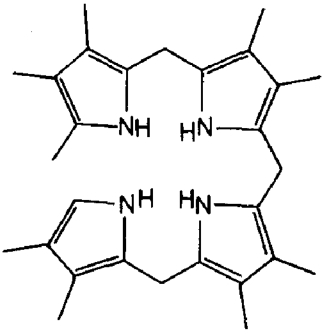
(98)



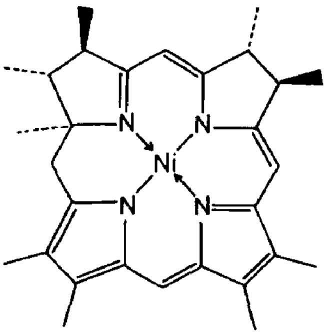
(99)

dissociation of nickel(II) to an N_2S_2 donor macrocycle have been described, dissociation occurring via two consecutive first order reactions showing no significant acid dependence, but accelerated by [$^-$OAc].[232]

Scheffold and coworkers have reported a series of selective alkylation experiments on nickel porphine complexes to yield optically active products.[233-236] The cyclization of a <u>seco-</u>-porphyrinogen (**100**) to the nickel tetrahydrocorrinate (**101**) and related diastereoisomers has been achieved,[237] while nickel(II) corrole[238] and corrin[239] derivatives have been synthesised. The luminescence of nickel(II) porphyrin complexes has been compared to the photophysical data for Zn^{II} and Mn^{II} porphyrin derivatives, [Ni(TPP)] being non-luminescent.[240] Metal incorporation into a tetracarboxylate derivative of TPP is particularly rapid and occurs via intramolecular transfer of metal ion from the peripheral carboxylate moieties to the porphyrin donor.[241]



(100)



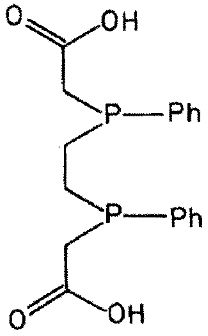
(101)

Octaalkylphthalocyanine (R = Me, ^{n}Bu) complexes of nickel(II) have been generated.[242] The cleavage of 4-pyridyl glycine derivatives[243] and the electrocatalytic reduction of O_2 to H_2O_2[244] have been achieved using nickel phthalocyanines.

4.3.6 **Phosphorus-donor ligands**

The cathodic behaviour of nickel(II) in anhydrous CH_3CN in the presence of $NaClO_4$ and phosphines has been assessed and related to the stabilities of nickel(II)/(I)/(0) products.[245,246] The single crystal X-ray structure of $(Ph_4As)[NiBr_3(PPh_3)]$ shows a tetrahedral nickel(II) centre with approximate C_3 symmetry with Ni-Br = 2.365, 2.368, 2.383 and Ni-P = 2.323 Å.[247] The variable temperature single crystal and powder magnetic susceptibility and transmission spectra for $[NiX_3(PPh_3)]^-$ ($X = Br^-$, I^-) have been analysed by the angular overlap model giving an analysis of PPh_3 as a strong σ-base and π-acid.[248] The ^{13}C n.m.r. spectrum of $[NiI_3(PPh_3)]^-$ has been reported,[249] while shifts in the ^1H and ^{13}C n.m.r. signals for $CHCl_3$ in the presence of $[NiX_2(PPh_3)_2]$ ($X = Cl^-$, Br^-, I^-) have been interpreted in terms of the formation of labile inner-sphere adducts of $CHCl_3$.[250] Complexation of $NiCl_2$ by $P(CH_2COOH)_3$ (L) under non-aqueous conditions yields the P-bound square planar species $[NiX_2(L)_2]$.[251]

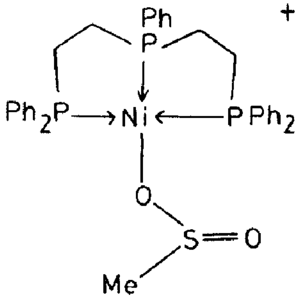
Square planar and square pyramidal nickel(II) complexes of O-phenylene bis(methylphenylphosphine) have been studied by variable temperature n.m.r. spectroscopy to elucidate the mechanisms of site exchange of axial Cl^-. This process was found to proceed by internal isomerisation of chelate rings and by intermolecular Cl^- exchange.[252] The single crystal X-ray structure of $[NiBr(LH)(LH_2)].H_2O$ (LH_2 = (**102**)) shows a square-based pyramidal structure with axial Br^-, Ni-P = 2.225,



(102)

2.232, 2.236, 2.215, Ni-Br = 2.587 Å, with non-coordinated H_2O and carboxylate functions.[253] Complexation of nickel(II) with $PhP[(CH_2)_3PH_{2-n}R_n]_2$ (L) affords the five coordinate $[NiX_2(L)]$ (X = Cl^-, Br^-) which is in equilibrium in solution with the square planar ionic species $[NiX(L)]^+$.[254] The coupling of alkyl Grignards with β-bromostyrene in the presence of dichloro (1,1'-bis(diphenylphosphino)ferrocene)nickel(II) has been described.[255] Reaction of NiX_2 with L (L = 2-[di(4-tolyl)-phosphinoethyl]diphenylphosphine) affords the square planar complex $[NiX_2(L)]$ (X = Cl^-, Br^-, I^-).[256] The X-ray structure of three polymorphs of trans-$[Ni(NCS)_2(P(CH_2CH_2CN)_3)_2]$ incorporating a P_2N_2 donor set has been described,[257] while treatment of $[Ni(acac)_2]$ with Et_2AlCl in the presence of Ph_3P afforded $[NiCl(PPh_3)_3]_2$ and $[Ni(acac)_2(PPh_3)]$; thermal decomposition of the former yielded $[NiCl_2(PPh_3)_2]$, while reaction of the latter with Et_2AlBr gave $[Ni(Br)(H)(PPh_3)_3]$ and $[NiBr_2(PPh_3)_2]$.[258] The single crystal X-ray structure of (**103**), prepared by reaction of

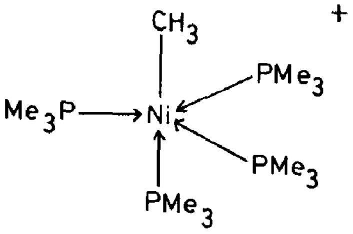
$[NiR(etp)]^+$ with SO_2, shows a distorted square planar nickel centre with Ni-P(cis to O) = 2.199, 2.214, Ni-P(trans to O) = 2.111, Ni-O = 1.937 Å.[259]



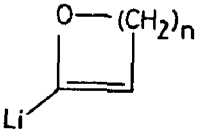
(103)

Reaction of $[Ni(CH_2SiMe_3)_2py_2]$ with L (L = $(PMe_3)_2$, $(PMe_2Ph)_2$, dppe, bipy, phen, tmen) affords the complexes $[Ni(CH_2SiMe_3)_2L]$.[108] The related species $[Ni(R)_2(PR_3)_2]$ (R = C_6Cl_5, mesityl, $Cl_2C{=}CCl$) have been prepared and the degree of rotation of the alkyl and phosphine ligands assessed by ^1H n.m.r. spectroscopy.[260] The metal vapour synthesis of $[Ni(CF_3)_2(PMe_3)_3]$ has been reported[261] while reaction of $[NiBr_2(PEt_3)_2]$ and $[Cd(CF_3)_2(CH_2OMe)_2]$ affords $[NiBr(CF_3)(PEt_3)_2]$ and $[Ni(CF_3)_2(PEt_3)_2]$.[262] The single crystal X-ray structure of $[Ni(CH_3)(PMe_3)_4]BPh_4$ (**104**) shows a slightly distorted C_{3v} symmetry with Ni-C = 2.074, Ni-P(axial) = 2.210, Ni-P(equ) = 2.256 Å, <CNiP(axial) = 179.4°, <CNiP(equ) = 83.8°.[263] The lithiation of coordinated PR_1R_2Me to $PR_1R_2CH_2Li$ in $[Ni(L)_2(PR_1R_2CH_3)_2]$ (L = 2,6-dimethoxyphenyl) occurs in

preference to lithiation of the aromatic ring[264]; amine substitution on $[Ni(Br)(2\text{-tolyl})(PPh_3)_2]$ occurs by replacement of



(104)



(105)

PPh_3 by less sterically hindered primary and secondary amines, py, 4-picoline, but not with tertiary amines.[265] Reaction of (105), LiR (n = 2,3) with $[NiCl(C_6Cl_5)(PPhMe_2)_2]$ affords $[Ni(R)(C_6Cl_5)(PPhMe_2)_2]$ which can be protonated by $HClO_4$ to the carbene product.[266] Treatment of $[Ni(C_2H_4)(PPh_3)_2]$ with one equivalent of triphenylcyclopropenylium perchlorate yields the cation $[Ni(C_3Ph_3)(PPh_3)_2]^+$ which was characterised structurally, Ni-P = 2.242, 2.234, Ni-C = 1.91, 2.02, 2.07 Å.[267] The single crystal X-ray structure of the cation $[Ni(C_3Ph_3)(triphos)]^+$, prepared by reaction of $[Ni(C_3Ph_3)(PPh_3)_2]^+$ with triphos, shows Ni-P = 2.301, 2.308, 2.322, Ni-C = 2.010, 2.036, 2.043 Å [268]; related cyclopropenyl complexes incorporating other tripod ligands were also synthesised.[268] Reaction of $[NiCl_2(PR_3)_2]$ with $R^1C{\equiv}CH$ (R^1 = $2\text{-}C_6H_4C{\equiv}CH$, $4\text{-}C_6H_4C{\equiv}CH$; R = Bu, Ph) affords the square planar species trans$[Ni(C{\equiv}CR^1)_2(PR_3)_2]$;[269] the role of related complexes in the catalytic trimerisation of acetylenes has been discussed.[270]

4.3.7 **Arsine-donor ligands**

Species of type [$NiX_2(L)_2$] and [$NiX_2(L)$] (X = halide, L = 2-phenylene*bis*(diphenylarsine), 2-phenylene*bis*(di-4-tolylarsine) have been prepared and their interconversion, magnetic and spin-crossover properties discussed.[271] Nickel(II) complexes of 2-phenylene*bis*(methylphenylarsine) have been found to be labile with respect to bidentate ligand redistribution between metal centres whereas the corresponding P-donor complexes are inert towards such processes.[252]

4.3.8 **Biological ligands**

Complexation of nickel(II) by a range of adrenaline,[272] tryptophan,[273] proline,[274] folic acid,[275] o-phospho-D.L.-serine,[276] adenosine,[277] purine[277] derivatives and a range of amino acids[278,279] has been reported in a series of papers.

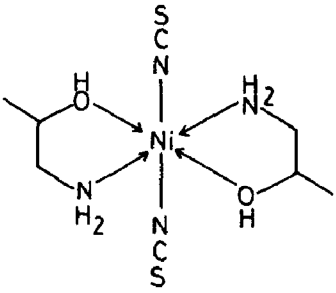
4.3.9 **Cyanides**

Single crystal polarised reflectance[280] and ^{13}C n.m.r. spectral[281] studies on $Ba[Ni(CN)_4].4H_2O$ and $K_2[Ni(CN)_4]$ respectively have been reported.[282] Substitution reaction of $[Ni(CN)_4]^{2-}$ with NO^-, generated from $Na_2N_2O_3$, affords $[Ni(CN)_3(NO)]^-$ in 3.6% yield at pH = 9.27 but in 30% yield at pH = 10.75.[283]

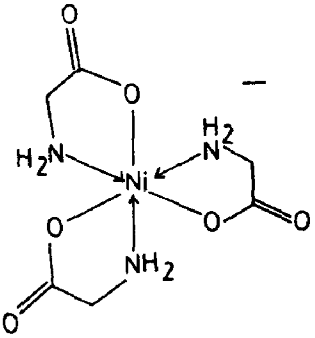
4.3.10 **Mixed-donor ligands**

4.3.10.1 N,O donors

Potentiometric, spectrophotometric and related studies on the binding of 2-amino-ethanol,[281] 1-amino-2-propanol, 3-amino-1-propanol[285], 1,3-diamino-2-propanol[286], nitriloacetates,[287-289] iminoacetates[289,290] and other amino acids[289-298] to nickel(II) have been reported. The single crystal X-ray structures of the (R,S) and (S,S) isomers of trans-$[Ni(NCS)_2(L)_2]$ **(106)** (L = 1-amino-2-propanol) have been described,[299] while the X-ray structure of $[Ni(NH_2CH_2COO)_3]^-$ **(107)** shows Ni-N = 2.091, Ni-O = 2.050, C-O(coord) = 1.264 and C-O(uncoord) = 1.238 Å, with both enantiometers existing in the crystals.[300] The acid catalysed dissociation of nickel (II) triglycine shows[301] an observed first order rate constant k where:-



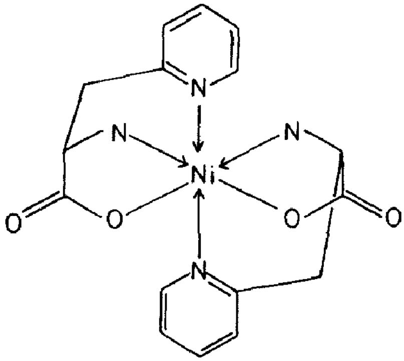
(106)



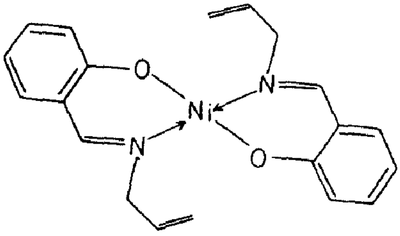
(107)

$$k = k_{H_2O} + k_H[H^+] + k_{HH}[H^+]^2 + (k_{HB} + k_{H_1HB}[H^+])[HB]$$

No general acid catalysis is observed when the axial coordination sites are blocked by coordinated solvent.[301] The adsorption of nickel glycinates on alumina[302] and the single crystal X-ray structure of bis(N,N'-dihydroxyethylglycinate)nickel(II)[303] have been reported. Reaction of bis[(2-pyridyl)alaninate]nickel(II) (**108**) with acetone affords the corresponding condensation product incorporating an N_4O_2 donor set.[304]

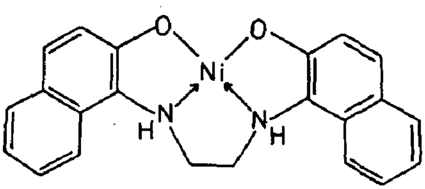


(108)

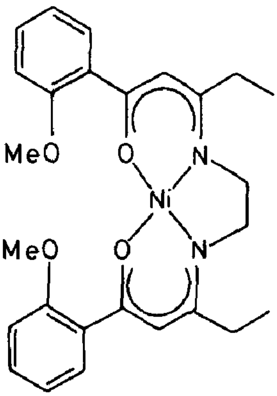


(109)

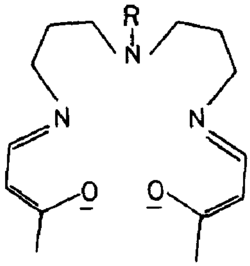
A wide range of Schiff-base ligand complexes of nickel(II) incorporating N_2O_2[159,305-309] and N_3O[160,310-314] donor sets have been synthesised. Single cystal X-ray structures of (**109**) (Ni-N = 1.905, Ni-O = 1.844, C=N = 1.323, C=C = 1.243 Å),[315] (**110**) (Ni-O = 1.849, Ni-N = 1.840 Å)[316] and (**111**) (Ni-O = 1.78, 1.87, Ni-N = 1.86, 1.91 Å)[317] have been reported. Halogenation



