6. Nickel 1993

Simon J. Higgins

CONTENTS

INTRODUCTION

This review covers the coordination chemistry of nickel for 1993. Reviews for 1990 and 1991 have also recently appeared in this series. Relevant references were obtained from the BIDS database using the keyword "nickel*". The years 1993–1994 (June) were checked, but only references dated 1993 are included. Additionally, the following journals were checked independently from the period January to December 1993: *Angew. Chem., Int. Ed., Engl., Helv. Chim. Acta, Inorg. Chem., Inorg. Chim. Acta, J. Am. Chem. Soc., J. Chem. Soc., Chem. Commun., J. Chem. Soc., Dalton Trans., J. Organometal. Chem., J. Phys. Chem., Organometallics , Polyhedron, Transition Metal Chemistry* and *Z. Anorg. Allg. Chem.*

Many papers describe nickel complexes with the same donor set but different formal oxidation states. As for the 1990 review the traditional subdivision by oxidation state and ligand type has been replaced by ligand type alone. In cases where the oxidation state is not obvious, it is stated explicitly. All $E_{1/2}$ values are quoted with respect to the saturated calomel electrode except where otherwise stated.

Nickel carbonyl clusters and organometallic complexes (other than mononuclear carbonyl complexes) have this year been specifically excluded. These are dealt with adequately elsewhere. Again, nickel complexes are widely employed in homogeneous catalysis, and many papers describing their applications in industrial processes and organic chemistry appear each year. However, only papers of particular interest for their coordination chemistry are treated here.

6.1 COMPLEXES WITH GROUP 14 DONOR LIGANDS

On treatment of $[Ni_6(CO)_{12}]^{2-}$ with $RSnCl_3$ (R = Me, Bu) in CH_3CN, the unusual trigonal bipyramidal Ni(II) complexes $[Ni(SnRCl_2)_4(CO)]^{2-}$ were formed [1], rare examples of stable Ni(II)–CO coordination. X–Ray studies showed that the CO occupies an equatorial site.

6.2 COMPLEXES WITH HALIDE AND PSEUDOHALIDE LIGANDS

6.2.1 Complexes with cyanide ligands

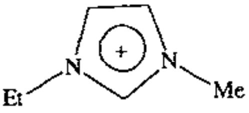
The coordination chemistry of Ni^{2+} with CN^- in liquid ammonia has been examined [2]. The only species detected spectroscopically (FTIR and Raman) were (ion–paired) $[Ni(CN)_4]^{2-}$, and

$[Ni(NH_3)_6]^{2+}$, in proportions depending on the mole ratio. Further coordination to give $[Ni(CN)_5]^{3-}$ at higher $[CN^-]$, as happens in aqueous solution, was not observed. A solid–state ^{13}C NMR spectroscopic study of $K_2[Ni(^{13}CN)_4].H_2O$ has been reported [3]. The chemical shift tensors are nearly axial, and have similar values to those in $[M(CN)_4]^{2-}$ (M = Pd, Pt), and CH_3CN.

A structural study of a series of inclusion complexes of type [(1,2-propanediamine)$Cd(NC)_4Ni$].nG, where G is a straight– or branched–chain alkane or related guest molecule (n = 0.3–0.5) has been reported [4]. Two structural types were observed, one for straight chain guests, the other for branched guests and α,ω–dihaloalkanes; for the latter molecules, weak halogen–H_2N hydrogen bonding appears to contribute to the structural preference.

6.2.2 *Complexes with halide and related ligands*

Rotationally–resolved electronic spectra of gas–phase $NiCl_2$, recorded using isentropically–expanded 'cold' beams, suggest that the molecule is linear; in inert gas matrices it is bent [5]. Simple chloro–complexes of Ni(II) continue to attract attention. The most unusual example this year is probably that found in the charge transfer salt $[ET]_3[NiCl_4].H_2O$ (ET = bis(ethylenedithio)tetrathiafulvalene); pairs of $[NiCl_4]^{2-}$ ions are linked by H–bonding through water molecules, and there are some short anion–cation distances. This results in a very distorted geometry, such that the $NiCl_4{}^{2-}$ ion approaches planarity (Cl–Ni–Cl angles 92.4(1)–95.2(1)°) [6]. The X–Ray crystal structure of $(emim)_2[NiCl_4]$ (emim = (**1**)) shows a network of hydrogen bonding, with all emim ring protons H–bonded to separate $[NiCl_4]^{2-}$ ions [7]. Such salts have been studied previously in ambient–temperature ionic liquids. The $[NiCl_4]^{2-}$ ion is also formed when $NiCl_2$ is dissolved in $ZnCl_2$–2NaCl eutectic; the standard potential of the Ni(II)/Ni(0) couple has been measured (–1.006 V *vs.* Cl_2(1 atm)/Cl^-) [8].



(**1**)

When $[NiCl_4]^{2-}$ is incorporated in the interlayers of a Mg–Al hydrotalcite–like clay, halogen exchange with alkyl bromides is possible under surprisingly mild conditions [9], ultimately producing intercalated $[NiBr_4]^{2-}$. The salt '(piperidinium)$_2[NiCl_4]$' is yellow, suggesting octahedral Ni(II), and the crystal structure confirms that the compound is (piperidinium)$_n$$\{[NiCl_3]Cl\}_n$, with chains of face–sharing $[NiCl_6]^{4-}$ octahedra in a structure related to that in $CsNiCl_3$ [10]. A review describing the application of neutron diffraction and isotope substitution (NDIS) to the study of aqueous cation structures has appeared; Ni^{2+} is particularly suitable for this technique as it has a large number of naturally–occurring isotopes with a range of neutron–scattering lengths [11]. The formation of complexes with Cl^-, Br^-, $SO_4{}^{2-}$ and ATP has been studied.

The complexation equilibria between Ni^{2+} and Cl^- in CH_3CN indicates that with increasing $[Cl^-]$, $[NiCl_x(CH_3CN)_{6-x}]^{(2-x)+}$ (x = 1,2), then tetrahedral $[NiCl_{4-x}(CH_3CN)_x]^{(2-x)-}$ (x = 1,0) form [12]. The ion $[MCl_4]^{2-}$ is less stable for M = Ni than either Cu or Zn; all reactions are more exothermic in CH_3CN than in the stronger donor solvent dmf.

The electronic spectrum of $[Ni(H_2O)_6](NO_3)_2$ dissolved in molten $Ca(NO_3)_2.4H_2O$ has been reported; it is thought that some displacement of water by nitrate ion occurs in this solvent [13].

The first example of a dinuclear Ni(II) complex with bridging $SeCN^-$ to be structurally characterised is $\{[Ni(NCSe)(L)]\}_2(\mu\text{-}SeCN)_2$ (L = $MeN(CH_2CH_2CH_2NH_2)_2$) [14]. The selenocyanate bridges in an end–to–end fashion so each Ni(II) is octahedrally coordinated by the tridentate L, a non–bridging nitrogen–bound $NCSe^-$ ion, the Se atom of one bridging $SeCN^-$ and the N atom of the second bridging $NCSe^-$. The complex is ferromagnetic as expected for this arrangement, with $J = 8.8\ cm^{-1}$.

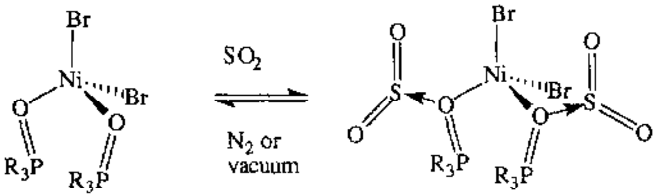
6.3 COMPLEXES WITH OXYGEN DONOR LIGANDS

6.3.1 Neutral ligands

A neutron and X–Ray diffraction study of $[Ni(H_2O)_6]SO_4$ at 25 K has been reported [15]. Changes in the electron distribution about the nickel in comparison with an earlier study at room temperature of $[Ni(D_2O)_6]SO_4$ [16] were interpreted as due to changes in the relative occupancy of the electronic energy levels with temperature. Another X–Ray study of the electron distribution in $[Ni(H_2O)_6]SO_4$ found four coplanar lobes of electron density at Ni; these each point to the S atoms of the nearest four SO_4^{2-} ions [17]. These findings contradict those from the earlier report on $[Ni(D_2O)_6]SO_4$. A careful re–examination of the structures of the ammonium Tutton salt and hexafluorosilicate salt of $[Ni(H_2O)_6]^{2+}$ has been reported [18]. As expected from ligand field considerations, the Ni–O bond is the shortest of any third row transition element (2.0418(8) Å for the Tutton salt).