(110)



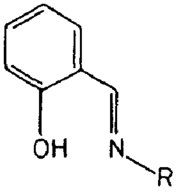
(111)



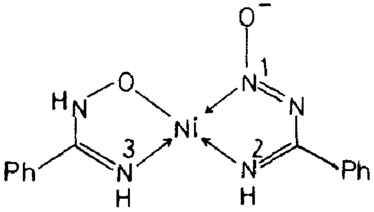
(112)

of [Ni(acacen)] with N-halo-succinimide leads to replacement of the methine proton by halide.[318,319] A series of high spin five coordinate complexes incorporating (**112**) (R = H, Ph, CH_3, CF_3) showing μ_{eff} = 3.3-4.3 BM have been generated.[320]

Complexes incorporating bidentate N,O donor ligands such as cytosine,[321] adenine-N-oxide,[322] pyrazole derivatives, [323-325] pyrrole and pyridine carboxylates[326] and keto-imines[54,136] have been generated. It was shown that the enthalpic factors that favour M-N(pyridine) bond formation are absent for pyrrolic M-N bonds,[326] while the degree of tetrahedral distortion in salicylaldimine complexes of (**113**) is controlled by substituent R.[151] The single crystal X-ray structure of (**114**) shows square planar nickel(II) with Ni-O = 1.849, Ni-N(1) = 1.856, Ni-N(2) = 1.831 and Ni-N(3) = 1.829 Å; the reactivity and interconversion of (**114**) to other derivatives was discussed.[327] Other papers on nickel complexes of mixed N,O ligands have appeared in the literature.[328-348]



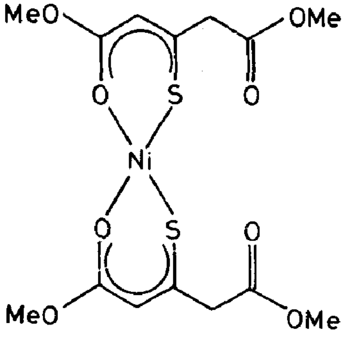
(113)



(114)

4.3.10.2 S,O donors

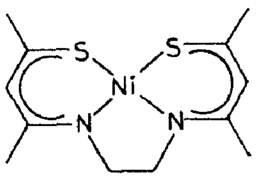
Studies on mixed S,O donor complexes[349] include the preparation of square planar and octahedral complexes of 1-methoxy-2-methylthioethane and 2-methoxyethanethiol[350] and thio-acac ligands.[351-353] The single crystal X-ray structure of $[NiL]^{2+}$ (**115**) shows a square planar complex with Ni-S = 2.14, Ni-O = 1.88 Å with long range interactions of 3.53 and 3.89 Å between Ni and other O donors; the corresponding triketo product $[Ni(L)_2(OH_2)_2]$ is found to be octahedral.[352,353]



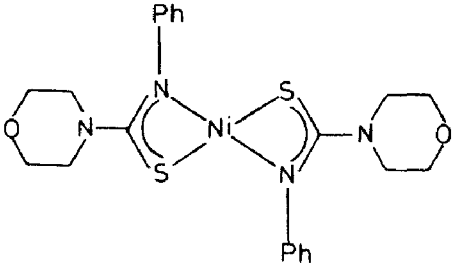
(115)

4.3.10.3 N,S donors

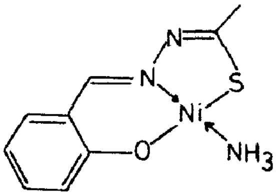
Thiosalicylohydrazide complexes of nickel(II) show a variety of bonding modes via N,O, N,S, O,S and N,O,S donors.[354,355] The single crystal X-ray structure of [Ni(S-acacen)] (**116**) shows a square planar structure with Ni-S = 2.139, 2.163 and Ni-N = 1.917, 1.923 Å;[356] these Ni-N distances are longer than found for the analogous N_2O_2 complex.[357] The structures of square planar species (**117**) (Ni-N = 1.888, Ni-S = 2.211 Å)[358] and (**118**) (Ni-N(imine) = 1.853, Ni-S = 2.146, Ni-O = 1.851 and Ni-N(NH_3) = 1.941 Å)[359] and the square bipyramidal complex (**119**) (Ni-N = 2.04, 2.05, Ni-S = 2.37, 2.38 Å)[360] have been described. The synthesis of a range of products incorporating thio-hydrazine ligands[361-363], mercapto acid amides[364] and 2-thiopicolinanilide[365] have been published, while the electronic structure of thionitrosyl complexes has been the subject of a CNDO study.[366]



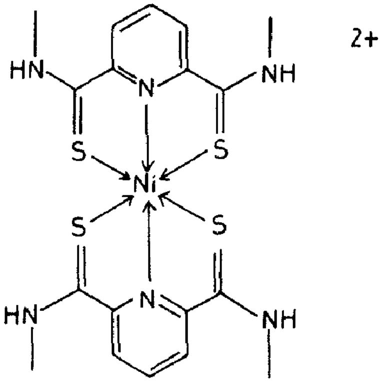
(116)



(117)



(118)

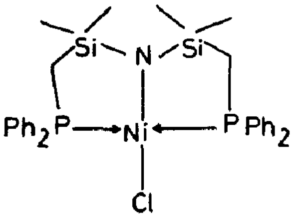


(119)

The electrochemical synthesis of N,N'-ethylene *bis*(monothioacetyl-acetoniminato)nickel(II) using nickel electrodes and the free ligand has been described.[3367]

4.3.10.4 Miscellaneous

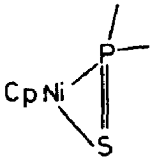
Phosphine triacetic acid, $P(CH_2COOH)_3$, binds via P- and two O-donors to nickel(II) under aqueous conditions.[251] The orange square planar complex (**120**) has been reported; at -80°C a bright green intermediate can be observed and was assigned as a paramagnetic tetrahedral species.[368] The preparation of species $[NiX_2(L)]$, $[NiX_2(L)_2]$ and $[Ni(NCS)(L)][Ni(NCS)_3(L)]$



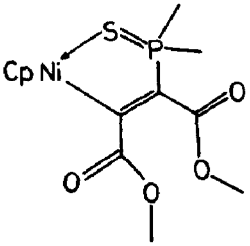
(120)

(L = 2,6-bis(diphenylphosphinomethyl)pyridine; X = ClO_4^-, NO_3^-) and related carbamoyl products have been prepared.[369] The tripod ligand tris(2-dimethylarsinoethyl)amine yields octahedral complexes of type $[NiX_2(L)]$ which are monomeric for X = Cl^-, Br^- and polymeric for X = NCS^-. [370]

The highly reactive derivative (**121**) was trapped by $MeO_2CC{\equiv}CCO_2Me$ to give (**122**).[371] The primary mercaptoalkylphosphines H_2PSH, $H_2PCH_2CH_2SH$ and $H_2PCH_2CHMeSH$ bind to nickel(II) to give planar bis-chelates, $[Ni(L)_2]$ in which the



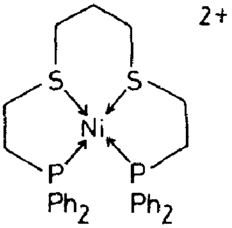
(121)



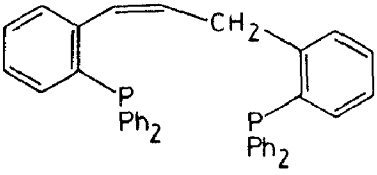
(122)

primary phosphine and thiol functions can be alkylated using K and alkyl halides.[372] The ligand 1,9-bis(diphenylphosphino)-3,7-dithianonane yields the square planar complex (**123**) on reaction with nickel(II) salts, Ni-P = 2.175, 2.196, Ni-S = 2.208, 2.218 Å.[373]

$NiCl_2$ reacts with the ligand (**124**) in 1,2-dimethoxyethane to yield the five coordinate species [NiCl(L)] in which nickel(II) is bound to two phosphines and the allylic function of (**124**).[374]



(123)

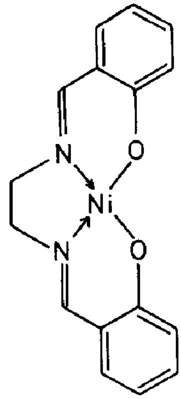


(124)

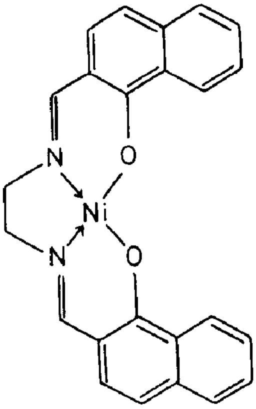
4.4. NICKEL(I)

The chemistry of nickel(I) compounds has been reviewed.[3] Reduction of $[Ni(acac)_2]$ with dibah affords a nickel(I) species that is involved in the catalytic addition of alkenyl zirconium to α,β-enones.[375] The single crystal X-ray structure of the $19e^-$ system [Ni(cp)(bipy)] shows Ni-N = 1.955, 1.958, Ni-C = 2.17-2.22 Å.[376].

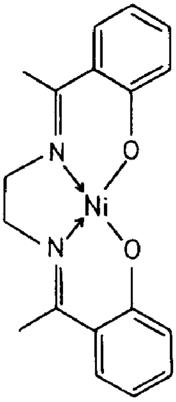
A range of nickel(I) complexes of tetraaza macrocycles have been generated by Pletcher and coworkers and found to react with alkyl bromides oxidatively to yield nickel(III) alkyl products[23] (see 4.2.3). These workers have also reduced electrochemically a



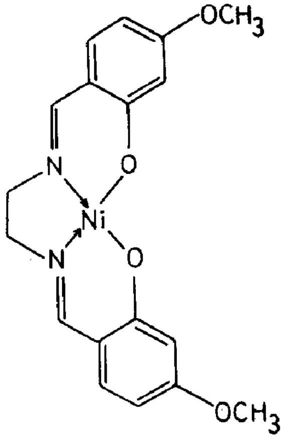
(125)



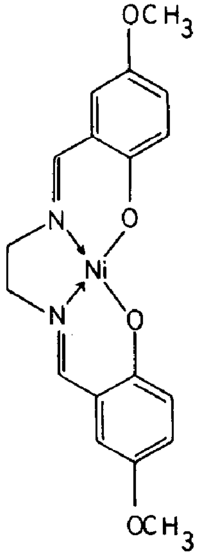
(126)



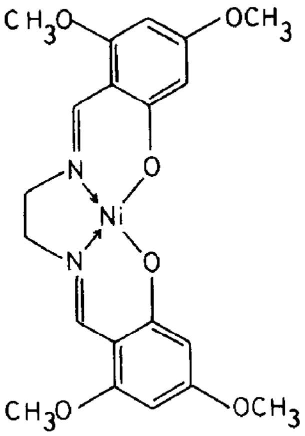
(127)



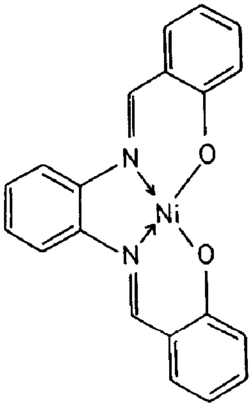
(128)



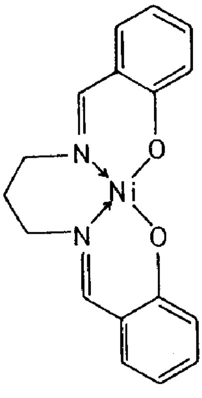
(129)



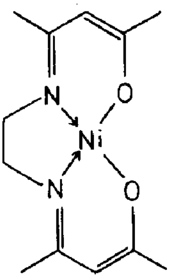
(130)



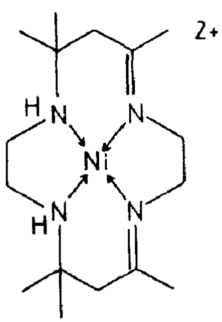
(131)



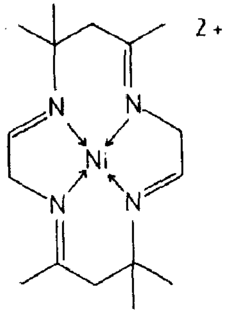
(132)



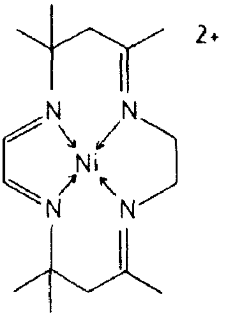
(133)



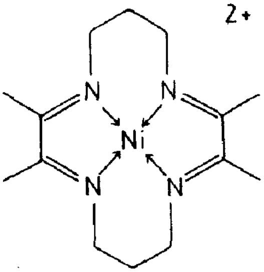
(134)



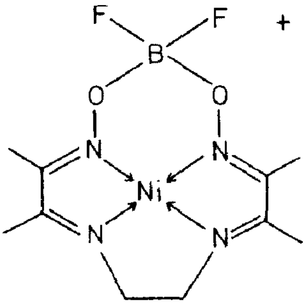
(135)



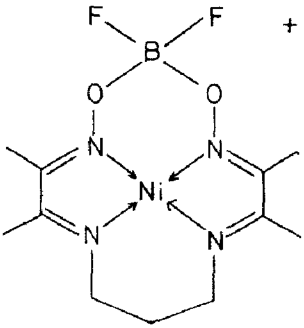
(136)



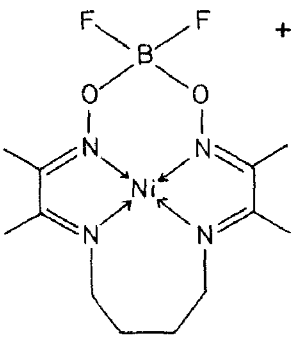
(137)



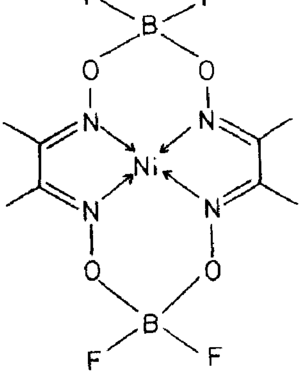
(138)



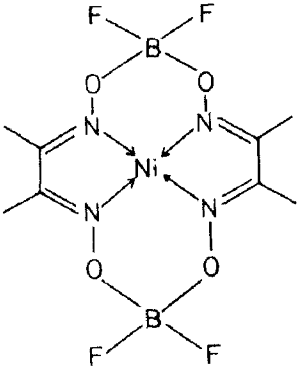
(139)



(14 0)

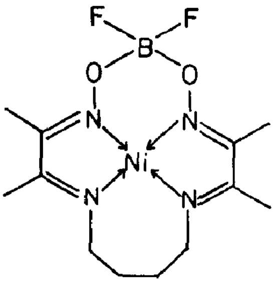


(141)



(142)

series of nickel(II) complexes, (**125**)-(**133**), incorporating N_2O_2 donor open chain ligands.[377] The nickel(I) and nickel(II)-ligand radical products were characterised by e.s.r. spectroscopy and their catalytic reactivity with alkyl bromides assessed.[377] E.s.r. spectroscopy has been used also to differentiate between metal and ligand based radical species in the reduced α-diimine macrocyclic complexes (**134-142**).[378] Both types of reduced complexes were found to bind CO to afford five coordinate d^9 nickel(I) adducts (typically $g_{\parallel} = 2.2$, $g_{\perp} = 2.1$) and the equilibrium binding constants determined electrochemically.[378] The one electron reduced product (**143**) exhibits dynamic valence isomerism with a thermal equilibrium existing between $[Ni^{II}(L^{\cdot-})]$ and $[Ni^{I}(L)]$; at 298K the equilibrium constant $K = 0.27$.[378] Macrocyclic-based radical species were found to show loss of