The water vapour pressure – temperature behaviour and thermodynamics of the dehydration of $[Ni(H_2O)_6](ClO_4)_2$ have been reported [19]. The species $[Ni(ClO_4)_2(H_2O)_4]$ and $[Ni(ClO_4)_2(H_2O)_2]$ are formed as the temperature is raised.

The tetrahedral complex $[NiBr_2(O{=}PPr^n{}_3)_2]$ has been found to react reversibly with SO_2, giving a ligand–bound adduct, $[Ni\{O(SO_2)PPr^n{}_3\}_2Br_2]$; it is suggested that the structure of the adduct is as represented in (2) [20].



(2)

6.3.2 *Anionic ligands*

6.3.2.1 *Oxides and related systems*

Since the discovery of high T_c superconductivity in hole–doped copper oxides, interest in the electronic structure of the late transition metal oxides has increased, and this is reflected in a number of papers this year. The system $Y_{2-x}Sr_xNiO_{4-\delta}$ has been studied. It shows one stable phase only, between 1100–1150°C, namely the stoichiometric Ni(III) oxide, $YSr_5Ni_3O_{11}$. This adopts the tetragonal K_2NiF_4 (T–type) structure, with oxygen vacancies in the nickel oxide planes [21]. The material is a semiconductor, exhibiting variable range 2–dimensional hopping behaviour. Another oxonickelate, $NaBa_2Ni(II)_2Ni(III)O_6$, has also been briefly described [22].

When Li^+ is doped into NiO giving $Li_xNi_{1-x}O$ (x = 0–0.4), charge compensation requires either formation of O^- or oxidation to Ni^{3+}. An EXAFS and X–Ray Absorption Near–Edge Structure (XANES) study of this system has been interpreted in terms of the predominant effect being oxidation to Ni^{3+} [23]; two different Ni–O bond lengths (2.07(1) and 1.94(1) Å), whose proportions changed with x, were found. Turning to phases containing exclusively Ni(II), a detailed study of the electronic spectrum of $NiTa_2O_6$, where the Ni^{2+} ions have D_{2h} symmetry, has been published [24]. The lowest energy transition is largely magnetic dipole in nature, but the other transitions are vibronic. The spinels $M_zNiMn_{2-z}O_4$ (M = Li, z = 0–0.66; M = Fe, z = 0–1; M = Zn, z = 0–1) have been prepared [25]. The electrical conductivity of these compounds has been interpreted in terms of the polaron hopping model.

An interesting nickel–antimony alkoxide cluster, $[Ni_6Sb_4O_4(OEt)_{16}(HOEt)_4]$, has been described [26]. This green complex was made by treatment of a mixture of $Sb(OEt)_3$ and KOEt with $NiBr_2$. X–Ray crystallography reveals a roughly tetrahedral arrangement of five–coordinated Sb(III) ions (with the stereoactive lone pair occupying the sixth position), and octahedral Ni(II) ions occupying positions roughly midway along the Sb–Sb edges. Each oxide ion is bonded to one Sb(III) and three Ni(II) ions.

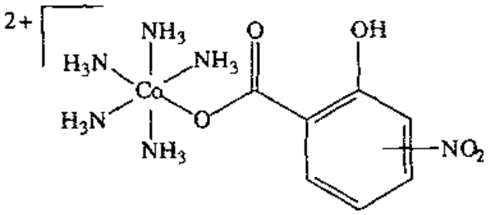
Oxides with metals in unusually low oxidation states continue to attract interest. Some unusual compounds of this type involving Ni(I), $RbNa_2NiO_2$ and KNa_2NiO_2, have been described this year [27]. These were prepared by prolonged treatment of Na_2NiO_2 with M_2O at 600°C.

Finally, a comprehensive ab initio study of gas–phase NiO_2 shows that the molecule adopts a side–on C_{2v} type arrangement [28], and is fairly well–described as $Ni^+O_2^-$.

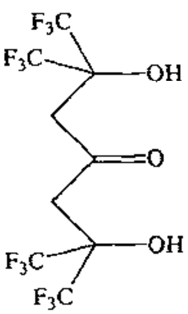
6.3.2.2 *RO^- and related ligands*

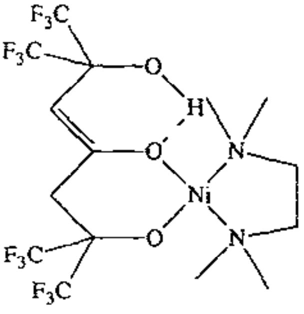
The presence of secondary organochlorine–metal bonding in Ni(II) complexes of 4–substituted 2,6–dichlorophenolate has been examined using structural and NQR spectroscopic methods [29]. For a range of 3d metal complexes of these ligands of the type $[M(OC_6H_2Cl_2X)_2(L)_2]$ (L = monodentate ligand), the strongest M···Cl–C interaction was found for Ni(II); this appears to be governed by octahedral site preference energy. The secondary bond in $[Ni(OC_6H_2Cl_3\text{-}O,Cl)_2(tmen)]$ is one of the shortest and strongest yet found (mean 2.611 Å); the geometry is pseudo-octahedral with *trans* oxygens and *cis* organochlorines.

The kinetics of the reversible binding of Ni(II) with Co(III) complexes of type (3) (and related systems with di– or multidentate Co(II)–amine complexes) have been studied by stopped–flow techniques [30]. The reaction proceeds via the phenoxide form of the ligand, giving a Ni(II)–salicylate chelate species.


(3)

The ligand (4) was previously thought to complex as an alkoxide–carbonyl didentate, with the remaining –OH group deprotonated, giving net neutral Ni(II) complexes with diamine co–ligands. However, X–Ray crystallography shows that, with tmen as co–ligand, the enol complex (5) is the true structure [31]. A range of heteronuclear complexes of type $[M^{II}\{Cr(A)(OH)_2\}_2]^{4+}$ (A = tetraamine), among them Ni(II) examples, has been isolated (as dithionate salts) [32]. Two forms of the complexes occur, depending on the nature of A. The first is more hydrated than the other, and it is suggested that the Cr complexes are singly bridging to Ni(II) in the former, and chelating in the latter. Correlation of magnetic with X–Ray crystallographic data suggests that in the complexes where the metals are linked by single bridges, antiferromagnetism is observed, but where they are linked by double bridges, weak ferromagnetism is seen.


(4)

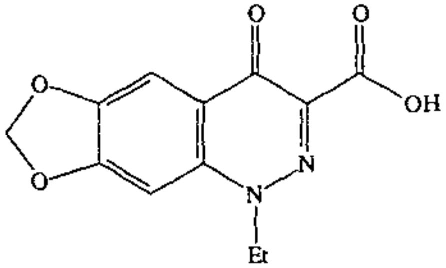

(5)

The stability constants of complexes formed by Ni(II) with 1–hydroxy–2–pyridone, of interest because of its potential therapeutic uses, have been reported [33]. This ligand gives stronger complexes than the related 1,4–dihydroxy–2–pyridinone and 1–methyl–3–hydroxy–2–pyridinone.

6.3.2.3 Carboxylic acid, amide and related ligands.

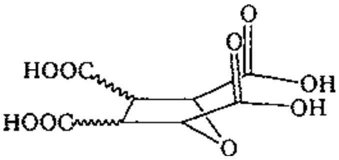
A number of novel carboxylato-bridged polymetallic complexes, including $[M^{III}_2NiO(O_2CCH_3)_6(py)_3]$.solv (M = Cr, Mn) have been prepared from the metal(II) acetates in pyridine (Cr) or ethanol–acetic acid–pyridine in air (Mn) [34]. The structure of the $Mn^{III}Co^{II}$ analogue shows an oxo–centred triangular core of metal ions, two bridging acetates linking each metal centre and terminal pyridine ligands, giving a roughly octahedral geometry at each metal. Unlike the mixed valence $Fe^{III}_2Fe^{II}$ analogue, IR spectroscopy establishes that these complexes are valence–localised at room temperature. Magnetic interactions in related complexes of Fe(III), including $[Fe_2NiO(O_2CCH_3)_6(py)_3]$, have been studied using inelastic incoherent neutron scattering (IINS), and the results compared with predictions from the Heisenberg–Dirac–Van Vleck spin–only magnetic coupling scheme [35]. Energy transfers of magnetic origin were observed consistent with transitions between low–lying energy levels of the exchange–coupled cluster, and excellent agreement with the theory was found. Differences in *J* values found using IINS and those measured with magnetic susceptibility–temperature experiments were small.

The structure of $[Ni(2\text{–phenoxybenzoate})_2(H_2O)_4]$ shows that the geometry is *trans*, with bond lengths Ni–O (carboxylate) 2.031(1) Å, Ni–OH_2 2.049(2), 2.104(2) Å [36]. Several metal complexes of the antibacterial compound cinoxacin (**6**), including $[Ni(6^-)_2(DMSO)_2].4H_2O$ and $Ni(6^-)_2.2H_2O$, have been prepared and characterised [37]. The crystal structure of the former consists of monomeric $[Ni(6^-)_2(DMSO)_2]$ units linked by extensive hydrogen bonding via the uncoordinated water molecules; the cinoxacins bind through one carboxylate oxygen and the exocyclic carbonyl oxygen atom.

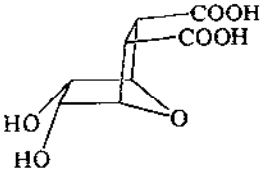


(**6**)

The crystal structure of the complex $[Ni(L)(bpy)(H_2O)_3]$ (H_2L = phthalic acid), obtained by reaction of piperidinium phthalate, bpy and $Ni(ClO_4)_2.6H_2O$ in ethanol, has been obtained. The phthalate dianion is bound *via* a single carboxylate oxygen, *trans* to one of the bpy nitrogens [38]. When $NiCl_2.6H_2O$ was treated with (**7**) (LH_4), partially deprotonated beforehand with Na_2CO_3, a complex $[Ni(LH_2)(H_2O)_3]$ was obtained, the X–Ray crystal structure of which showed LH_2^{2-} coordinated *fac* through two deprotonated carboxylates in positions 2 and 5, and the 1–ether oxygen [39]. The complex, and a mixed Co–Ni complex prepared similarly, decomposed to oxides at very low temperatures. A very similar complex of the ligand (**8**) has also been described; the crystal structure shows the same donor set and geometry [40].

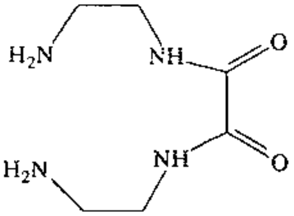


(7)



(8)

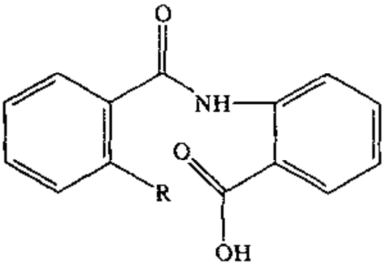
Turning to other simple dicarboxylic acids, a dinuclear nickel(II) complex, [{(acac)(tmen)Ni}$_2$(oxalate)], has been prepared. The crystal structure shows that the molecule is centrosymmetric, with bridging five-membered chelate ring oxalate dianion [41]. There is weak antiferromagnetic interaction between the nickel(II) centres. The crystal structure of *trans*–$K_2[Ni(ox)_2(H_2O)_2].4H_2O$ has been determined. The molecule is centrosymmetric, and isomorphous with the Pd(II) and Pt(II) analogues, although in the latter, the axial water molecules are not coordinated [42]. The design of ferromagnetic complexes attracts much attention from coordination chemists. Reaction of the salt $[Cr(salen)(ox)]^-$ with $NiCl_2.6H_2O$ and 1,4,7,10–tetraazadodecane (L) in $MeOH/H_2O$ affords the oxalate-bridged complex $[(salen)Cr(\mu\text{–}ox)Ni(L)]^+$, isolated as the BPh_4^- salt [43]. This is ferromagnetic, and on the basis of the spin Hamiltonian $H = -2JS_{Cr}.S_{Ni}$, $J = +4.6\ cm^{-1}$. The salt $KCa[Cr(L)_3].6H_2O$ (H_2L = dithiooxalic acid) reacts with the square planar $[Ni(L')](ClO_4)_2$ (L' = *rac*–5,5,7,12,12,14–Me_6–cyclam) (1:3) in $MeOH/H_2O$ to precipitate a red–brown tetrametallic complex, $[Cr(\mu\text{–}L)_3\{Ni(L')\}_3]$ [44]. This complex is also ferromagnetic; $J = +5.9\ cm^{-1}$. The central Cr(III) is coordinated by the six sulfur atoms, and each Ni(II) ion is coordinated by a folded, *cis* macrocycle and the two oxygens of the bridging dithiooxalate ligands. The complex $[Cu(oxamidobis\{N,N'\text{–}propionate\})]^{2-}$ complexes to Ni(II) *via* the exocyclic amido oxygens to afford a dinuclear complex of stoichiometry $NiCu(L)(H_2O)_5.3.5H_2O$, the crystal structure of which reveals discrete NiCu dimers, with the Ni(II) coordinated octahedrally to four water molecules in addition to the amido oxygens [45]. The fifth water is loosely coordinated, axially, to Cu(II). There is strong intramolecular antiferromagnetic coupling.



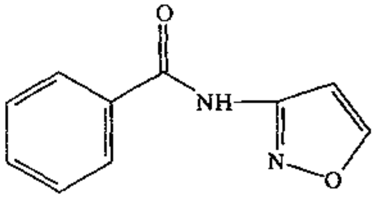
(9)

The complexation behaviour of various sugar acids, for example D–glucoheptanoic, D–gluconic, D–galactonic, D–ribonic, with Ni(II) in water has been studied [46]. Interaction is weak, even at high pH. Chelation of Ni(II) by a terminal carboxyl group oxygen and the neighbouring (deprotonated) sugar –OH group is proposed; the green colour suggests octahedral Ni(II). A

Ni(II)–cyclohexylbutyrate complex has been employed as a modifier for a carbon paste electrode for the electrochemical determination of lipoic acid [47].

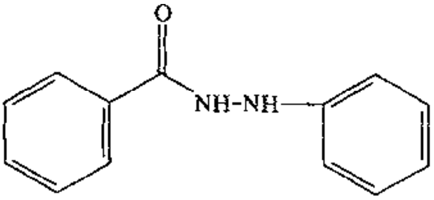


R = –H; **(10a)**
R = –NH$_2$; **(10b)**

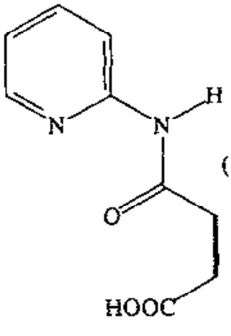


(11)

Several complexes [Cu(oxae)NiL$_2$](ClO$_4$)$_2$.H$_2$O (L = bpy, phen and derivatives) have been described [48]; H$_2$oxae = (**9**). Spectroscopic evidence suggests that the Cu(II) is square planar and the Ni(II) six–coordinate and chelated to the oxamido unit *via* the oxygens. Antiferromagnetic behaviour is observed for two examples. The coordination behaviour of nickel(II) with a range of amide and amide–carboxylic acid ligands (**10**)-(**13**) has been examined [49]. The ligands (**10**) form octahedral [NiL$_2$(H$_2$O)$_2$] (**10a**) and [NiL$_2$] (**10b**) with the ligand probably coordinated through the deprotonated carboxyl group, the amide nitrogen and (**10b**) the aryl–NH$_2$ group. The other ligands coordinate *via* the amide oxygen, based on IR spectroscopic evidence; all complexes isolated were octahedral. The ligands (**13**) (bond in bold represents –CH$_2$CH$_2$– or *o*–C$_6$H$_4$) behaved exclusively as pyridine–(amide oxygen) didentates, and octahedral complexes [NiL$_2$X$_2$] were isolated with a range of Ni(II) salts.