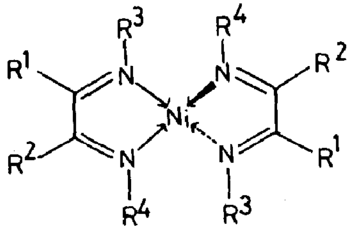
(143)

$\nu_{C=N}$ stretching vibration bands in the 1500-1700 cm^{-1} region with new bands appearing at lower frequencies;[379] ^{15}N labelling experiments confirmed these lower frequencies to involve imine-type vibrations.[379]

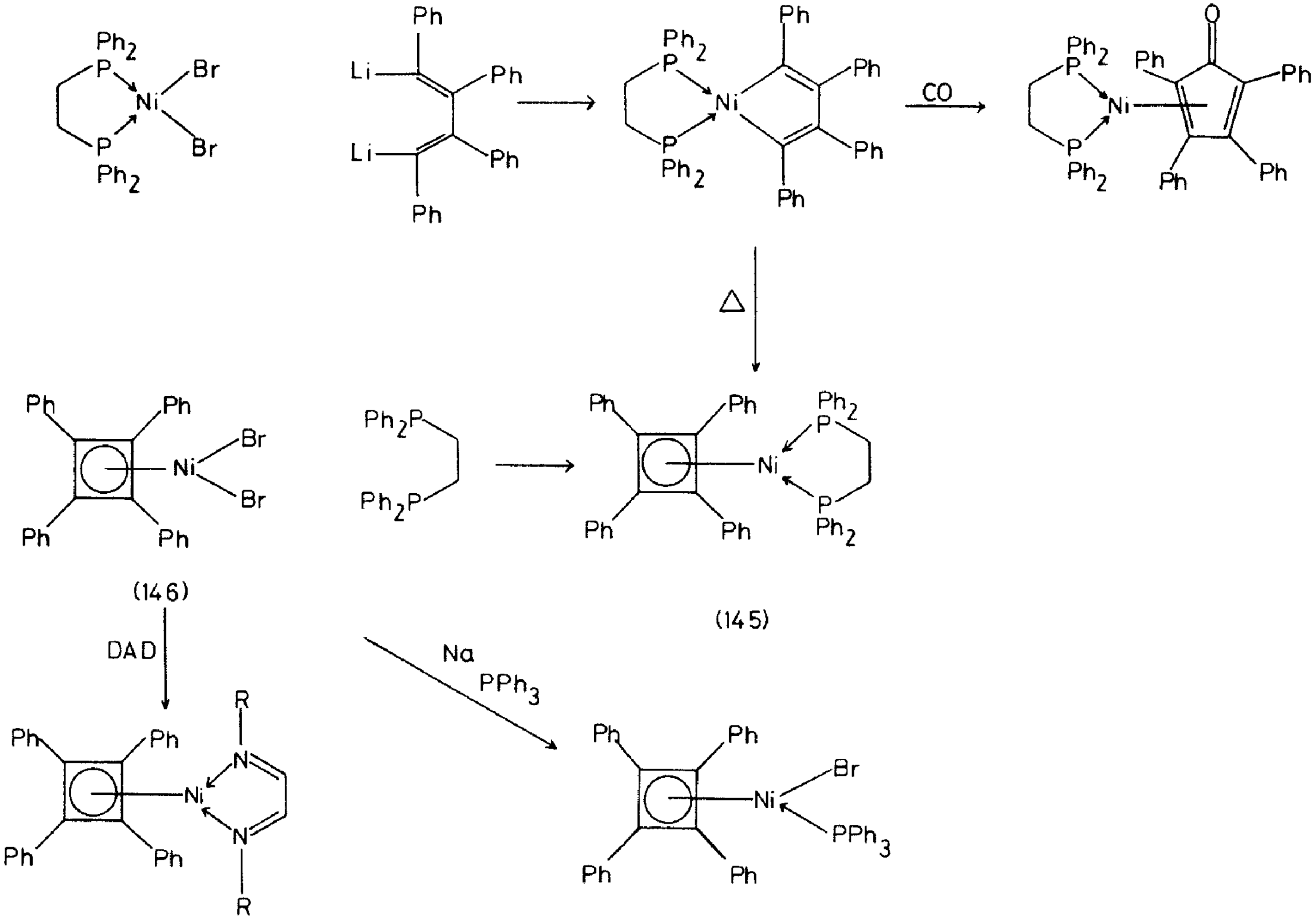
A range of nickel(I) phosphine species have been synthesised. The single crystal X-ray structures of [Ni(L)](ClO$_4$) ((L) = (tris(2-diphenylphoshinoethyl)phosphine)[380] and [Ni(L)(PPh$_3$](ClO$_4$) ((L) = tris(2-diphenylarsinoethyl)amine)[381] show trigonal pyramidal and trigonal bipyramidal stereochemistries respectively with non-coordinated ClO$_4^-$ anions. Evidence for the formation of [Ni(P(OEt)$_3$)$_4$]$^+$ as an intermediate in the nickel-catalysed Arbuzov reaction[382] and in the electrochemical reduction of Ni(ClO$_4$)$_2$ in CH$_3$CN in the presence of P(OEt)$_3$[245,246] has been presented. The reduction of [NiBr(diphos)$_2$]$^+$, [NiBr$_2$(PR$_3$)$_2$] and trans-[NiBr(Ph)(PPh$_3$)$_2$] yields nickel(I) halo-phosphine products[383-385] while the selective cis-isomerization of 1-pentene catalysed by [NiX(PPh$_3$)$_3$] (X = halide, pseudo-halide) shows a first order dependence on 1-pentene;[386] a mechanism involving metal hydride addition-elimination was indicated by isotopic exchange studies.[386] Reaction of [NiCl(PPh$_3$)$_3$]$_2$ with CH$_3$CN in the presence of TlPF$_6$ affords [Ni(NCCH$_3$)(PPh$_3$)$_3$]$^+$;[258] treatment of [NiX$_2$(PCy$_2$Ph)$_2$] (X = Cl$^-$, Br$^-$, I$^-$) with Na gives the nickel(I) dimer [Ni(μ-PCy$_2$)(PCy$_2$Ph)]$_2$ which reacts with CO to yield [Ni(μ-PCy$_2$)(CO)$_2$]$_2$.[387,388] [NiBr(C$_4$Ph$_4$)(PPh$_3$)] has been prepared by treatment of [NiBr$_2$(C$_4$Ph$_4$)] with Na and PPh$_3$; the iodo derivative was prepared from [Ni(C$_4$Ph$_4$)(cot)],I$_2$ and PPh$_3$.[389] A range of nickel(I) bipy species of type [Ni(Cp)L$_2$] (L = PR$_3$; L$_2$ = diphos, arphos, bipy, phen) have been synthesised by electrochemical reduction of nickel(II) precursors, by reaction of [NiCl(PPh$_3$)$_3$] with NaCp or by treatment of [Ni(cp)NO], [Ni(cp)CO]$_2$ or [Ni(cp)(CH$_2$PPh$_3$)$_2$]$^+$ with excess of L.376.

4.5 NICKEL(O)

The reduction of [Ni(acac)$_2$] at a Hg electrode yields the two electron reduction product [Ni(acac)$_2$]$^{2-}$ which decomposes to the metal plus two equivalents of acac$^-$.[390] A range of nickel(O) diazadiene complexes [Ni(DAD)$_2$] have been prepared by ligand substitution reactions on nickel(O) precursors, or, more efficiently, by direct reduction of the nickel(II) precursors.[391,392] The single crystal X-ray structure of [Ni(L)$_2$] (**144**) (R^1 = R^2 = H, R^3 = R^4 = cyclohexyl) shows two orthogonal chelate rings bound to tetrahedrally coordinated nickel(O).[391] For R^1 = R^2 = H, R^3 = R^4 = 2,6-dimethylphenyl however a dihedral angle of 44° is observed between the two chelate rings, the conformation (D_{2d} nickel(O) or D_{2h} formally nickel(II)) being dictated by the substituents of the aryl moieties on R^3 and R^4.[392] The related tetraazadiene species [Ni(Ar$_2$N$_4$)$_2$] transfers the ligand Ar$_2$N$_4$ to nickel(O) centres in the presence of RNC to afford [Ni(CNR)$_2$(Ar$_2$N$_4$)].[393]



(144)



(146)

(145)

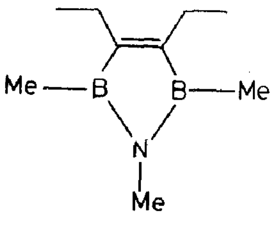
(147)

The interaction of diazacyclopentadiene and 9-diazafluorene ligands with nickel(0) centres has been reported.[394] Treatment of these products with COS was found to yield metal carbonyl, dithiocarbonate or metal sulphide-thiol species.[394]. The reaction of nickel(0) tetramethylethylenediamine fragments with heteroolefins such as benzil, aldehydes and α,β-unsaturated carbonyls (L) gives the four coordinate products [Ni(L)(tmen)]; the analogous diphosphine species $[Ni(L)(PR_3)_2]$ were also prepared.[395] [Ni(cod)(bipy)] reacts with maleic anhydride (L) to afford $[Ni(bipy)(L)_2]$ in which L is coordinated via the alkenyl function and [Ni(bipy)(L)] where additional coordination of the carbonyl moiety occurs.[132] The cyclobutadiene complex (**145**) has been prepared,[396,397] while treatment of (**146**) with diazadiene ligands yields (**147**).[398]

The electrochemical reduction of nickel(II) in the presence of phosphines to yield nickel(0) phosphine complexes has been described in several reports.[245,246,383-385,399] The equilibrium between $[Ni(PPh_3)_4]$ and $[Ni(PPh_3)_3]$ has been monitored at low temperature by ^{31}P n.m.r. spectroscopy, the phosphines in $[Ni(PPh_3)_4]$ being found to be equivalent.[400] A photoelectron spectroscopic study of $[Ni(PPh_3)_4]$ has been reported.[38] Reaction of $[Ni(PF_3)_4]$ with alkyl lithium and Grignard reagents affords $[Ni(PF_3)_{4-n}(PF_2R)_n]$ (n = 1-3), $[Ni(PF_3)_3(PF_2R)(PFR_2)]$ and $[Ni(PF_3)_3(PR_3)]$.[401] An ab initio SCF-MO study on the bonding in $[Ni(C_2H_2)(PH_3)_2]$ and $[Ni(C_2H_4)(PH_3)_2]$ has been reported.[402] Substitution of PH_3 with NH_3 greatly strengthens the back donation between nickel and C_2H_4, while the energy component for C_2H_2 on nickel is greater than that for C_2H_4.[402] The single crystal X-ray structure of [Ni(C_2H_4)(PPh_3)$_2$] has been redetermined and shows C-C = 1.391, Ni-P = 2.148, 2.158, Ni-C = 1.959, 1.978 Å with the protons of coordinated ethylene situated in a plane 0.17 Å from the C atoms.[403] The solution behaviour of [Ni(hex-1-ene)(PCy_3)$_2$] was monitored by ^{31}P n.m.r. spectroscopy and found to form [Ni(hex-1-ene)$_2$(PCy_3)] in the presence of excess of hex-1-ene.[404] The role of nickel(0) phosphines in the polymerisation of butadiene has been discussed.[405-407]

Treatment of [Ni_3(cp)$_3$(CO)$_2$] with excess of PPh_3 in refluxing thf gives [Ni(cp)$_2$], [Ni(CO)$_2$(PPh_3)$_2$] and [Ni(CO)(PPh_3)$_3$],[408] while reduction of [$NiCl_2$(PCy_2Ph)$_2$] with Na in the presence of CO affords [Ni(CO)$_2$(PCy_2Ph)$_2$].[388] The single crystal X-ray structure of [Ni(CO)$_2$(PCy_3)$_2$] shows a distorted tetrahedral configuration with Ni-P = 2.257, 2.264, Ni-C = 1.75, C-O = 1.17 Å, <PNiP = 122.8°.[409] The oxidative addition of organic halides to nickel(0) centres to yield nickel(II) alkyl products has been described.[383,384,410-412]

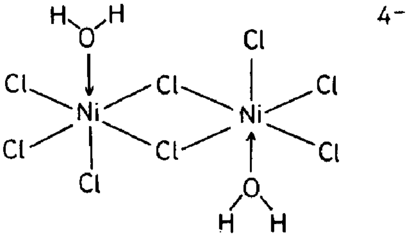
Reaction of $Ni(CO)_4$ with (L) ((L) = **148**) gives the bis-sandwich complex [Ni(L)$_2$].[413]



(148)

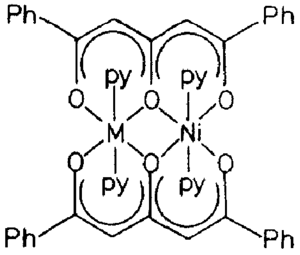
4.6 POLYNUCLEAR COMPLEXES

The structure of $CaNi_5H_5$ has been discussed.[414] The single crystal X-ray structure of $[Ni_2Cl_8(OH_2)_2]^{4-}$ **(149)** shows octahedral nickel(II) with chloro bridges, Ni-Cl = 2.407, 2.409, Ni-Cl (bridge) = 2.430, Ni-O = 2.123 Å.[415] Powder magnetic susceptibility measurements on **(149)** in the range 2-240K shows ferromagnetic exchange between the nickel centres with J/k = 11.7K, D/k = -4.9K, z'J'/k = -0.76 and g = 2.297.[415]



(149)

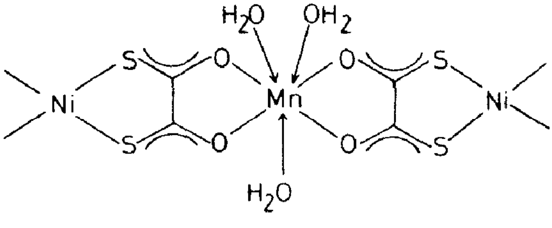
Reaction of $Ni(OAc)_2$ with RCOOH in toluene yields the proposed mixed carboxylate dimers of stoichiometry $[Ni(OAc)_{2-n}(O_2CR)_n]$ (R = Me,Et).[416] The single crystal X-ray structure of $[Ni_4(OAc)_2(OMe)_4(L)_4]^{2+}$ shows a $Ni_4(OMe)_4$ cube with two acetates capping opposite faces and four isocyanides ((L) = 2,5-dimethyl-2,5-diisocyanohexane) capping the four remaining faces.[417] The structure of $[(L)Ni(O_2CCMe_3)_4Ni(L)]$ (L = quinaldine) shows Ni-Ni = 2.75, Ni-N = 2.07 Å with four bridging carboxylates.[418] Treatment of $[Ni(acac)_2]$ with Ph_3AsO affords the binuclear species $[Ni_2(acac)_4(OAsPh_3)]$ incorporating a bridging Ph_3AsO ligand, Ni-O(As) = 2.11, 2.28 Å and one of the oxygens from an acac$^-$ ligand acting as the other bridging group, Ni-O = 2.00, 2.22 Å.[419] A single crystal e.s.r. study on Ni^{II}/Cu^{II} and Ni^{II}/Co^{II} bunuclear complexes of triketonates has shown antiferromagnetic interactions between the metal centres in (**150**).[420] A dimeric octrahedral nickel structure has been