(12)



(13)

Finally, EXAFS has been employed to study the solution structure of divalent transition metal ions, including nickel, in dmf and dma. Unsurprisingly, the data for Ni(II) are best fitted by a [NiL$_6$]$^{2+}$ model, although there is some evidence that the Ni(II)–O bond in [Ni(dma)$_6$]$^{2+}$ is elongated owing to steric crowding [50].

6.3.2.4 β-Diketonato and related ligands.

Some Ni(II) complexes of simple functionalised β–diketonates have been reported [51]. Thin films of nickel have been made by chemical vapour deposition, using [Ni(acac)$_2$] as substrate [52]. Electron ionisation positive ion mass spectra have been reported for Ni(II)–β–diketonates and monothio–β–diketonates [Ni(RC(X)CHC(O)R')$_2$] (X = O,S; R = Ph, 2–thienyl, 5–Me–2–thienyl, 2–naphthyl; R' = $-CF_2H$, $-CF_3$, $-C_2F_5$, n–C_3F_7) [53]. For X = O, the molecular ion $[NiL_2]^+$ is prominent in all cases. Fragmentation is principally by loss of R' radicals, followed by loss of even–electron species affording Ni–containing ions. For X = S, fragmentation of $[NiL_2]^+$ affords mainly L^+, and some of the other fragment ions contain Ni(I). The electronic structure and optical spectra of [M(acac)$_2$] (M = Ni, Pd, Pt) has been the subject of a theoretical study using a semi-empirical approach (INDO/S–SCF–CI) [54]. The markedly different electronic spectra of the Ni(II) and Pd(II) complexes are accounted for by this approach; the increase in covalency from Ni(II) to Pt(II) is clear from the calculated decrease in charge at the metal centre and increase in mixing of metal and ligand orbitals, particularly the highest occupied π_3 ($3b_{2g}$) and d ($8a_g$ and $3b_{2g}$) orbitals. This raises the energies of these with respect to the other occupied frontier orbitals and reduces the HOMO-LUMO separation. The increased separation of the pairs of highest occupied and lowest unoccupied orbitals reduces the configuration interaction, and it is this which affects the appearance of the electronic spectra significantly.

6.3.2.5 Phosphate, silicate and related ligands

There is much current interest in the substitution of transition metals into aluminophosphate structures. A blue Ni(II)–aluminophosphate of formula $0.4NiO{:}0.8Al_2O_3{:}1.0P_2O_5{:}1.5en{:}50H_2O$ has been prepared from $Ni(OAc)_2.4H_2O$, $Al(OiPr)_3$, P_2O_5 and ethylenediamine as template [55]. X–Ray crystallography established that the nickel(II) ions are coordinated to two framework oxygens, a water molecule and two ethylenediamine molecules (one didentate, the other unidentate). Other protonated ethylenediamines are present in the lattice. The nickel(II) ions link aluminophosphate layers. The crystal structure of a layered vanadyl(IV) phosphate, $Ni_{0.5}VOPO_4.2H_2O$, has been independently reported by two groups [56, 57]. Whereas $Ni_{0.5}VOPO_4.1.5H_2O$ (typically the major product of the hydrothermal synthesis employed) is orthorhombic, $Ni_{0.5}VOPO_4.2H_2O$ is tetragonal. The nickel(II) centre is coordinated by two *trans*–V^{IV}=O groups and four water molecules; the Ni(II) ions thus link $VOPO_4^-$ sheets.

A series of diphosphates $AM_3(P_2O_7)_2$ (A = Ca, Sr, Ba; M = Ni) has been made by a hydrothermal method [58]. X–Ray crystallographic data show that the structure consists of infinite chains of edge sharing MO_6 octahedra, connected by P_2O_7 bridges to form a 3-dimensional superstructure with channels parallel to the b axis. Two lamellar Ni(II) oxophosphorus compounds, $Ni(HPO_3).H_2O$ (a) and $NiCl(H_2PO_2).H_2O$ (b), have been prepared, from $NiCl_2.6H_2O$ and H_3PO_3/KOH at 180°C, and from $NiCl_2.6H_2O$ and H_2PO_2 at room temperature, respectively [59]. The structures of both compounds have been solved using the Rietveld powder diffraction method. The structure of (a) consists of *cis*–Ni_2O_8 zig-zag chains of edge-sharing octahedra, interconnected by phosphate bridges. In (b), distorted $NiCl_2O_3(H_2O)$ octahedra are linked into dimers by edge sharing, and the dimers are further connected by Cl^- bridges, giving a layer structure.

The crystal structure of $Sr_2Ni(PO_4)_2$ [60] shows Ni(II) ions occupying two sites with octahedral geometry (average Ni–O 2.08(2) Å) and separated by ≥ 4.8 Å. There are sheets of PO_4^{3-} and Ni^{2+} ions, linked by Ni–O bonds to form tunnels, in which are located eight–coordinate Sr^{2+} ions. The structure of lithium nickel phosphate has been re–examined using the Rietveld powder method. The structure is related to olivine, with hexagonal close–packed oxygen atoms; Li and Ni occupy half the octahedral sites and P, $^1/_8$ of the tetrahedral sites [61]. Moving to a study with a rather different emphasis, the effect of various metal ions, including Ni(II), on the rate of hydrolysis of cyclic and linear condensed phosphate oligomers has been examined [62]. The rate is, it appears, affected by both the degree of complex formation and the nature of the bonding in the complex.

Finally, the global distribution of Co(II) and Ni(II) in the earth's mantle and core are important in constraining models of the chemical evolution of the earth. Until recently, the effect of pressure on the partitioning between these phases had been ignored. The crystal field spectra of doped silicate glasses quenched from high-temperature, high-pressure melts shows that the coordination, and therefore the partitioning, of these elements changes with pressure. Thus, Ni(II) is in a distorted octahedral site at all pressures, but Co(II) changes from tetrahedral to octahedral coordination with increasing pressure [63].

6.4 COMPLEXES WITH SULFUR AND SELENIUM DONOR LIGANDS

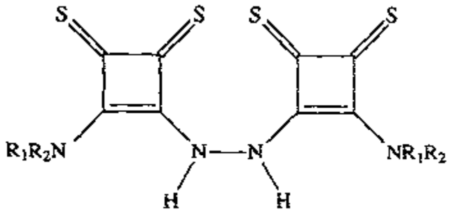
6.4.1 Complexes of alkanethiol and related ligands

There has been a revival of interest lately in toroidal nickel thiolate complexes $[Ni(SR)]_n$ (n = 4,5,6,8). Extended Hückel calculations have been employed to probe structural aspects of these complexes [64]. In the case of 3– and 4–membered rings, where the nickel atoms are displaced out of the toroid, this is attributable to repulsive metal–metal interactions. Sulfur–sulfur interactions do not apparently play an important rôle in determining structure; the dominant effect is maximisation of Ni–S bond strength.