(150)

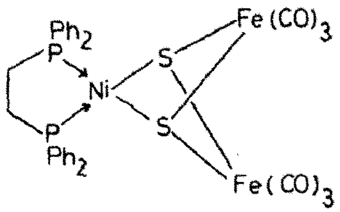
proposed for the product [$Ni_2(L)_2$] formed on binding a tetraone ligand (L) with nickel(II).[421] The synthesis and magnetic properties of [$Ni_4(L)_8$] (L = 9,10-phenanthrenesemiquinone) have been reported.[70]

[$Ni(S_2C_2O_2)_2$]$^{2-}$ reacts with $MnSO_4$ to yield a black Ni^{II}/Mn^{II} chain complex [$Ni(S_2C_2O_2)[Mn(OH_2)_3](O_2C_2S_2)Ni]_n$ (**151**) with dithiooxalate bridging Ni^{II} and seven coordinate Mn^{II} ions, Ni-S = 2.167-2.178 Å.[422] The product follows the Curie law expected for Mn^{II} down to 34K.[422] Treatment of [$Ni(S_2CNEt_2)_2$] with [MS_4]$^{2-}$ (M = Mo,W) in water/acetone affords [$Ni(S_2CNEt_2)$-(MS_4)]$^-$, while reaction of $NiNO_3$ and [MOS_3]$^{2-}$ gives the

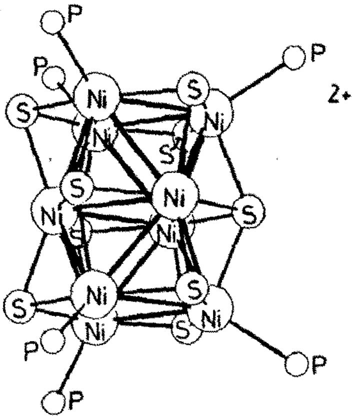


(151)

corresponding trimer $[Ni(MOS_3)_2]^{2-}$ incorporating an NiS_4 donor set.[423] $[Ni(diphos)_2]$ inserts into the S-S bond of $[Fe_2(\mu-S_2)-(CO)_6]$ to give (**152**) under mild conditions.[424] Reaction of $NiBF_4$ with H_2S in $CH_2Cl_2/EtOH$ in the presence of PEt_3 affords $[Ni_9(\mu_4-S)_3(\mu_3-S)_6(PEt_3)_6]^{2+}$, (**153**), the single crystal X-ray structure of which shows a confacial bioctahedron of Ni_9 atoms held together by bridging S atoms with the planes 2.1 Å apart and the six Ni atoms in the outer layers each bound to a PEt_3 ligand. The six S atoms of the outer layers each triply bridge Ni atoms (Ni-S = 2.175 Å) while the three S atoms of the inner layer each quadruply bridge Ni atoms (Ni-S = 2.230 Å).[425]



(152)

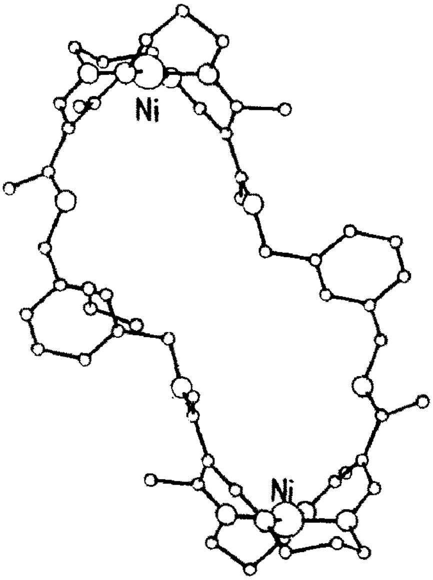


(153)

The structure of $[Ni_2Cl_2(en)_4](BPh_4)_2$ shows bridging chloro ligands with Ni-Cl = 2.403, 2.503 Å. The ferromagnetic exchange between nickel centres was found to vary with counter-ion in the order $Cl^- < ClO_4^- < BPh_4^-$.[426] Bis(cyclohexane-1,2-bis(2'-pyridylhydrazonato))dinickel(II) shows a short Ni-Ni distance of

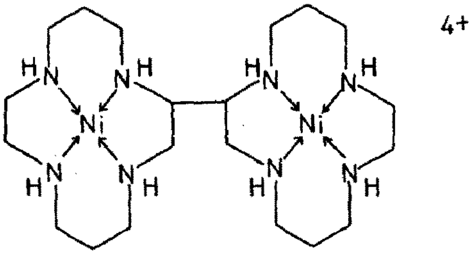
2.809 Å.[427] A series of mixed nickel-lead,[428] -mercury,[428-430] -cadmium, -zinc[429] and -copper[431] products incorporating bridging NCS^- and $NCSe^-$ ligands have been generated, while mixed nickel-copper species with histidine and histamine ligands have been studied potentiometrically.[432] The magnetic interactions in Cu^{II} and Co^{II} doped samples of [bis(N,N'-bis(2-diethylamino)-ethyl)(2-hydroxyethylamino)]dinickel(II),[433] and in polymeric nickel(II) materials incorporating isonicotinic acid[434] and trimeric benzotriazolyl derivatives[435] have been discussed. A range of metal triazole complexes have been reported;[436,437] the single crystal X-ray structure of $[Ni_2(NCS)_4(OH_2)(L)_4]$ (L = 4-ethyl-1,2,4-triazole) shows a binuclear complex bridged by three triazole ligands with terminal NCS^- ligands. The co-ordination around the distorted octahedral nickel centres is completed by one terminally bound triazole ligand on one metal (NiN_6 donor set) with a bound H_2O on the other (NiN_5O donor set).[437] Structural data on $[Ni_2Br_2(tu)_8](NO_3)_2$ has been reported.[96]

The chemistry of covalently linked dimeric porphyrins has been reviewed.[438] Dimeric macrocyclic species of type (**154**) have been generated;[224,428] the single crystal structure of the xylyl bridged dinickel species shows a Ni-Ni separation of 13.6 Å with a cavity of 3.87-6.18 Å in width.[439] The bridging of $[Ni(dmgBF_2)_2]$ units has been achieved using 4,4'-bipy to give a binuclear species with Ni-Ni separation of 3.909 Å and the nickel atom 0.2 Å out of the plane of the macrocycle, Ni-N = 1.85, Ni-N(bipy) = 2.35 Å.[220,440] By contrast in the presence of benzimidazole, dimeric units of $[Ni(dmgBF_2)_2]_2$ are formed

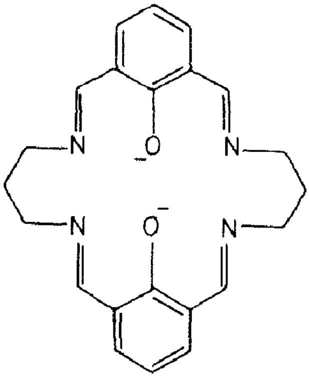


(154)

sandwiched between layers of benzimidazole via π-π interactions with a Ni-Ni distance of 3.358 Å and the metal sitting in the plane of the macrocycle.[441] The coupling of cyclam units to form $[Ni_2(cyclam)_2]^{4+}$ (**155**) has been described,[442] while binuclear Ni/Cu and Ni/Ni complexes of (**156**) have been prepared and studied electrochemically.[443,444] The oxidative dimerisation of $[Ni(L)]^{2+}$ (L = (**12**)) via nickel(III) intermediates has been described.[20]

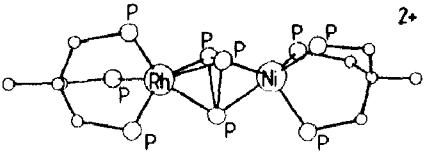


(155)

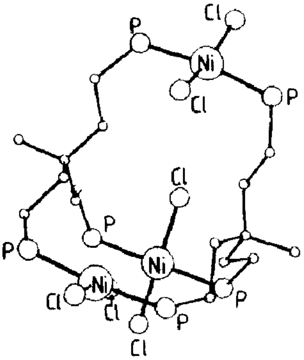


(156)

The synthesis and structures of a series of nickel tripod complexes have been reported by Sacconi and coworkers. Reaction of $[Rh(triphos)(P_3)]$ with $[Ni(OH_2)_6]^{2+}$ in $CH_2Cl_2/EtOH$ in the presence of triphos affords the dark red complex $[(triphos)Ni(\mu\text{-}P_3)Rh(triphos)]^{2+}$ (**157**) which has a Rh-Ni distance of 4.401 Å;[445] the related species $[(triphos)Co(\mu\text{-}P_3)Ni(etriphos)]^{2+}$ has also been prepared.[446] The trimeric products $[Ni_3Cl_4(Etnp_3)_2]^{2+}$,[447] $[Ni_3Cl_6(etriphos)_2]$[448] and $[Ni_3Cl_6(etp)_2]$ (**158**)[449] have been generated; the single crystal X-ray structure of (**158**) shows an array of nickel atoms with the tripod ligand being monodentate to each metal centre, Ni-P = 2.23, Ni-Cl = 2.16 Å.[449] Related chain polynuclear species have been generated with arsine tripod ligands.[370]

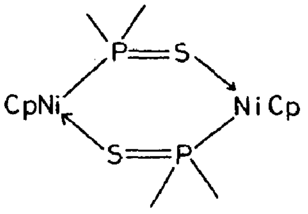


(157)

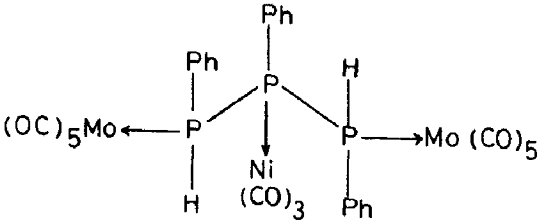


(158)

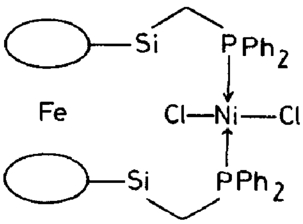
The use of metallobis(phosphonates) in the synthesis of heterometallic complexes has been demonstrated by the reactivity of $[Ni(cp)\{(P(OMe)_2O\}_2H]$ and $[Ni(cp)\{P(OMe)_2O\}_2]X$ ($X = Tl^+$, NH_4^+) with metal acetylacetonates and chlorides to give a wide range of tri- and tetra-nuclear compounds of type $[Ni(cp)\{P(OMe)_2O\}_2]_nM$ ($n = 2,3$; $M = Co^{II}, Cu^{II}, Zn^{II}, VO, Al^{III}, Cr^{III}, Fe^{III}$), $[Ni(cp)\{P(OMe)_2O\}_2]_2Ni(NH_3)_2$, $[Ni(cp)\{P(OMe)_2O\}_2]Ni(acac)$, $[Ni(cp)\{P(OMe)_2O\}_2]Pd(allyl)$, $[Ni(cp)\{P(OMe)_2O\}_2]Rh(cod)$ and $[Ni(cp)\{P(OMe)_2O\}_2]_2Ni$.[450] Treatment of $[Ni(cp)_2]$ with Me_2HPS affords (**159**) in 40% yield;[371] while the single crystal X-ray stucture of (**160**) shows a threo-threo configuration of the ligand with P-P = 2.241, Mo-P = 2.512, 2.520, Ni-P = 2.222 Å.[451] The incorporation of $NiCl_2$ fragment into ferrocene derivatives to yield (**161**) and related species has been illustrated.[255,452]



(159)

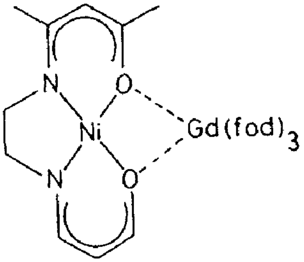


(160)

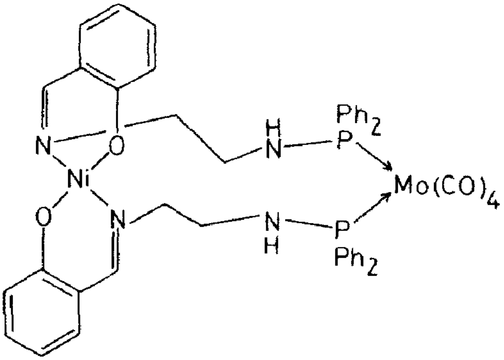


(161)

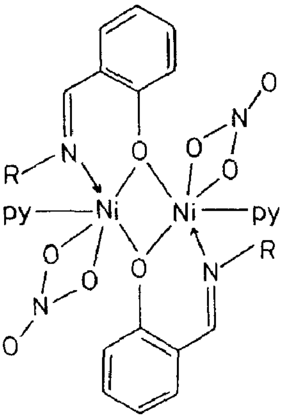
The ^{13}C and ^{1}H spin lattice relaxation rates in [Ni(acacen)] are effected by [Gd(fod)$_3$] presumably via formation of an adduct of type (**162**).[453] A series of binuclear species based on salicylaldimino type ligands have been generated.[454-458] A single crystal e.s.r. study on a [Ni(salen)Co(hfa)$_2$] derivative has been reported,[456] while the single crystal X-ray structure of (**163**) shows a Ni-Mo distance of 5.679 Å.[457] A range of derivatives of (**164**) have been synthesised and characterised crystallographically.[455] The distorted trigonal bipyramidal



(162)

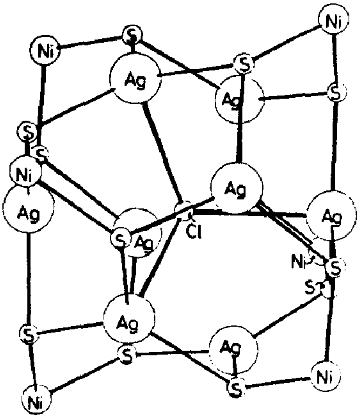


(163)



(164)

complex [Ni(L)(L')] (L = $GaMe_2(N_2C_5H_7)(OCH_2CH_2NMe_2)$; L' = $GaMe_2(N_2C_5H_7)_2$) has been structurally characterised, L being co-ordinated meridonally with O in an equatorial position and two N donors bound axially, Ni-O = 1.993, Ni-N (pz, axial) = 2.072, Ni-N(amine) = 2.229, Ni-N(equ) = 2.005, 2.006 Å.[459] Reaction of $NiCl_2$ with penicillamine (L) in the presence of $AgNO_3$ affords the unusual cluster species $[Ag_8Ni_6(L)_{12}Cl]^{5-}$ (**165**) which is based on a Cl^- centred Ag^I_8 cube inscribed into an icosahedron of S donor



(165)

atoms. Each S function bridges between two Ag^I and a Ni^{II} ion with the six Ni^{II} atoms lying at the apices of an octahedron.[460] Other polynuclear nickel products have been reported.[461-468]

Dedicated to Martin Nelson and Tony Stephenson.

References

1 A.A.G. Tomlinson, **Coord. Chem. Rev., 37,** (1981), 221.

2 D.H. Antonsen, **Kirk-Othmer Encycl. Chem. Technol., 15,** (1981), 801, 3rd Edition, J. Wiley and Sons, N.Y. [**Chem. Abstr., 95,** (1981), 143228].