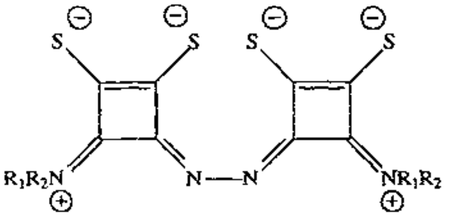
The question of the exact geometry of $[Ni(SR)_4]^{2-}$ complexes is of interest since some Ni–containing metalloenzymes are thought to have sites of this type (where RS^- is cysteinyl), and since Ni(II) substitution is often employed as a way of studying other metalloenzymes with these sites. A crystal structure of a new polymorph of $[NEt_4]_2[Ni(SPh)_4]$ (orthorhombic; Ni–S (average) = 2.296(4) Å) has appeared [65]. The geometry at nickel is tetragonally compressed tetrahedral. A range of structures of the related $[NEt_4]_2[M(2\text{–}PhC_6H_4S)_4].2CH_3CN$ (including M = Ni) has also been published [66]. The complexes all crystallise in space group $I\bar{4}c2$, which imposes S_4 symmetry on the anions; all therefore have tetragonally–compressed geometry, although the compression is greatest for Ni(II), as expected for a d^8 ion.

(13A)

The crystal structures of the compounds $[M(L)_4](BF_4)_2$ (L = **(13A)**; M = Zn, Ni) have been examined [67]. The ligands bind only *via* the sulfur, and the bond lengths in the ligand show that the zwitterion form is a significant contributor to the overall structure. In this case, the Zn(II) complex has almost regular tetrahedral geometry, but the Ni(II) complex is significantly distorted, with *trans*–S–Ni–S angles of *ca.* 85°. The bis(dithiasquareamide) ligands **(14)** have been prepared, and their coordination chemistry with nickel(II) explored [68]. FAB–MS and spectroscopic data support a formulation as square planar $[Ni_2(L^{2-})_2]$, with each nickel(II) centre coordinated to two S^- donors from each ligand; species with mixed *N,S*–donor sets could not be made. In pyridine solution, the complexes are thermochromic, with temperature–dependant axial coordination of pyridine presumably responsible for this.



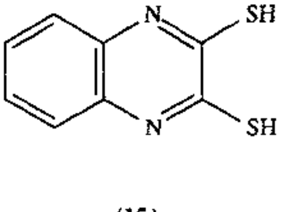
(14)

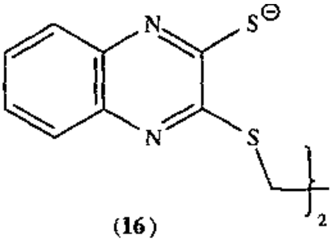


(14a)

The dithioamide ligand quinoxaline–2,3–dithiol H_2L **(15)** reacted with $NiCl_2$ in hot EtOH affording blue–green $[Ni(H_2L)_2]^{2+}$. With RO^-/ROH, this gave red $[Ni(L)_2]^{2-}$ with the ligand *S*-bound as a dithiolate. Treatment of the latter with 1,2–dibromoethane gave a neutral complex [Ni(L')] (H_2L' = **(16)**), and with MeI *trans*–[Ni(L")$_2$] (L" as **(16)** but RSMe, not $RSCH_2CH_2SR$) [69]. Interestingly, both $[Ni(L)_2]^{2-}$ and $[Ni(H_2L)_2]^{2+}$ reportedly undergo reversible one–electron oxidations in CH_3CN at quite similar potentials (+0.12 V and +0.32 V respectively). Although the peak–to–peak separation for the latter was large (180 mV), coulometry confirmed that both complexes were stable in solution, and ESR spectra were consistent with a square planar, $(d_{xy})^1$ Ni(III) formulation for both forms.

The crystal structure of $[Ni(fac\text{–}\{Co(aet)_3\})_2]Cl_2.3H_2O$ (aet = 2–aminoethanethiolate anion) has been reported [70]. The Ni(II) has distorted octahedral coordination, with the six thiolate ligands forming bridges from the two *fac*–$[Co(aet)_3]$ subunits. The average Ni–S distance (2.400(1)Å) is longer than in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (2.238(1) Å), which is square planar at nickel(II).


(15)


(16)

6.4.2 *Metalloenzymes with Ni–thiol sites*

There has been extensive recent interest in the FeNi hydrogenases present in methanogenic archaeobacteria. These usually contain Fe–S clusters, and a single nickel site which if demetallated renders the enzyme inactive. The redox chemistry of the protein is complex. Two oxidised, catalytically inactive forms, A and B, exhibit different rhombic ESR spectra. Under H_2, these signals initially disappear, then are replaced by another rhombic spectrum characteristic of the active enzyme (C). Finally, this too disappears; the fully–reduced enzyme is ESR-silent. These changes have been interpreted in terms of all nickel oxidation states from 0 to IV; considerable controversy surrounds the area, and this continues this year.

An ESR study of a Ni(II)–substituted rubredoxin has been adduced as evidence that the active C form of FeNi hydrogenases (which earlier work suggested is a Ni–H complex) is Ni(III), as is the photolysed C–form (referred to as C^*, which is not a Ni–H complex) [71]. Upon oxidation of the Ni(II)–rubredoxin with ferricyanide, an ESR signal strikingly similar to that of NiFe hydrogenase C^* was observed. On treatment of the Ni(III)–rubredoxin with CN^-, the ESR signal changed to one very similar to that of NiFe hydrogenase C. A resonance Raman study of the complex $[Ni(SPh)_4]^{2-}$, Ni(II)–substituted rubredoxins and Ni(II)–substituted desulforedoxins has been interpreted in terms of tetragonally–elongated NiS_4 cores in the rubredoxins, and a distorted square planar core in the desulforedoxin, with Ni–cysteinate bonding important in all these enzymes [72].

In contrast, two studies employing ESR, electron–nuclear double resonance (ENDOR) and X–Ray absorption (XAS) spectroscopies found no evidence of bond length changes during any of the redox processes referred to above, and concluded that the oxidation state of nickel in FeNi hydrogenases does not change during the catalytic cycle [73]. Further, the XAS results suggested a $NiS_{2\pm1}(N/O)_{3\pm1}$ site, with 5– or 6–coordinate Ni. The photolysis process of the C form of the enzyme has been studied using ENDOR and H/D exchange experiments, and these support the assignment of a Ni-H species to this form [74]. The bond valence sum (BVS) method has been applied to FeNi hydrogenases (and other metalloenzymes), and the theory has been used to check the conclusions of the latter two papers [75]. No inconsistencies with the conclusions could be found ; however, the BVS method cannot be used to test the presence of Ni–H species, which makes the exercise less valuable. It is clear that this field will continue to provoke investigation.

Some FeNi hydrogenases also contain Ni–bound Se (from selenocysteine). An example of a FeNiSe hydrogenase has been studied using ESR spectroscopy. As isolated, the enzyme had a rhombic spectrum. On illumination, this was replaced by a second rhombic spectrum. Hyperfine ^{77}Se coupling to the 'dark' signal was highly anisotropic, but after illumination, the splitting was nearly isotropic. These changes were interpreted as a change from a $(d_{z^2})^1$ state to a $(d_{x^2-y^2})^1$ state on photolysis, the putative H$^-$ binding site being *cis* to the RSe$^-$ ligand [76].

IR Spectroscopy has been employed to study the binding of CO and ^{13}CO (inhibitors of hydrogenase activity) to the nickel site in hydrogenases [7]. Finally, a review of bacterial hydrogenases has been published [78].

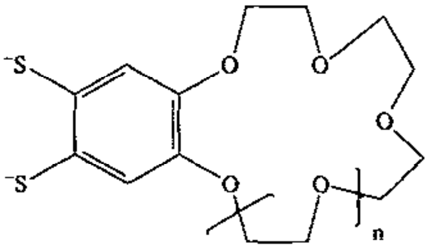
Turning now to Ni–containing CO dehydrogenase (CODH) enzymes, some kinetic evidence has been published which suggests that the oxidation of CO to CO_2 occurs at one site, and the coupled synthesis of acetyl–CoA occurs at a separate site, activated by reduction towards CO binding for acetyl synthesis [79]. It is known that CODH has an $(\alpha\beta)_3$ quaternary structure. Treatment of the protein with phen resulted in removal of *ca.* 0.3 Ni per subunit [80]. Further, the partially demetallated enzyme did not give the ESR signal characteristic of the enzyme active form, nor was it catalytically active. This suggests that the nickel in one subunit is rather different, and may be the active site.

6.4.3 *Xanthate, dithiocarbamate and related ligands*

The complex $[Ni(EtOCS_2)_2]$ has been employed as a diamagnetic host lattice for a Cu(II) complex in ^{1}H and ^{19}F ENDOR studies [81]. Electronic and MCD spectra of $[Ni(EtOCS_2)_2]$ in CH_3CN have been recorded, together with those of the Pd(II) and Pt(II) analogues. The intense bands are assigned to LMCT from S orbitals to the empty $3d_{x^2-y^2}$ orbital. The most intense band is assigned to a $S\sigma \rightarrow 3d_{x^2-y^2}$ transition [82]. An attempt to make mixed *N,S*–donor complexes by treating $[Ni(R_2NCS_2)_2]$ with en failed; either no reaction occurred or $[Ni(en)_3](R_2NCS_2)_2$ was the product [83]. On standing (in air) for several days, solutions of the latter precipitated $[Ni(en)_3](S_2O_3)$. Electrospray mass spectrometry has been used to characterise the products formed when metal–dtc complexes, including $[Ni(R_2NCS_2)_2]$ (R = Et, benzyl) are treated with $NOBF_4$ [84]. Peaks due to $[Ni(R_2NCS_2)_3]^+$ were seen, together with weak peaks due to $[Ni(R_2NCS_2)_2]^+$; however, the intensity of the latter increase with ion source energy, confirming that they are daughter ions. The crystal structure of a mixed ligand complex, $[Ni(^iPr_2NCS_2)(PhC(S)CHC(S)Ph)]$, has been determined. It has no mirror symmetry, and four different Ni–S distances [85].

6.4.4 *1,2-Dithiolene and related ligands*

The second-order hyperpolarisabilities of $[Ni(S_2C_2H_2)_2]^{2-}$, $[Ni(S_2C_2Me_2)_2]^{2-}$ and *trans*–$[Ni\{SC(Me)=C(Me)SMe\}_2]$ have been computed using the coupled Hartree–Fock–perturbed CNDO approach [86]. The results have been compared with those for tetrathiafulvalene (TTF). All the Ni(II) complexes had higher polarisabilities and hyperpolarisabilities than TTF. Also with optical second–order applications in mind, a series of complexes $[Ni\{SC(R^1)=C(R^2)S\}_2]^{2-}$ has been examined, in both CH_2Cl_2 solution and in a polymethylmethacrylate host, using Z–scan and degenerate four–wave mixing methods. The complexes have the advantage that by varying the substituents, the absorption band can be tuned between 770 and 935 nm [87].



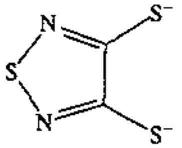
(17) n = 1
(18) n = 2

Crown ether–dithiolene ligands H_2L **(17)** and **(18)** (above) have been synthesised, as have their nickel complexes $[Et_4N][Ni(L)_2]$ [88]. Electrochemistry and spectroscopy indicate that the new ligands are similar to $(1,2\text{-}S_2C_6H_4)^{2-}$, but more electron–rich. IR Spectroelectrochemistry has been used to characterise further the redox chemistry of $[Ni(mnt)_2]^{2-}$ (mnt = *cis*–1,2–dicyanoethylene–1,2–dithiolate dianion) [89]. Although both the redox processes (a) and (b) (below) are reversible on the voltammetric timescale, reversible changes in ν_{CN} were only seen for process (a).

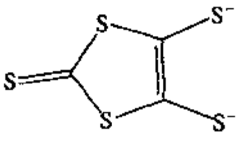
$$[Ni(mnt)_2]^{2-} + e^- \rightleftharpoons [Ni(mnt)_2]^- \quad (a)$$

$$[Ni(mnt)_2]^- + e^- \rightleftharpoons [Ni(mnt)_2] \quad (b)$$

The complex $[Bu_4P][Ni(\mathbf{19})_2]$, synthesised by I_2 oxidation of the dianion, has been structurally characterised [90]. Whereas the dianion is centrosymmetric, planar and monomeric, the monoanion is rendered dimeric by interaction between nickel and a sulfur from a neighbouring molecule (Ni–S = 2.385 Å), giving an approximately square pyramidal geometry. Crystal structures of $[R_4N]_2[Ni(\mathbf{20})_2]$ (R = Et, Bu) have also been published this year [91]. The tetraethylammonium salt had a layer–type structure, in which cation and anion were parallel to the *ab* plane and alternated along the *c* axis. The tetrabutylammonium salt, in contrast, adopted a much looser structure with anions in centrosymmetric sites and cations in holes between the anions.



(19)

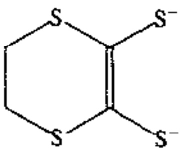


(20)

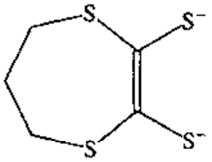
Better orbital overlap and electronic properties may result in improved electrical properties in conducting salts of these anionic complexes. One strategy recently tried has been the use of organometallic cations, and the crystal structure of $[Co(cp)_2][Ni(dmit)_2]$ (dmit = (**20**)) has been published this year [92]. The Ni(II) geometry is planar, with a shuttle shaped D_{2h} conformation. There are sheets of S···S connected anionic stacks, with pairs of cations between them.

Another strategy is to incorporate Se, with its spatially more extended orbitals, into the ligand. Electrochemical oxidation of $[Me_4N][Ni(dmise)_2]$ (dmise = (**20**) with C=S replaced by C=Se) gave a compound α–$[Me_4N][Ni(dmise)_2]_2$. Using $[Bu_4N][Ni(dmise)_2]$ in the presence of excess $[Me_4N][PF_6]$, needles of β–$[Me_4N][Ni(dmise)_2]_2$ also formed. The two structures showed differences in molecular packing; both exhibit many short intermolecular S...S contacts, and the α structure also has some very short Se····Se distances. Both are low bandgap [E_g 0.08 eV (α), 0.05 eV (β)] semiconductors [93].

Complexes $[Ni(L)_2]^{n-}$ (L = (**21**)) are interesting as, unlike the $[dmit]^{2-}$ complexes, they can be electrochemically oxidised, to mixed–valence cationic complexes. The redox chemistry of $[R_4N][Ni(L)_2]$ has been studied using microelectrode techniques [94]. As well as a quasi–reversible one–electron reduction ($E \approx -0.7$ V) and oxidation ($E \approx 0.0$ V), a further irreversible oxidation (Epa $\approx +0.90$ V) was observed, corresponding to the formation of $[Ni(L)_2]_3(BF_4)_2$. The mechanism involves one–electron oxidation to $[Ni(L)_2]^+$ followed by fast chemical processes leading either to formation of the solid mixed valence complex, or to decomposition.



(**21**)



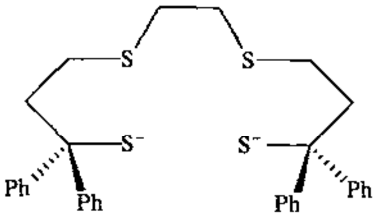
(**22**)

Complexes of the analogous ligand (**22**) have been described this year. The crystal structure of the complex $[Et_4N][Ni(\mathbf{22})_2]$ reveals an unusual packing motif, with double layers of planar anions. The 1,3–propane bridges lie in a chair conformation [95]. Two salts of [Ni(1,2–dithiooxalato–*S,S'*)$_2$]$^{2-}$ have also been reported. The 2–methylpyridinium salt has mixed layers of planar anions and cations held together electrostatically, and there is an extensive N–H···O and CH...O H–bonding, and some π–π cation–anion interaction [96]. The quinolinium salt has layers of planar anions and cations stacked along one axis in an ...ACCACC... sequence apparently dictated by strong π–π interactions [97].