3 K. Nag and A. Chakravorty, **Coord. Chem. Revs., 38** (1980), 87.

4 K.O. Christie, **Inorg. Chem., 16,** (1977), 2238.

5 P. Charpin, M. Lance, T.B. Huy and R. Bougon, **J. Fluor. Chem., 17,** (1981), 479.

6 H. Saarinen, J. Korvenranta and E. Näsäkkälä, **Acta Chem. Scand. Ser. A, 34,** (1980), 443.

7 P.J. Heaney, A.G. Lappin, R.D. Peacock and B. Stewart, **J. Chem. Soc., Chem. Commun.,** (1980), 769.

8 A.G. Lappin, M.C.M. Laranjeira and L. Youde-Owei, **J. Chem. Soc., Dalton Trans.,** (1981), 721.

9 H. Frouzanfar and D.H. Kerridge, **J. Inorg. Nucl. Chem., 42,** (1980), 1381.

10 R.I. Haines and A. McAuley, **Coord. Chem. Rev., 39,** (1981), 77.

11 P.T. Manoharan, J.H. Noordik, E. de Boer, and C.P. Keijzers, **J. Chem. Phys., 74,** (1981), 1980.

12 W. Dietzsch, J. Lerchner, J. Reinhold, J. Stach, R. Kirmse, G. Steimecke and E. Hoyer, **J. Inorg. Nucl. Chem., 42,** (1980), 509.

13 J.C. Brodovitch, R.I. Haines and A. McAuley, **Can. J. Chem., 59,** (1981), 1610.

14 T. Sakurai, J-I. Hongo, A. Nakahara and Y. Nakao, **Inorg. Chim. Acta, 46,** (1980), 205.

15 J.M.T. Raycheba and D.W. Margerum, **Inorg.Chem., 20,** (1981), 1441.

16 A. Bencini, L. Fabbrizzi and A. Poggi, **Inorg. Chem., 20,** (1981), 2544.

17 J.C. Brodovitch and A. McAuley, **Inorg. Chem., 20,** (1981), 1667.

18 E. Zeigerson, G. Ginzburg, J.Y. Becker, L.J. Kirschenbaum, H. Cohen and D. Meyerstein, **Inorg. Chem., 20,** (1981), 3988.

19 W.A. Welsh, J. Otutakowski and P.M. Henry, **Can. J. Chem.**, 59, (1981), 697.

20 G. Ferraudi and S. Muralidharan, **Inorg. Chem.**, 20, (1981), 4262.

21 P. Morliere and L.K. Patterson, **Inorg. Chem.**, 20, (1981), 1458.

22 D.G. Batyr and L. Ya. Kistruga, **Koord. Chim.**, 7, (1981), 274.

23 J.Y. Becker, J.B. Kerr, D. Pletcher and R. Rosas, **J. Electroanal. Chem. Interfacial Electrochem.**, 117, (1981), 87.

24 G. Smith and J.K. Kochi, **J. Organomet. Chem.**, 198, (1980), 199.

25 B.P. Mishra and D.V.R. Rao, **J. Inst. Chem. (India)**, 52, (1980), 155.

26 S.N. Bhattacharyya, N.C. Saha and P. Neto, **J. Phys. Chem.**, 85, (1981), 300.

27 M.F. Rudolf, **Bull. Acad. Pol. Sci. Ser. Chim.**, 27, (1979), 815; [**Chem. Abstr.**, 94, (1981), 071920].

28 K. Yvon, J. Schefer and F. Stucki, **Inorg. Chem.**, 20, (1981), 2776.

29 J. Schefer, P. Fischer, W. Halg and F. Stucki, **J. Less-Common Met.**, 74, (1980), 65.

30 W.E. Wallace, H.E. Flotow and D. Ohlendorf, **J. Less-Common Met.**, 79, (1981), 157.

31 J.C. Archard, C. Lartigue and A. Percheron-Guegan, **J. Less-Common Met.**, 79, (1981), 161.

32 L.C. Belkbir, E. Joly, N. Gerard and J.C. Archard, **J. Less-Common Met.**, 73, (1980), 69.

33 P.S. Bagus and C. Bjoerkman, **Phys. Rev.**, 23, (1981), 461.

34 B.M. Andreev, A.N. Perevezentsev and V.V. Shitikov, **Zh. Fiz. Khim.**, 55, (1981), 1993; [**Chem. Abstr.**, 95, (1981), 157441].

35 A. Morvillo and A. Turco, **J. Organomet. Chem.**, 208, (1981), 103.

36 A.N. Nesmeyanov, L.S. Isaeva, G.I. Drogunova and L.N. Morozova, **J. Organomet. Chem.**, 195, (1980), C13.

37 A.W. Potts, D. Law and E.P.F. Lee, **J. Chem. Soc., Faraday Trans. 2, 77**, (1981), 797.

38 A. Baldy, A. Durocher, H. Rzehak and Y. Limouzin-Maire, **Bull. Soc. Chim. Fr. Pt. 1**, 1-2, (1981), 67.

39 S. Cummings, J.E. Enderby, G.W. Neilson, J.R. Newsome, R.A. Howe, W.S. Howells and A.K. Soper, **Nature, 287**, (1980), 714.

40 S.B. Ivanov, Yu. N. Mikhailov and V.G. Kuznetsov, **Zh. Strukt. Khim., 22**, (1981), 188; [**Chem. Abstr., 95**, (1981), 016419].

41 A. Leclaire and M.M. Borel, **Acta Crystallogr.** B, **36**, (1980), 3088.

42 A. Leclaire and M.M. Borel, **Acta Crystallogr.** B, **36**, (1980), 3090.

43 H. Montgomery, **Acta Crystallogr.** B, **36**, (1980), 2121.

44 T.E. Jenkins and J. Lewis, **Spectrochim. Acta A, 37**, (1981).

45 M.S. Verma and H.L. Nigam, **Indian J. Chem., Sect. A, 20**, (1981), 727.

46 A.B. Kunz, **J. Phys. (C), 14**, (1981), L455.

47 C. Platte and M. Troemal, **Acta Crystallogr.** B, **37**, (1981), 1276.

48 X. Solans and C. Miravitlles, **Acta Crystallogr.** B, **37**, (1981), 1407.

49 W. VanDoorne and M. Hannink, **Synth. React. Inorg. Met.-Org. Chem., 11**, (1981), 15.

50 S.S. Sandhu and J.M. Sharma, **J. Inorg. Nucl. Chem., 42**, (1980), 1193.

51 W. Jaehning, **Z. Chem., 20**, (1980), 421.

52 T.M. Che and K. Kustin, **Inorg. Chem., 20**, (1981), 509.

53 S. Komiya, A. Yamamoto and T. Yamamoto, **Chem. Lett.**, (1981), 193.

54 T. Yamamoto, T. Kohara and A. Yamamoto, **Bull. Chem. Soc. Jap., 54**, (1981), 2010.

55 A.T. Pilipenko, L.I. Savranskii and V.P. Kobylyashnyi, **Dokl. Akad. Nauk. SSR, 254**, (1980). 678.

56 S. Shibata, M. Ohta and R. Tani, **J. Mol. Struct., 73**, (1981), 119.

57 G.J. Bullen, R. Mason and P. Pauling, Inorg. Chem., 4, (1965), 456.

58 S. Kudo, A. Iwase and N. Tanaka, Bull. Chem. Soc. Jap., 54, (1981), 207.

59 A. Lodzinska, E. Danilczuk, Z. Czerniawska and M. Klobukowski, Pol. J. Chem., 54, (1980), 2119.

60 Y. Saito, T. Takeuchi, Y. Fukuda and K. Sone, Bull. Chem. Soc. Jap., 54, (1981), 196.

61 H. Hoshino, Y. Fukuda and K. Sone, Bull. Chem. Soc. Jap., 54, (1981), 420.

62 A. Samantarag, P.K. Panda and B.K. Mohapatra, J. Indian Chem. Soc., 58, (1981), 408.

63 G. Albertin, E. Bordignon, A. Orio, G. Pellizzi and P. Tarasconi, Inorg. Chem., 20, (1981), 2862.

64 M.L. Morris and R.D. Koob, Inorg. Chem., 20, (1981), 2737.

65 P.F. Richardson and R.W. Kreilick, Inorg. Chem., 20, (1981), 1978.

66 J.M. Huggins and R.G. Bergman, J. Am. Chem. Soc., 103, (1981), 3002.

67 V.T. Kasumov, M.K. Guseinova and A.A. Medzidov, Zh. Strukt. Khim., 22, (1981), 90; [Chem. Abstr., 95, (1981), 017258].

68 M.S. Masoud and F. Elzaway, Talanta, 27, (1980), 766.

69 K. Lal and R.K. Shukla, J. Indian Chem. Soc., 58, (1981), 115.

70 M.W. Lynch, R.M. Buchanan, C.G. Pierpoint and D.N. Hendrickson, Inorg. Chem., 20, (1981), 1038.

71 A. Paduan-Filho, E. Sinn, R.D. Chirico and R.L. Carlin, Inorg. Chem., 20, (1981), 2688.

72 F.J. Iaconianni, L.L. Pytlewski, C.M. Mikulski and N.M. Karayannis, Inorg. Chim. Acta, 53, (1981), L21.

73 I.S. Ahuja, R. Singh and L. Sriramulu, Transition Met. Chem., 5, (1980), 373.

74 M.F. Rudolf, Bull. Acad. Pol. Sci. Ser. Chim., 27, (1979), 747; [Chem. Abstr., 93, (1980), 194951].

75 N. Hilje and O.A. Serra, Ing. Cienc. Quim., 4, (1980), 144.

76 A. Kircheiss, U. Pretsch and U. Borth, **Z. Chem.**, **20**, (1980), 349.

77 W. Marty, **Synth. React. Inorg. Met. Org. Chem.**, **11**, (1981), 411. [**Chem. Abstr.**. 95, (1981), 125317]

78 R.M. Issa, S.E. Zayan, T.M. El-Shamy and G.B. El-Hefnawey, **Monatsch. Chem.**, **111**, (1980), 1413.

79 C. Preti and G. Tosi, **J. Coord. Chem.**, **10**, (1980), 209.

80 M. Chaabouni, J.L. Pascal and J. Potier, **C.R. Seances Acad. Sci. Ser. C.**, **291**, (1980), 125.

81 H.D. Lutz, W. Eckers and B. Engelen, **Z. Anorg. Allg. Chem.**, **475**, (1981), 165.

82 J.R. Lusty, **J. Coord. Chem.**, **10**, (1980), 243.

83 L. Alagna, A.A.G. Tomlinson, C. Ferragina and A. La Ginestra, **J. Chem. Soc., Dalton Trans.**, (1981), 2376.

84 R. Boca, **J. Mol. Catal.**, 10, (1981), 187.

85 J. Lakaj, F. Pavelcik, V. Kettmann, J. Masaryk, V. Vrakel and J. Garaj, **Acta Crystallogr. B**, **37**, (1981), 926.

86 M. Maltese, G. Zennaro, B. Martini, R. Croce, S.N. Cesaro and M. Spoliti, **J. Mol. Struct.**, **66**, (1980), 65.

87 S. Wingefors, **Acta Chem. Scand. Ser. A**, **34**, (1980), 327.

88 K.S. Bose, **J. Inorg. Nucl. Chem.**, **42**, (1980), 1515.

89 A. Vogler and H. Kunkely, **Angew. Chem.**, **93**, (1981), 399.

90 W. Dietzsch, J. Kaiser and R. Richter, **Z. Anorg. Allg. Chem.**, **477**, (1981), 71.

91 W.-H. Pan, J.P. Fackler and H.-W. Chen, **Inorg. Chem.**, **20**, (1981), 856.

92 R. Hemmer, H.A. Brune and U. Thewalt, **Z. Naturforsch., B; Anorg. Chem., Org. Chem.**, **36**, (1981), 78.

93 A. Vlcek, **Inorg. Chim. Acta**, **43**, (1980), 35.

94 P. Cassoux, L. Interrante and J. Kasper, **C.R. Seances Acad. Sci., Ser. C.**, **29**, (1980), 25.

95 H. Hartmann, E. Uhlemann, W. Huebner, E. Ludwig, L. Beyer, M. Walter and E. Hoyer, **Z. Chem.**, **21**, (1981), 271.

96 T. Sramko, A. Sirota and M. Dunaj-Jurco, **Proc. Conf. Coord. Chem.**, **8**, (1980), 417; [**Chem. Abstr.**, **94**, (1981), 131458].

97 E.S. Raper, M.E. O'Neill and J.A. Daniels, **Inorg. Chim. Acta**, 41, (1980), 201.

98 M.E. O'Neill, E.S. Raper and J.A. Daniels, **Inorg. Chim. Acta**, 54, (1981), L25.

99 S. Manogaran and D.N. Sathyanarayana, **Bull. Soc. Chim. Belg.**, 90, (1981), 427.

100 D.G. Batyr, B.M. Boloyan and E.V. Popa, **Koord. Khim.**, 7, (1981), 737; [**Chem. Abstr.**, 95, (1981), 034626].

101 D.T. Haworth and R.S. Czernuszewicz, **Spectrosc. Lett.**, 13, (1980), 765.

102 E.M. Khairy, A.F. Shoukry and J. Ahmad, **Indian J. Chem. Sect.A**, 20, (1981), 421.

103 Ya. I. Tur'yan and I.I. Moskatov, **Zh. Obshch. Khim.**, 51, (1981), 1412; [**Chem. Abstr.**, 95, (1981), 121838].

104 T. Takahashi and T. Koiso, **Bull. Chem. Soc. Jap.**, 53, (1980), 3400.

105 J.B. Hodgson, G.C. Percy and D.A. Thornton, **J. Mol. Struct.**, 66, (1980), 81.

106 M. Gerloch and M.R. Manning, **Inorg. Chem.**, 20, (1981), 1051.

107 J.M. Coronas, C. Polo and J. Sales, **Inorg. Chim. Acta**, 48, (1981), 87.

108 E. Carmona, F. Gonzalez, M.L. Poveda, J.L. Atwood and R.D. Rodgers, **J. Chem. Soc., Dalton Trans.**, (1981), 777.

109 A. Lewartowska, S. Brzozowski and W. Kemula, **J. Mol. Struct.**, 75, (1981), 113.

110 J. Lipkowski, **J. Mol. Struct.**, 75, (1981), 13.

111 T. Krogulec and Z. Galus, **J. Electroanal. Chem. Interfacial Electrochem.**, 117, (1981), 109.

112 G. Hartmann, P.G. Jones, R. Mews and G.M. Sheldrick, **Z. Naturforsch. B; Anorg. Chem., Org. Chem.**, 35, (1980), 1191.

113 S. Bhaduri, K.R. Sarma and B.A. Narayan, **Transition Met. Chem.**, 6, (1981), 206.

114 S.A. Bhaduri, I. Bratt, B.F.G. Johnson, A. Khair, J.A. Segal, R. Walters and C. Zuccaro, **J. Chem. Soc., Dalton Trans.**, (1981), 234.