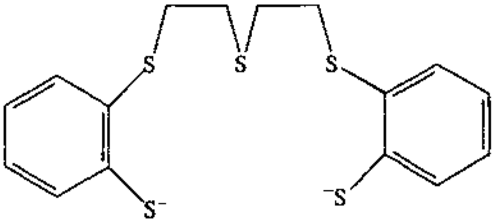
6.4.5 Complexes with mixed R_2S/RS^- donor sets

Nickel complexes of this group of ligands are of interest in biomimetic work. The oxidation of nickel–bound thiolates by dioxygen has been explored for complexes of multidentate ligands including $S(CH_2CH_2S^-)_2$. Reaction of the dithiol with $Ni(OAc)_2$ gave the thiolate–bridged dimer $[Ni(L)]_2$ [98]. Reaction of this with $(Et_4N)CN$ gave planar $Et_4N[Ni(L)(CN)]$, the crystal structure of which showed a highly distorted square planar arrangement, with *trans*– thiolates. The thioether donor lies significantly out of the plane defined by nickel and the other three donor atoms. This complex reacted with dioxygen to give a planar complex of the mixed thiolate–sulfinate ligand $S(CH_2CH_2S^-)(CH_2CH_2SO_2)$. Isotopic labelling studies show that the sulfinate oxygens in each molecule derive mainly from single O_2 molecules.

The ligand H_2L (H_2L = **(23)**) reacted with $Ni(OAc)_2$ in toluene to afford dark violet [Ni(L)], the crystal structure of which shows a distorted square planar arrangement [99]. Cyclic voltammetry shows that [Ni(L)] undergoes one–electron reduction at –1.33 V, which shifts to more positive potentials and becomes irreversible in the presence of CO. This, and IR spectroscopic data, suggest that the Ni(I) complex binds CO. Moreover, the complex is electrocatalytic for CO_2 reduction. Thus, the complex mimics two of the suggested rôles of the nickel site in NiFe CO dehydrogenases.



(23)

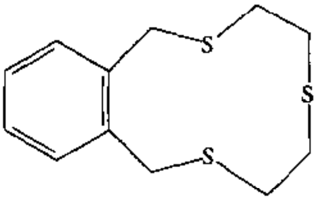


(24)

A nickel–promoted reductive C–S bond cleavage has been reported, which occurs when solutions of the Ni(I) complex of **(24)** are electrogenerated [100]. The product was identified by cyclic voltammetry and spectroscopy as $[Ni(o\text{–}C_6H_4S_2)_2]^{2-}$. ESR and NMR evidence suggests a one–electron mechanism, involving reduction to a formally 19 electron nickel(I) species, $(d_{x^2-y^2})^1 \rightarrow$ S–C σ^* electron transfer and concomitant C–S cleavage, extrusion of $CH_2{=}CH_2$, followed by a further one-electron reduction and extrusion of ethylene sulfide.

6.4.6 *Complexes with thioether and related macrocyclic ligands*

The coordination chemistry of some intermediate–ring trithioether macrocycles has been explored, in the hope that their moderate binding ability might make them useful in membrane–based ion–selective electrodes [101]. The ligand **(25)**, with $[Ni(H_2O)_6](BF_4)_2$ in nitromethane–acetic anhydride, afforded violet octahedral $[Ni(\mathbf{25})_2](BF_4)_2$. The crystal structure shows a distinctly compressed geometry, with the cyclophane units mutually *trans*. The ligand field strength of **(25)** is intermediate between that of [9]-ane-S_3 and [12]-ane-S_3, and comparable with that of other 10–membered ring trithioethers.

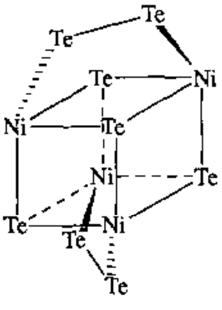


(25)

Some interesting diphosphine-[9]-ane-S_3 mixed ligand complexes of nickel(II) have been described this year [102]. These were synthesised by treatment of $[Ni(L–L)Cl_2]$ (L–L = diphosphine) with [9]-ane-S_3 in the presence of PF_6^-; a common side–product was $[Ni([9]\text{-ane-}S_3)_2]^{2+}$. With dppm, dppe, dmpe and $(cyclo–C_6H_{11})_2PCH_2CH_2P(cyclo–C_6H_{11})_2$, five–coordinate, low–spin $[Ni(L–L)([9]\text{-ane-}S_3)](PF_6)_2$ salts were isolated; the crystal structure of the dppe complex confirmed that the geometry is distorted square based pyramidal. With the tridentate $MeC(CH_2PPh_2)_3$, a five–coordinate complex with a single free phosphine donor atom was isolated (crystallographic evidence). Cyclic voltammetry of the Ni(II) dications in CH_3CN showed a single one–electron chemically reversible reduction at between –0.32 and –0.70 V, and a second irreversible reduction at between –0.86 and –1.48 V. On the basis of ESR spectroscopic evidence, the product of the first process is assigned as pyramidal d^9 Ni(I); superhyperfine coupling shows both phosphines remain coordinated. The product of the second process is probably d^{10} Ni(0) and tetrahedral, with an η^1–bound diphosphine.

6.4.7 *Chalcogenide clusters*

The Fe_4S_4 cluster in ferrodoxin from *pyrococcus furiosus* readily exchanges one Fe for other transition metal ions; a Mössbauer study of the $NiFe_3S_4$ protein, and the cyanide–treated $NiFe_3S_4$ protein, has been reported [103]. In contrast to $ZnFe_3S_4$ which shows a localised Fe^{2+} site ($S = {}^5/_2$), the $NiFe_3S_4$ species ($S = {}^3/_2$) and the CN^--treated complex show the same quadrupole splittings and isomer shifts, although analysis of the magnetic hyperfine data does reveal three distinguishable sites. Isomer shift data suggests some transfer of Fe d–electron density to Ni.



(26)

Some unusual NiTe cluster compounds have been prepared; treatment of $[Ph_4P]_2[Ni(Se_4)_2]$ with $Te{=}PEt_3$ [104] afforded $[Ph_4P]_4[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ (structure as in **(26)**; each Ni–Ni diagonal not bridged by Te_2^{2-} is bridged by Te_3^{2-}, not shown) rather than the hoped-for $[Ni(Te_4)_2]^{2-}$ species. The *formal* oxidation state of nickel in this complex is therefore +4.

6.5 COMPLEXES WITH MIXED N,S–DONOR SETS

6.5.1 Metalloenzymes

Nickel(II)–substituted *pseudomonas aeruginosa* azurin has been studied by 2D ^1H NMR spectroscopy [105]. The binding site consists of two histidine nitrogen atoms and a cysteine-S^- (strongly bound), a glycine carbonyl oxygen and methionine –SMe (weakly bound); NOESY and COSY techniques were used to assign 15 paramagnetically-shifted resonances belonging to these ligands. The variation in the spectra with pH allowed subtle changes in the metal binding site to be probed [106].

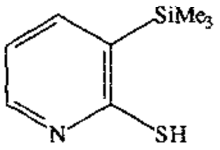
6.5.2 Nitrogen–thiolate and related donor sets

Two complexes of nickel(II) with D– and L–penicillamine (β,β'–dimethylcysteine, $H_2NCH(CMe_2CS^-)COO^-$), have been described [107]. These are $Tl_2[Ni(H_2O)_6][Ni(D\text{–}pen)(L\text{–}pen)]_2.[NiSCN)_2(H_2O)_4]$ (A) made by reaction of $Ni(NO_3)_2.6H_2O$, D,L–penicillamine, KSCN and $TlNO_3$ in water, and $Tl[Ni(D\text{–}Pen)(D\text{–}penH)].H_2O$ (B), made by reaction of $Ni(OAc)_2.4H_2O$, $TlNO_3$ and D–penicillamine in water. The penicillamine complex in (A) is square planar, and the ligands act as thiolate–amine donors; both carboxylate groups are deprotonated but are not coordinated. In (B), the geometry is also *cis*–square planar, with penicillamines acting as amine–thiolate ligands. One protonated and one deprotonated carboxyl group, again not coordinated, are present.