115 B.N. Figgis, P.A. Reynolds, A.H. White, G.A. Williams and S. Wright, **J. Chem. Soc., Dalton Trans.**, (1981), 997.

116 H. Kuma, K. Motobe, W. Mori and S. Yamada, **Bull. Chem. Soc. Jap.**, 53, (1980), 3214.

117 U. Engelhardt, B. Friedrich and I. Kirner, **Z. Naturforsch. B; Anorg. Chem., Org. Chem.**, 36, (1981), 791.

118 L.V. Shmelev and A.N. Kitaigorodskii, **Zh. Fiz. Khim.**, 54, (1980), 1951; [**Chem. Abstr.**, 93, (1980), 212774].

119 B. Lenarcik and M. Wisniewski, **Pol. J. Chem.**, 54, (1980), 1869; [**Chem. Abstr.**, 94, (1981), 163514].

120 W. Van Riel, H.O. Desseyn, W. Van de Mieroop and A.T.H. Lenstra, **Transition Met. Chem.**, 5, (1980), 330.

121 M. Klinga, **Cryst. Struct. Commun.**, 10, (1981), 521.

122 H. Koehler, V.F. Bolelij and V.V. Skopenko, **Z. Anorg. Allg. Chem.**, 468, (1980), 179.

123 G.A. Bottomley and L.G. Glossop, **Aust. J. Chem.**, 34, (1981), 699.

124 R.A. Read and D.N. Margerum, **Inorg. Chem.**, 20, (1981), 3143.

125 E. Iwamoto, T. Fujiwara and Y. Yamamoto, **Inorg. Chim. Acta**, 43, (1980), 95.

126 A. Yamagishi and M. Soma, **J. Chem. Soc., Chem. Commun.**, (1981), 539.

127 A. Yamagishi, **J. Chem. Soc., Chem. Commun.**, (1981), 1168.

128 A. Yamagishi, **J. Chem. Soc., Chem. Commun.**, (1981), 1128.

129 M.G. Burnett, V. McKee and S.M. Nelson, **J. Chem. Soc., Dalton Trans.**, (1981), 1492.

130 T.L.J. Huang and D.G. Brewer, **Can. J. Chem.**, 59, (1981), 1689.

131 H. Hoberg and A. Herrera, **Angew. Chem.**, 92, (1980), 951.

132 E. Uhlig, G. Fehske and B. Nestler, **Z. Anorg. Allg. Chem.**, 465, (1980), 141.

133 Yu. A. Ol'dekop, N.A. Maier, A.A. Erdman and V.P. Prokopovich, **Dokl. Akad. Nauk. SSSR.**, 257, (1981), 647.

134 R. Knorr and A. Weiss, **Chem. Ber.**, 114, (1981), 2104.

135 V.B. Rana, D.P. Singh and M.P. Teotia, **Transition Met. Chem.**, 6, (1981), 189.

136 N.V. Thakkar and B.C. Holdar, **J. Inorg. Nucl. Chem.**, **42**, (1980), 843.

137 D. Dorn, D. Linke and E. Uhlig, **Z. Anorg. Allg. Chem.**, **468**, (1980), 153.

138 Yu. A. Simonov, M.M. Botoshanskii and I.I. Bulgak, Koord. Khim., 7, (1981), 612.

139 W. Keim, R. Appel, A. Storeck, C. Krueger and R. Goddard, **Angew. Chem.**, 93, (1981), 91.

140 T. Yamamoto, T. Kohara and A. Yamamoto, **Bull. Chem. Soc. Jap.**, **54**, (1981), 1720.

141 P.D.I. Fletcher and V.C. Reinsborough, **Can.** J. **Chem.**, 59, (1981), 1361.

142 V. Leovac, M. Babin, V. Canic and N.V. Gerbeleu, **Z. Anorg. Allg. Chem.**, **471**, (1980), 227.

143 A.N. Speca, C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski and N.M. Karayannis, **Inorg. Chim. Acta**, **46**, (1980), 235.

144 E. Uhlig and M. Doering, **Z. Chem.**, 21, (1981), 73.

145 R.B. Jordan, J. **Coord. Chem.**, 10, (1980), 239.

146 Y. Kojima, **Chem. Lett.**, 1, (1981), 61.

147 A.P. Zuur, W.L. Driessen and P.L.A. Everstijn, **Inorg. Nucl. Chem. Lett.**, 17, (1981), 15.

148 R.S. Srivastava, **Inorg. Chim. Acta**, 55, (1981), L71.

149 J. Terheijden, W.L. Driessen and W.L. Groenevald, **Transition. Met. Chem.**, 5, (1980), 346.

150 L.K. Peterson and H.E.W. Rhodes, **Inorg. Chem. Acta**, **45**, (1980), L95.

151 U. Reiffer, M. Schumann, K.J. Wannowius and H. Elias, **Transition Met. Chem.**, 5, (1980), 272.

152 K. Kumar and P.C. Nigam, **Inorg. Chem.**, **20**, (1981), 1623.

153 I. Endo, S. Horikoshi and S. Utsuno, **J. Chem. Soc.**, **Chem. Commun.**, (1981), 296.

154 A.S. Abushamleh and H.A. Goodwin, **Aust.** J. **Chem.**, 33, (1980), 2171.

155 A.S. Abushamleh and H.A. Goodwin, **Aust. J. Chem.**, **34**, (1981), 313.

156 M.G.B. Drew, J. Nelson and S.M. Nelson, **J. Chem. Soc., Dalton Trans.**, (1981), 1685.

157 M.G.B. Drew, J. Nelson and S.M. Nelson, **J. Chem. Soc., Dalton Trans.**, (1981), 1691.

158 N.A. Bailey and D.E. McKenzie, **Inorg. Chim. Acta**, **43**, (1980), 205.

159 M.P. Teotia, I. Singh and V.B. Rana, **Transition Met. Chem.**, 6, (1981), 60.

160 M.M. Aly and F.A. El-Said, **J. Inorg. Nucl. Chem.**, **43**, (1981), 287.

161 A.N. Singh, **Indian J. Chem. Sect. A**, **19**, (1980), 587.

162 K.P. Balakrishnan, **J. Inorg. Nucl. Chem.**, **43**, (1981), 695.

163 M. Takahashi and T. Iwamoto, **J. Inorg. Nucl. Chem.**, **43**, (1981), 253.

164 C.C. Hwang, Y.H. Yu, Y.S. Horng and C.C. Liao, **J. Chin. Chem. Soc.**, **28**, (1981), 1; [**Chem. Abstr.**, **95**, (1981), 161156].

165 M.I. Ermakova, I.A. Shikhova and N.I. Latosh, **Zh. Obshch. Khim.**, **51**, (1981), 174.

166 R.C. Agarwal, V. Singh and G.K. Agrawal, **J. Inorg. Nucl. Chem.**, **42**, (1980), 1073.

167 G.M. Kurdyumov, O.I. Agapova and O.V. Ivanov, **Zh. Neorg. Khim.**, **26**, (1981), 677; [**Chem. Abstr.**, **94**, (1981), 198261].

168 V. Divjakovic, B. Ribar and V.M. Leovac, **Z. Kristallogr.**, **154**, (1981), 83; [**Chem. Abstr.**, **94**, (1981), 093992].

169 P. Krautil and R. Robson, **J. Coord. Chem.**, **10**, (1980), 7.

170 A.D. Toleva, N.V. Gerbeleu and G.P. Syrtsova, **Zh. Neorg. Khim.**, **26**, (1981), 1288; [**Chem. Abstr.**, **95**, (1981), 053968].

171 D.G. Batyr, B.M. Baloyan and E.V. Popa, **Koord. Khim.**, **7**, (1981), 648; [**Chem. Abstr.**, **95**, (1981), 053947].

172 M. Mohan and B. Das Paramhans, **Gazz. Chim. Ital.**, **111**, (1981), 35; [**Chem. Abstr.**, **95**, (1981), 034593].

173 I.S. Maslennikova, **Zh. Fiz. Khim.**, **55**, (1981), 1038; [**Chem. Abstr.**, **94**, (1981), 201194].

174 V.L.R. Murthy, S.V.J. Lakshman, Proc. Indian Acad. Sci. Ser. Chem. Sci., 90, (1981), 225. [Chem. Abstr., 95, (1981) 12330].

175 M.G. Ivanov, I.I. Kalinichenko and I.I. Olikov, Koord. Khim., 7, (1981), 1091; [Chem. Abstr., 95, (1981), 123224].

176 K.G. Sharma, R.S. Shakhawat and R.K. Mehta, Proc. Indian Natl. Sci. Acad. Part A, 46, (1980), 494. [Chem. Abstr. 95, (1981), 121800].

177 R.A. Jain and A.K. Jain, Thermochim. Acta, 46, (1981), 61; [Chem. Abstr., 95, (1981), 121795].

178 K.G. Sharma, R.P. Mathur and R.K. Mehta, J. Indian. Chem. Soc., 58, (1981), 225.

179 N.B. Das, A. Nayak and B.B. Mahapatra, J. Indian Chem. Soc., 58, (1981), 337.

180 K. Satpathy, T. Mahana and R.K. Patel, J. Indian Chem. Soc., 58, (1981), 350.

181 S. Randhawa, B.S. Pannu and S.L. Chopra, J. Indian Chem. Soc., 58, (1981), 437.

182 L.D. Dave and S.K. Thampy, Indian J. Chem. Sect. A, 20, (1981), 405.

183 R.N. Kapadia, Indian J. Chem. Sect. A., 20, (1981), 525.

184 V.V. Ramanujam and V.M. Selvarajan, Indian J. Chem. Sect. A, 20, (1981), 633.

185 M.S. Masoud, M.M. Osman and T.M. Salem, Indian J. Chem. Sect. A, 20, (1981), 584.

186 N. Saha, and K.M. Datta, Indian J. Chem. Sect. A, 20, (1981), 402.

187 C. Natarajan and N. Hussain, Indian J. Chem. Sect. A, 20, (1981), 307.

188 R.S. Srivastava, L.D.S. Yadav and R.K. Khare, Indian J. Chem. Sect. A, 20, (1981), 516.

189 S. Ghosh and P.K. Ray, J. Indian Chem. Soc., 58, (1981), 533.

190 D.S. Rao and M.C. Ganorkar, J. Indian Chem. Soc., 58, (1981), 217.

191 R.C. Aggarwal and D.S.S. Narayana, Indian J. Chem. Sect. A., 20, (1981), 419.

192 B.T. Thaker, J. Indian Chem. Soc., 57, (1980), 682.

193 M.F. Rudolf, Bull. Acad. Pol. Sci. Ser. Sci. Chim., 28, (1980), 43; [Chem. Abstr., 95, (1981), 015559].

194 M.F. Rudolf, Bull. Acad. Pol. Sci. Ser. Sci. Chim., 27, (1979), 757; [Chem. Abstr., 93, (1980), 228067].

195 P. Paoletti, Pure Appl. Chem., 52, (1980), 2433.

196 J.S. Alper and L.J. Zompa, J. Inorg. Nucl. Chem., 42, (1980), 1693.

197 M. Nonoyama, Transition Met. Chem., 5, (1980), 269.

198 L. Fabrizzi, M. Micheloni, P. Paoletti, A. Poggi and A.B.P. Lever, J. Chem. Soc., Dalton Trans., (1981), 1438.

199 A. Dei, Inorg. Chim. Acta, 53, (1981), L155.

200 A. Dei, L. Fabrizzi and P. Paoletti, Inorg. Chem., 20, (1981), 4035.

201 L. Hertli and T.A. Kaden, Helv. Chim. Acta, 64, (1981), 33.

202 R.W. Hay and P.R. Norman, Inorg. Chim. Acta, 45, (1980), L139.

203 A.E. Merbach, P. Moore and K.E. Newman, J. Magn. Res., 41, (1980), 30.

204 J.H. Coates, D.A. Hadi, S.F. Lincoln, H.W. Dodgen and J.P. Hunt, Inorg. Chem., 20, (1981), 707.

205 E.J. Billo, Inorg. Chem., 20, (1981), 4019.

206 K. Toriumi and T. Ito, Acta Crystallogr. B, 37, (1981), 240.

207 T. Ito and K. Toriumi, Acta Crystallogr. B, 37, (1981), 88.

208 T. Ito, Y. Tsutsumi, Y. Hiratsuka, K. Mochizuki and M. Fujimoto, Bull. Chem. Soc. Jap., 54, (1981), 931.

209 K. Mochizuki, M. Fujimoto, H. Ito and T. Ito, Bull. Chem. Soc. Jap., 53, (1980), 2535.

210 T. Ito, K. Toriumi and H. Ito, Bull. Chem. Soc. Jap., 54, (1981), 1096.

211 T. Ito, H. Ito and K. Toriumi, Acta Crystallogr. B, 37, (1981), 1412.

212 J.W. Krajewski, Z. Urbanczyk-Lipkowska and P. Gluzinski, Pol. J. Chem., 54, (1980), 2189; [Chem. Abstr., 95, (1981), 016414].

213 W. Bachman, S. Bürki and T.A. Kaden, **J. Chem. Soc., Chem. Commun.,** (1981), 158.

214 M. Kodama and E. Kimura, **J. Chem. Soc., Dalton Trans.,** (1981), 694.

215 B.J. Fisher and R. Eisenberg, **Report 1980, TR-1, Order No. AD-A091344;** [**Chem. Abstr., 94,** (1981), 164701].

216 J.W.L. Martin, J.H. Timmons and A.E. Martell, **J. Coord. Chem., 10,** (1980), 251.

217 B.K. Coltrain and S.C. Jackels, **Inorg. Chem., 20,** (1981), 2032.

218 O.P. Anderson, **Acta Crystallogr. B, 37,** (1981), 1194.

219 D.M. Adams and D.C. Stevens, **Inorg. Chem., 20,** (1981), 525.

220 F.S. Stephens, R.S. Vagg and E.C. Watton, **Inorg. Chim. Acta, 47,** (1981), 97.

221 W. Fedder, F. Umland and E. Hohaus, **Z. Anorg. Allg. Chem., 471,** (1980), 77.

222 K. Uhle and R. Genz, **Z. Chem., 21,** (1981), 142.

223 D.H. Busch, D.J. Olszanski, J.C. Stevens, W.P. Schammel, M. Kojima, N. Herron, L.L. Zimmer, K.A. Holter and J. Mocak, **J. Am. Chem. Soc., 103,** (1981), 1472.

224 D.H. Busch, S.C. Jackels, R.C. Callahan, J.J. Gryzybowski, L.L. Zimmer, M. Kojima, D.J. Olszanski, W.P. Schammel, J.C. Stevens, K.A. Holter and J. Mocak, **Inorg. Chem., 20,** (1981), 2834.

225 K.J. Takeuchi, D.H. Busch and N. Alcock, **J. Am. Chem. Soc., 103,** (1981), 2421.

226 K. Sakata, M. Hashimoto, N. Tagami and Y. Murakami, **Bull. Chem. Soc. Jap., 53,** (1980), 2262.

227 S.D. Lehr and K.A. Holter, **Synth. React. Inorg. Met-Org. Chem., 10,** (1980), 607; [**Chem. Abstr., 94,** (1981), 040608].

228 V.B. Rana, D.P. Singh, P. Singh and M.P. Teotia, **Transition Met. Chem., 6,** (1981), 36.

229 M. Gerloch and L.R. Hanton, **Inorg. Chim. Acta, 49,** (1981), 37.

230 R. Kruse and E. Breitmaier, **Chem. Ber., 114,** (1981), 832.

231 K.R. Adam, G. Anderegg, K. Hendrick, A.J. Leong, L.F. Lindoy, H.C. Lip, M. McPartlin, R.J. Smith and P.A. Tasker, **Inorg. Chem., 20,** (1981), 4048.

232 L.F. Lindoy and R.J. Smith, **Inorg. Chem.**, 20, (1981), 1314.

233 H.C. Mez, J. Leoliger, U. Vogel, M. Meier and R. Scheffold, **Helv. Chem. Acta, 64**, (1981), 1098.

234 U. Vogel, K. Meier, J. Loeliger and R. Scheffold, **Helv. Chim. Acta, 64**, (1981), 1113.

235 K. Meier, R. Scheffold and P. Engel, **Helv. Chim. Acta, 64**, (1981), 1496.

236 K. Meier and R. Scheffold, **Helv. Chim. Acta, 64**, (1981), 1505.

237 C. Angst, C. Kratky and A. Eschenmoser, **Angew. Chem.**, 93, (1981), 275.

238 Y. Murakami, Y. Matsuda, K. Sakata, S. Yamada, Y. Tanaka and Y. Aoyama, **Bull. Chem. Soc. Jap.**, 54, (1981), 163.

239 N.D. Pekel and T.A. Malent'eva, **Zh. Obshch. Khim., 49**, (1979), 2706; [**Chem. Abstr.**, 93, (1981), 196790].

240 A. Harriman, **J. Chem. Soc., Faraday Trans. 1**, 76, (1980), 1978.

241 D.A. Buckingham, C.R. Clark and W.S. Webley, **J. Chem. Soc., Chem. Commun.**, (1981), 192.

242 E.A. Cuellar and T.J. Marks, **Inorg. Chem.**, 20, (1981), 3766.

243 P. Bukall and I. Ugi, **Heterocycles**, 15, (1981), 381.

244 H. Behret, H. Binder, G. Sandstede and G.G. Scherer, **J. Electroanal. Chem. Interfacial Electrochem.**, 117, (1981), 29.

245 G. Bontempelli, F. Magno, G. Schiavon and B. Corain, **Inorg. Chem.**, 20, (19i81), 2579.

246 G. Schiavon, G. Bontempelli and B. Corain, **J. Chem. Soc., Dalton Trans.**, (1981), 1074.

247 L.R. Hanton and P.R. Raithby, **Acta Crystallogr. B**, 36, (1980), 2417.

248 M. Gerloch and L.R. Hanton, **Inorg. Chem.**, 20, (1981), 1046.

249 I. Bertini, C. Luchinat and E. Borghi, **Inorg. Chem.**, 20, (1981), 303.

250 A.N. Kitaigorodskii, A.V. Kessenikh and A.V. Bulatov, **Zh. Fiz. Khim.**, 55, (1981), 1200.

251 J. Podlahova, Collect. Czech. Chem. Commun., 45, (1980), 1477.

252 N.K. Roberts and S.B. Wild, Inorg. Chem., 20, (1981), 1892.

253 J. Podlahova, B. Kratochvil and V. Langer, Inorg. Chem., 20, (1981), 2160.

254 M. Baacke, S. Hietkamp, S. Morton and O. Stelzer, Chem. Ber., 114, (1981), 2568.

255 T. Hayashi, M. Konishi, K. Yokota and M. Kumada, Chem. Lett., (1980), 767.

256 N.D. Sadanani, A. Walia, P.N. Kapoor and R.N. Kapoor, J. Coord. Chem., 11, (1981), 39.

257 B.M. Foxman, P.L. Goldberg and H. Mazurek, Inorg. Chem., 20, (1981), 4368.

258 A.N. Nesmeyanov, L.S. Isaeva, L.N. Morozova, P.V. Petrovskii, B.L. Tumanskii, B.V. Lokshin and Z.S. Klemenkova, Inorg. Chim. Acta, 43, (1980), 1.

259 C. Mealli, M. Peruzzini and P. Stoppioni, J. Organomet. Chem., 192, (1980), 437.

260 M. Wada and K. Sameshima, J. Chem. Soc., Dalton Trans., (1981), 240.

261 D.W. Firsich and R.J. Lagow, J. Chem. Soc., Chem. Commun., (1981), 1283.

262 L.J. Krause and J.A. Morrison, J. Chem. Soc., Chem. Commun., (1981), 1282.

263 A. Gleizes, A. Kerkeni, M. Dartiguenave, Y. Dartiguenave and H.F. Klein, Inorg. Chem., 20, (1981), 2372.

264 M. Wada, J. Chem. Soc., Chem. Commun., (1981), 680.

265 Y. Nakamura, K. Maruya and T. Mizoroki, Bull. Chem. Soc. Jap., 53, (1980), 3089.

266 M. Wada, Y. Koyama and K. Sameshima, J. Organomet. Chem., 209, (1981), 115.

267 C. Mealli, S. Midollini, S. Moneti and L. Sacconi, Angew. Chem., 92, (1980), 967.

268 C. Mealli, S. Midollini, S. Moneti and L.Sacconi, J. Organomet. Chem., 205, (1981), 273.

269 R. Nast and A. Beyer, J. Organomet. Chem., 204, (1981), 267.

270 P. Bicev, A. Furlani and M.V. Russo, **Gazz. Chim. Ital.**, **110**, (1980), 25.

271 S.S. Sandhu, S. Baweja and S.S. Parmar, **Transition Met. Chem.**, 5, (1980), 299.

272 A. Gergely, T. Kiss, G. Deak and I. Sovago, **Inorg. Chim. Acta**, 56, (1981), 35.

273 R. Battini, G.G. Battistuzzi, G. Grandi, L. Menabue, G.C. Pellacani, M. Saladini and A.B. Corradi, **J. Chem. Soc., Dalton Trans.**, (1981), 1665.

274 K.J. Ahmed, A. Habib and S.Z. Haider, **J. Bangladesh Acad. Sci.**, **4**, (1980), 85; [**Chem. Abstr.**, **94**, (1981), 201124].

275 Ya. D. Fridman, V.F. Nazarov and M.G. Levina, **Koord. Khim.**, 6, (1980),1442; [**Chem. Abstr.**, 93, (1980), 193009].

276 T.M. Che and K. Kustin, **J. Inorg. Biochem.**, **13**, (1980), 267.

277 H. Loennberg and J. Arpalahti, **Inorg. Chim. Acta**, 55, (1981), 39.

278 B. Jezowska-Trzebiatowska and L. Latos-Grazynski, **J. Inorg. Nucl. Chem.**, **42**, (1980), 1079.

279 M.S. El-Ezaby and T.E. El-Khalafawy, **J. Inorg. Nucl. Chem.**, 43, (1981), 831.

280 R.L. Musselman, J.B. Cornelius and R.M. Trapp, **Inorg. Chem.**, 20, (1981), 1931.

281 R.E. Wasylishen, G.L. Neufeld and K.J. Friesen, **Inorg. Chem.**, 20, (1981), 637.

282 E.L. King, **Inorg. Chem.**, **20**, (1981), 2350.

283 F.T. Bonner and M.J. Akhtar, **Inorg. Chem.**, 20, (1981), 3155.

284 R.D. Hancock, **Inorg. Chim. Acta**, **49**, (1981), 145.

285 J.M. Antelo, F. Arce, J. Casado and A. Varela, **Ann. Chim.**, 71, (1981), 209.

286 P.O. Lumme, P. Tilus and M. Orama, **Finn. Chem. Lett.**, 1-2, (1981), 11.

287 T. Matsusinovic and I. Filipovic, **Talanta**, 28, (1981), 199.

288 D. Banerjea, T.A. Kaden and H. Sigel, **Inorg. Chem.**, **20**, (1981), 2586.

289 T.B. Field and W.A.E. McBryde, **Can. J. Chem.**, 59, (1981), 555.

290 Y.K. Sze and W.A.E. McBryde, **Can. J. Chem.**, **58**, (1980), 1795.

291 E. Farkas, B. Beke and A. Gergely, **Magy. Kem. Foly.**, **86**, (1980), 345; [**Chem. Abstr.**, **93**, (1980), 211038].

292 F. Bigoli, E. Leporati and M.A. Pellinghelli, **J. Chem. Soc., Dalton Trans.**, (1981), 1961.

293 F. Bigoli, E. Leporati and M.A. Pellinghelli, **J. Chem. Soc., Dalton Trans.**, (1981), 1531.

294 M. Claude, M. Paris, J.P. Scharff, M. Aplincourt and R.P. Hugel, **J. Chem. Res. Synop.**, **7**, (1981), 222.

295 R.S. Sandhu and R.K. Kalia, **Ann. Chim.**, **70**, (1980), 625.

296 E. Farkas, A. Gergely and E. Kas, **J. Inorg. Nucl. Chem.**, **43**, (1981), 1591.

297 L. Latos-Grazynski and B. Jezowska-Trzebiatowska, **J. Coord. Chem.**, **10**, (1980), 159.

298 L. Latos-Grazynski and B. Jezowska-Trzebiatowska, **J. Inorg. Nucl. Chem.**, **43**, (1981), 1249.

299 G. Nieuwpoort and G.C. Verschoor, **Inorg. Chem.**, **20**, (1981), 4079.

300 C.F. Campana, D.F. Shepard and W.M. Litchman, **Inorg. Chem.**, **20**, (1981), 4039.

301 C.E. Bannister and D.W. Margerum, **Inorg. Chem.**, **20**, (1981), 3149.

302 K.W. Hipps and U. Mazur, **Inorg. Chem.**, **20**, (1981), 1391.

303 E.B. Chuklanova and T.N. Polynova, **Koord. Chim.**, **7**, (1981), 944.

304 S.R. Ebner and R.J. Angelici, **Inorg. Chem.**, **20**, (1981), 2971.

305 E. Kwiatkowski and M. Kwiatkowski, **Inorg. Chim. Acta**, **42**, (1980), 197.

306 Y. Nishida, S. Kida, S. Cremer and K. Nakamoto, **Inorg. Chim. Acta**, **49**, (1981), 85.

307 K.R. Levan and C.A. Root, **Inorg. Chem.**, **20**, (1981), 3566.

308 K.R. Levan and C.A. Root, **J. Org. Chem.**, **46**, (1981), 2404.

309 H. Kuma and S. Yamada, **Bull. Chem. Soc. Jap.**, **53**, (1980), 3218.

310 S. Balt, J. Meuldijk and W.E. Renkema, **Inorg. Chim. Acta**, 43, (1980), 173.

311 S. Balt, J. Meuldijk and W.E. Renkema, **Transition Met. Chem.**, 5, (1980), 357.

312 B. Chiswell, **Inorg. Chim. Acta**, 41, (1980), 165.

313 K.P. Balakrishnan and V. Krishnan, **J. Coord. Chem.**, 10, (1980), 181.

314 P.R. Shukla and P. Takroo, **Indian J. Chem. Sect. A**, 20, (1981), 305.

315 S.C. Bhatia, J.M. Bindlish, A.R. Saini and P.C. Jain, **J. Chem. Soc., Dalton Trans.**, (1981), 1773.

316 F. Akhtar, **Acta Crystallogr. B**, 37, (1981), 84.

317 U. Casellato, P.A. Vigato, R. Graziani and M. Vidali, **Inorg. Chim. Acta**, 49, (1981), 173.

318 Y. Fujii, M. Ito and K. Akiyama, **Bull. Chem. Soc. Jap.**, 54, (1981), 2527.

319 T. Nagahara, K. Kasuga and Y. Yamamoto, **Inorg. Chim. Acta**, 47, (1981), 37.

320 Y-Y. Chen, D.E. Chu, B.D. McKinney, L.J. Willis and S.C. Cummings, **Inorg. Chem.**, 20, (1981), 1885.

321 M. Goodgame and K.W. Johns, **Inorg. Chim. Acta**, 46, (1980), 23.

322 C.M. Mikulski, F.J. Iaconianni, L.L. Pytlewski, A.N. Speca and N.M. Karayannis, **Inorg. Chim. Acta**, 46, (1980), L47.

323 W.L. Driessen and P.L.A. Everstijn, **Inorg. Chim. Acta**, 41, (1980), 179.

324 N. Saha and K.M. Datta, **J. Inorg. Nucl. Chem.**, 43, (1981), 1405.

325 N.R. Shah and J.R. Shah, **J. Inorg. Nucl. Chem.**, 43, (1981), 1583.

326 R. Aruga, **Aust. J. Chem.**, 34, (1981), 501.

327 L. Malatesta, G. La. Monica, M. Manassero and M. Sansoni, **Gazz. Chim. Ital.**, 110, (1980), 113; [**Chem. Abstr.**, 93, (1980), 214578].

328 J.E. Poldoski and T.J. Bydalek, **J. Inorg. Nucl. Chem.**, 43, (1981), 119.

329 R.S. Srivastava, **J. Inorg. Nucl. Chem., 42,** (1980), 1526.

330 M.P. Teotia, J.N. Gurtu and V.B. Rana, **J. Inorg. Nucl. Chem., 42,** (1980), 821.

331 N.S. Bhave and R.B. Kharat, **J. Inorg. Nucl. Chem., 42,** (1980), 977.

332 C.D. Rao, B.K. Mohapatra and S. Guru, **J. Inorg. Nucl. Chem., 42,** (1980), 1195.

333 R.L. Dutta and A. Bhattacharya, **J. Inorg. Nucl. Chem., 42,** (1980), 1205.

334 S. Murakami, **J. Inorg. Nucl. Chem., 43,** (1981), 335.

335 C.P. Saxena and P.V. Khadikar, **J. Inorg. Nucl. Chem., 43,** (1981), 603.

336 K. Ogura, S. Murakami and K. Seneo, **J. Inorg. Nucl. Chem., 43,** (1981), 1243.

337 B.A. Jani and P.K. Bhattacharya, **J. Indian Chem. Soc., 58,** (1981), 207.

338 M.S. Mayadeo and R.L. Ganti, **J. Indian Chem. Soc., 58,** (1981), 614.

339 G.S. Sanyal, A.B. Modak and A.K. Mudi, **Indian J. Chem. Sect. A, 20,** (1981), 510.

340 R.C. Das, M.K. Misra and S.K. Mohanty, **Indian J. Chem. Sect. A, 20,** (1981), 528.

341 I. Ahmed and F. Akhtar, **Indian J. Chem. Sect. A, 20,** (1981), 737.

342 M. Kastner, S. Jonsdottir and G. Klar, **Chem.-Ztg., 105,** (1981), 232.

343 F. Brezina and J. Kamenicek, **Z. Chem., 21,** (1981), 233.

344 G. Bouet and J. Jolivet, **C.R. Seances Acad. Sci. Ser. 2, 292,** (1981), 1139.

345 M.K. Hassan, M.I. Ismail and Z.H. Khalil, **Ann. Chim., 71,** (1981), 337.

346 M.K. Hassan, M.I. Ismail and Z.H. Khalil, **Curr. Sci., 49,** (1980), 935.

347 Yu. Ya. Kharitonov and G.V. Tsintsadze, **Koord. Chim., 6,** (1980), 1874; [**Chem. Abstr., 94,** (1981), 075967].

348 A.E. Shvelashvili and E.B. Miminoshvili, **Koord. Khim., 6,** (1980), 1251; [**Chem. Abstr. 93,** (1980), 213704].

349 S.K. Tiwari, S. Jain, A. Kumar and K.C. Tiwari, **J. Indian Chem. Soc**, 57, (1980), 571.

350 B.C. Bloodworth, B. Demetriou and R. Grzeskowiak, **Inorg. Chim. Acta**, 53, (1981), L85.

351 L. Beyer, R. Kirmse, J. Stach, R. Szargan and E. Hoyer, **Z. Anorg. Allg. Chem.**, **476**, (1981), 7.

352 U. Casellato, P.A. Vigato, R. Graziani, M. Vidali and B. Acone, **Inorg. Chim. Acta**, **45**, (1980), L79.

353 R. Graziani and M. Vidali, **Transition Met. Chem.**, 6, (1981), 166.

354 P.K. Biswas and N.R. Chaudhuri, **J. Chem. Soc., Dalton Trans.**, (1981), 2176.

355 P.K. Biswas and N.R. Chaudhuri, **J. Chem. Soc., Dalton Trans.**, (1981), 2385.

356 D. Attanasio, G. Dessy, V. Fares and G. Pennesi, **Mol. Phys.**, **40**, (1980), 269.

357 F. Cariati, F. Morazzoni, C. Busetto, G. Del Pireo and A. Zazzetta, **J. Chem. Soc., Dalton Trans.**, (1976), 342.

358 C. Janakiram-Sayala, W.P. Bosman, J. Willemse and J.A. Cras, **Recl. Trav. Chim. Pays-Bas**, **99**, (1980), 314.

359 E. Gyepes, F. Pavelcik and A. Beno, **Collect. Czech. Chem. Commun.**, **46**, (1981), 975.

360 C. Kratky, J. Schurz, E. Gagliardi and A. Popitsch, **Monatsh. Chem.**, **112**, (1981), 721.

361 S. Chandra, K.B. Pandeya and R.P. Singh, **Transition Met. Chem.**, 5, (1980), 257.

362 L. El-Sayed, A. El-Toukhy, N. El Kady and M.F. Iskander, **Transition Met. Chem.**, 5, (1980), 293.

363 K.F. Belyaeva, V.N. Biyushkin and V.A. Neverov, **Koord. Chim.**, 7, (1981), 433; [**Chem. Abstr.**, **94**, (1981), 183813].

364 R.S. Thakur and C.S. Bhandari, **J. Inst. Chem. (India)**, 53, (1981), 33; [**Chem. Abstr.**, **94**, (1981), 215410].

365 M. Molina, C. Melios and N. Barelli, **Talanta**, 28, (1981), 69.

366 S. Millefiori, A. Millefiori and G. Granozzi, **Inorg. Chim. Acta**, **48**, (1981), 233.

367 A. Cinquantini, R. Seeker, R. Cini and P. Zanello, Inorg. Chim. Acta, 53, (1981), L201.

368 M.D. Fryzuk and P.A. MacNeil, J. Am. Chem. Soc., 103, (1981), 3592.

369 P. Giannoccaro, C.F. Nobile, G. Vasapollo and A. Sacco, Congr. Naz. Chim. Inorg., [Atti], 13th., (1980), 100.

370 P. Dapporto, M. Peruzzini and P. Stoppioni, Inorg. Chim. Acta, 47, (1981), 213.

371 E. Lindner, F. Bouachir and W. Hiller, J. Organomet. Chem., 210, (1981), C37.

372 K. Issleib and W. Gans, Z. Anorg. Allg. Chem., 475, (1981), 116.

373 K. Aurivillius and G.I. Bertinsson, Acta Crystallogr. B, 37, (1981), 72.

374 M.A. Bennett and H. Neumann, Aust. J. Chem., 33, (1980). 1251.

375 F.M. Dayrit and J. Schwartz, J. Am. Chem. Soc., 103, (1981), 4466.

376 E.K. Barefield, D.A. Krost, D.S. Edwards, D.G. VanDerveer, R.L. Trytko, S.P. O'Rear and A.N. Williamson, J. Am. Chem. Soc., 103, (1981), 6219.

377 C. Gosden, J.B. Kerr, D. Pletcher and R. Rosas, J. Electroanal. Chem. Interfacial Electrochem., 117, (1981), 101.

378 R.R. Gagne and D.M. Ingle, Inorg. Chem., 20, (1981), 420.

379 R.R. Gagne, D.M. Ingle and G.C. Lisensky, Inorg. Chem., 20, (1981), 1991.

380 S. Midollini, S. Moneti, A. Orlandini and L. Sacconi, Cryst. Struct. Commun., 9, (1980), 1141.

381 S. Midollini, S. Moneti, A. Orlandini and L. Sacconi, Cryst. Struct. Commun., 9, (1980), 1153.

382 T.M. Balthazor and R.C. Grabiak, J. Org. Chem., 45, (1980), 5425.

383 S. Sibille, M. Troupel, J.-F. Fauvarque and J. Perichon, J. Chem. Res. Synop., (1980), 147.

384 S. Sibille, J.C. Folest, J. Coulombeix, M. Troupel, J.-F. Fauvarque and J. Perichon, J. Chem. Res. Synop., (1980), 268.

385 G. Schiavon, G. Bontempelli, M. De Nobili and B. Corain, **Inorg. Chim. Acta, 42**, (1980), 211.

386 H. Kanai, K. Kushi, K. Sakanoue and N. Kishimoto, **Bull. Chem. Soc. Jap., 53**, (1980), 2711.

387 C.F. Nobile, P. Gianoccaro, G. Vasapollo and A. Sacco, **Congr. Naz. Chim. Inorg., 13**, (1980), 105.

388 C.F. Nobile, G. Vasapollo, P. Gianoccaro and A. Sacco, **Inorg. Chim. Acta, 48**, (1981), 261.

389 H. Hoberg, W. Richter and C. Froehlich, **J. Organomet. Chem., 213**, (1981), C49.

390 O. Sock, P. Lemoine and M. Gross, **Electrochim. Acta, 26**, (1981), 99.

391 M. Svoboda, H. Tom Dieck, C. Krueger and Y-H. Tsay, **Z. Naturforsch. B; Anorg. Chem., Org. Chem., 36**, (1981), 814.

392 H. Tom Dieck, M. Svoboda and T. Greiser, **Z. Naturforsch. B; Anorg. Chem., Org Chem., 36**, (1981), 823.

393 P. Overbosch, G. Van Koten and K. Vrieze, **J. Organomet. Chem., 208**, (1981), C21.

394 J.A. Ibers, T.R. Gaffney and K. Schramm, **Coord. Chem., 21**, (1980), 141.

395 D. Walther, **J. Organomet. Chem., 190**, (1980), 393.

396 H. Hoberg and W. Richter, **J. Organomet. Chem., 195**, (1980), 347.

397 H. Hoberg and W. Richter, **J. Organomet. Chem., 195**, (1980), 355.

398 H. Hoberg and C. Froehlich, **J. Organomet. Chem., 209**, (1981), C69.

399 J. Grobe and B.H. Schneider, **Z. Naturforsch., B; Anorg. Chem., Org. Chem., 36**, (1981), 8.

400 R. Mynott, A. Mollbach and G. Wilke, **J. Organomet. Chem., 199**, (1980), 107.

401 T. Kruck and G. Maeueler, **Z. Anorg. Allg. Chem., 475**, (1981), 156.

402 K. Kitaura, S. Sakaki and K. Morokuma, **Inorg. Chem., 20**, (1981), 2292.

403 W. Dreissig and H. Dietrich, **Acta Crystallogr. B, 37**, (1981), 931.

404 A. Musco, I. Georgii and B.E. Mann, **Inorg. Chim. Acta, 45,** (1980), L149.

405 P. Heimbach, J. Kluth, H. Schenkluhn and B. Weimann, **Angew. Chem., 92,** (1980), 567.

406 P. Heimbach, J. Kluth, H. Schenkluhn and B. Weimann, **Angew. Chem., 92,** (1980), 569.

407 A. Sisak, H. Schenkluhn and P. Heimbach, **Acta Chim. Acad. Sci. Hung., 103,** (1981), 37; [**Chem. Abstr., 93** (1980), 220258].

408 D.L. Beach and T.P. Kobylinski, **J. Inorg. Nucl. Chem., 42,** (1980), 1504.

409 A. Del. Pra, G. Zanotti, L. Pandolfo and P. Segala, **Cryst. Struct. Commun., 10,** (1981), 7.

410 B. Hipler and E. Uhlig, **J. Organomet. Chem., 199,** (1980), C27.

411 E. Uhlig and W. Poppitz, **Z. Anorg. Allg. Chem., 477,** (1981), 167.

412 M.F. Semmelhack, P. Helquist, L.D. Jones, L. Keller, L. Mendelson, L.S. Ryono, J.G. Smith and R.D. Stauffer, **J. Am. Chem. Soc., 103,** (1981) 6460.

413 W. Siebert, H. Schmidt and R. Full, **Z. Naturforsch. B; Anorg. Chem., Org. Chem., 35,** (1980), 873.

414 K. Ensslen, H. Oesterreicher and E. Bucher, **J. Less-Common Met., 77,** (1981), 287.

415 C.P. Landee and R.D. Willett, **Inorg. Chem., 20,** (1981), 2521.

416 B.P. Baranwal, G.K. Parashar and R.C. Mehrotra, **Monatsh. Chem., 111,** (1980), 1203.

417 W.L. Gladfelter, M.W. Lynch, W.P. Schaefer, D.N. Hendrickson and H. B. Gray, **Inorg. Chem., 20,** (1981), 2390.

418 N.I. Kirillova, Yu. T. Struchkov, M.A. Porai-Koshits, A.A. Pasynskii, A.S. Antsyshkina, L.Kh. Minacheva, G.G. Sadikov, T.Ch. Idrisov and V.T. Kalinnikov, **Inorg. Chim. Acta, 42,** (1980), 115.

419 J.H. Binks, G.J. Dorward, R.A. Howie and G.P. McQuillan, **Inorg. Chim. Acta, 49,** (1981), 251.

420 L. Banci, A. Bencini, C. Benelli, A. Dei and D. Gatteschi, **Inorg. Chem., 20,** (1981), 1399.

421 G.L. Stucky, R.J. Bowman, M.W. Stutzman and L.T. Taylor, J. Inorg. Nucl. Chem., **42**, (1980), 1257.

422 A. Gleizes and M. Verdaguer, J. Am. Chem. Soc., **103**, (1981), 7373.

423 K.P. Callahan and E.J. Cichon, Inorg. Chem., **20**, (1981), 1941.

424 D. Seyferth, R.S. Henderson and M.K. Gallagher, J. Organomet. Chem., **193**, (1980), C75.

425 C.A. Ghilardi, S. Midollini and L. Sacconi, J. Chem. Soc., Chem. Commun., (1981), 47.

426 I.B. Konche-Waksman, Y. Journaux and O. Kahn, Transition. Met. Chem., **6**, (1981), 176.

427 N.A. Bailey, D.E. McKenzie and J.M. Worthington, Inorg. Chim. Acta, **43**, (1980), 145.

428 P.P. Singh, N. Singh and D.D.S. Yadav, J. Inorg. Nucl. Chem., **43**, (1981), 77.

429 P.P. Singh, A.K. Gupta and A.K. Srivastava, J. Coord. Chem., **10**, (1980), 199.

430 P.P. Singh, S. Kumar, M.P. Reddy, Inorg. Chem., **20**, (1981), 2711.

431 S.A. Khan, J. Inorg. Nucl. Chem., **42**, (1980), 919.

432 P. Amico, G. Arena, P.G. Daniele, G. Ostacoli, E. Rizzarelli and S. Summartano, Inorg. Chem., **20**, (1981), 772.

433 L. Banci, A. Bencini, A. Dei and D. Gatteschi, Inorg. Chem., **20**, (1981), 393.

434 J.R. Allan, G.M. Baillie and N.D. Baird, J. Coord. Chem., **10**, (1980), 171.

435 P.D.W. Boyd and R.L. Martin, J. Chem. Soc., Dalton Trans., (1981), 1069.

436 G. Vos, J.P. Haasnoot and W.L. Groeneveld, Z. Naturforsch. B.; Anorg. Chem., Org. Chem., **36**, (1981), 802.

437 G. Vos, A.J. de Kok and G.C. Verschoor, Z. Naturforsch. B.; Org. Chem., **36**, (1981), 809.

438 D. Dolphin, J. Hiom and J.B. Paine III, Heterocycles, **16**, (1981), 417.

439 D.H. Busch, G.G. Christoph, L.L. Zimmer, S.C. Jackels, J.J. Grzybawski, R.C. Callahan, M. Kojima, K.A. Holter, J. Mocak, N. Herron, M. Chavan and W.P. Schammel, **J. Am. Chem. Soc., 103,** (1981), 5107.

440 F.S. Stephens and R.S. Vagg, **Inorg. Chim. Acta, 42,** (1980), 139.

441 F.S. Stephens and R.S. Vagg, **Inorg. Chim. Acta, 43,** (1980), 77.

442 E.K. Barefield, D. Chueng, D.G. Van Derveer and F. Wagner, **J. Chem. Soc., Chem. Commun.,** (1981), 302.

443 R.R. Gagne, C.L. Spiro, T.J. Smith, C.A. Harmann, W.R. Thies and A.K. Shiemke, **J. Am. Chem. Soc., 103,** (1981), 4073.

444 C.L. Spiro, S.L. Lambert, T.J. Smith, E.N. Duesler, R.R. Gagne and D.N. Hendrickson, **Inorg. Chem., 20,** (1981), 1229.

445 C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, **J. Am. Chem. Soc., 103,** (1981), 1448.

446 C. Bianchini, M. Di Vaira, A. Meli and L. Sacconi, **Inorg. Chem., 20,** (1981), 1169.

447 C. Bianchini, C. Mealli, A. Meli and L. Sacconi, **Inorg. Chim. Acta, 43,** (1980), 223.

448 C. Bianchini, A. Meli, A. Orlandini and L. Sacconi, **J. Organomet. Chem., 209,** (1981), 219.

449 F. Cecconi, S. Midollini, A. Orlandini and L. Sacconi, **Inorg. Chim. Acta, 42,** (1980), 59.

450 H. Werner, N.K. Tri, C. Friebel, P. Koehler and D. Reinen, **Z. Naturforsch. B.; Anorg. Chem., Org. Chem., 36,** (1981), 322.

451 O. Stelzer, S. Morton and W.S. Sheldrick, **Acta Crystallogr., B, 37,** (1981), 439.

452 N.E. Schore, L.S. Benner and B.E. Labelle, **Inorg. Chem., 20,** (1981), 3200.

453 J.Y. Lee, D.A. Hanna and G.W. Everett, **Inorg. Chem., 20,** (1981), 2004.

454 T. Izumitani, H. Okawa and S. Kida, **Chem. Lett.,** (1981), 483.

455 R.J. Butcher, C.J. O'Connor and E. Sinn, **Inorg. Chem., 20,** (1981), 3486.

456 L. Banci, C. Benelli and D. Gatteschi, **Inorg. Chem., 20,** (1981), 4397.

457 C.S. Kraihanzel, E. Sinn and G.M. Gray, **J. Am. Chem. Soc.,** 103, (1981), 960.

458 M. Louey, P.D. Nichols and R. Robson, **Inorg. Chim. Acta, 47,** (1981), 87.

459 K.S. Chong, S.J. Rettig, A. Storr and J. Trotter, **Can. J. Chem., 58,** (1980), 1091.

460 P.J.M.W.L. Birker, J. Reedijk and G.C. Verschoor, **Inorg. Chem., 20,** (1981), 2877.

461 T.F. Zafiropoulos, S.P. Perlepes, P.V. Ioannou, J.M. Tsangaris and A.G. Galinos, **Z. Naturforsch. B; Anorg. Chem., Org. Chem., 36,** (1981), 87.

462 M.M. Aly and A.M. Shalaby, **Monatsh. Chem., 111,** (1980), 935.

463 I. S. Ahuja, R.S. Singh and C.L. Yadava, **J. Mol. Struct., 68,** (1980), 333.

464 S. Khanna, R. Kumar and G.K. Chaturvedi, **Indian J. Chem. Sect. A, 19,** (1980), 766.

465 P. Vigato, U. Casellato, B. Acone, M. Vidali and D.F. Fenton, **Inorg. Nucl. Chem. Lett., 16,** (1980), 489.

466 R.L. Dutta and A.K. Sarkar, J. **Inorg. Nucl. Chem., 43,** (1981), 180.

467 N.S. Bhave and R.B. Kharat, J. **Inorg. Nucl. Chem., 43,** (1981), 414.

468 A.C. Dash, M.S. Dash and S.K. Mohapatra, J. **Inorg. Nucl. Chem., 43,** (1981), 1074.