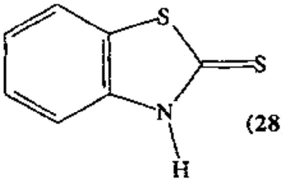
Dark green [Ni(dmit)(piperidine)$_2$] and red $[Bu_4N][Ni(dmit)_2(piperidine)_2]$ ($dmit^{2-}$ = **(20)**) have been prepared by the reaction of $[Bu_4N]_2[Zn(dmit)_2]$ with piperidine and $NiSO_4.6H_2O$ [108]. Since the band at 517 nm seen in the electronic spectrum of the 2:1 complex was absent from the spectrum of the 1:1 complex, this band, previously assigned to an internal dmit transition, has been re–assigned to an inter–dmit transition.

The equilibrium and kinetics of extraction of Ni(II) by 8–mercaptoquinoline in two–phase systems has been examined [109]. Unlike 8–quinolinol, the thia analogue shows considerable interfacial activity, probably associated with the more ready formation of the zwitterionic form.

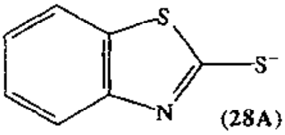
The electro-oxidation of nickel foil in solutions of HL (HL = **(27)**) afforded the complex $[Ni(L)_2]$ [110]. When the electrolyte contained bpy or phen, $[Ni(L)_2(L')]$ (L' = bpy, phen) were obtained. On the basis of spectroscopic data, these are respectively square planar and octahedral, with L^- chelating in the thiolate form. The sacrificial anode method has also been used to prepare complexes of benzothiazole–2–thione HL (HL = **(28)**) [111]. Again, complexes $[Ni(L)_2]$ and $[Ni(L)_2(L')]$ (L' = bpy, phen) were isolated. These were rather insoluble, but magnetic and spectroscopic data suggest that they are planar and octahedral respectively, with the ligand N,S^-–chelating as **(28A)**.



(27)

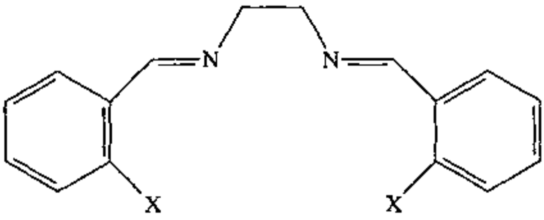


(28)



(28A)

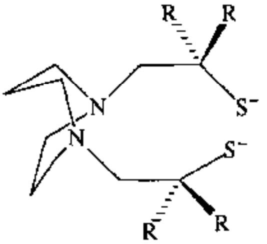
Attempts to mimic the nickel coordination environment in hydrogenases (*q.v.*) has stimulated work on mixed thiolate–amine multidentate donor ligands. On refluxing (**29**) with $NiCl_2.6H_2O$ in EtOH, golden crystals of [Ni(L)] (L = (**30**)) formed [112]. The corresponding dithiolate–diamine *N,N'*–bis(*o*–mercaptobenzyl)ethylenediamine (H_2L'), prepared by Na/NH_3 reduction of (**30**), reacted with $Ni(OAc)_2$ to afford [Ni(L')]. The crystal structures of [Ni(L)] and [Ni(L')] showed the geometry about Ni(II) to be square planar, with similar Ni–S bond lengths, but rather different Ni–N bond lengths (1.85, 1.95 Å respectively). Whereas [Ni(L)] shows a quasi–reversible reduction at −1.36 V, and an irreversible oxidation at $E_p{}^a = +1.00$ V, [Ni(L')] shows no reduction but an irreversible oxidation at $E_p{}^a = +0.59$ V.



X = $-S^tBu$ (**29**)
X = $-S^-$ (**30**)

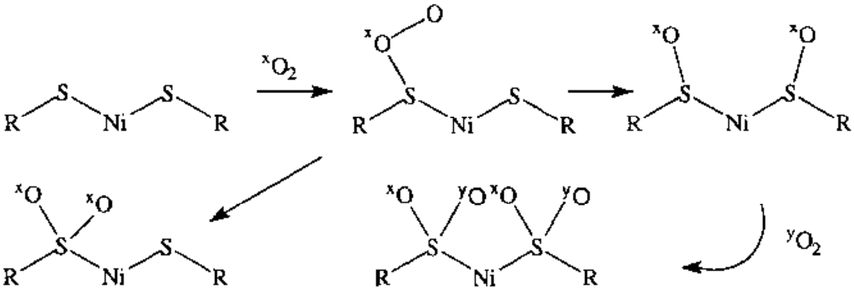
The oxidation of nickel–bound thiolates by dioxygen has been explored for complexes of multidentate ligands including $S(CH_2CH_2S^-)$ (see section 6.4.5) and $RN(CH_2CH_2SH)_2$ (R = CH_3, $MeSCH_2CH_2$, $PhCH_2SCH_2CH_2$, $Ph_2CHCH_2CH_2$, $PhCH_2$; H_2L) [98]. With $Ni(OAc)_2$, these afford thiolate–bridged square planar dimers $[Ni(L)]_2$, which on treatment with $[Et_4N]CN$ gave square planar $[Et_4N][Ni(L)CN]$. In the latter, the thiolate donors are *trans* and the fourth donor atom is the tertiary amine. Upon reaction with dioxygen, one thiolate sulfur is oxidised to the sulfinate, which remains coordinated (*via* sulfur) to Ni(II).

A study of the reaction of [Ni(L)] (L = (**31**)) with labelled dioxygen makes an interesting comparison with the latter work [113]. Interestingly, while this complex reacts with dioxygen to afford a mixture of neutral complexes of the corresponding sulfinate (RSO_2^-)–thiolate and bis–sulfinate ligands, the isolated sulfinate–thiolate complex is totally unreactive to dioxygen (although it does react with H_2O_2). The apparent paradox was resolved using laser desorption ionisation FT ion cyclotron resonance mass spectra of the products of reactions with $^{16}O_2/^{18}O_2$ mixtures, which revealed that the bis–sulfinate forms *via* an intermediate bis–sulfenate, as shown in Scheme 1.



R = –H (**31**)

R = –CH_3 (**32**)

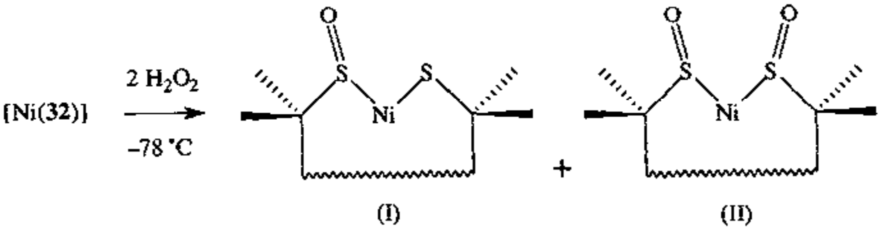


sulfinate–thiolate

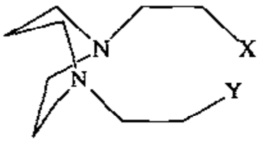
bis–sulfinate

Scheme 1

When Ni(II)–coordinated thiolates react with H_2O_2, sequential single oxygen atom transfer to afford coordinated RSO_2^- has often been postulated to proceed *via* intermediate, unstable nickel–sulfenate (RS(O)–Ni) species. The first examples of such complexes to be isolated and characterised have been described this year [114]. On reaction of [Ni(L)] (L = (**32**)) with two equivalents of H_2O_2 at –78°C, complexes (I) and (II) were isolated. X–Ray crystallography established distances of Ni–SR (2.148(3) Å) and Ni–S(O)R (2.162(3) Å) for (I). That (II) was the bis-sulfenate complex was established by ^1H NMR spectroscopy and a preliminary X–Ray study. Interestingly, at room temperature (I) afforded the sulfinate–thiolate complex when treated with one equivalent of H_2O_2, but at –78°C it gave (II).

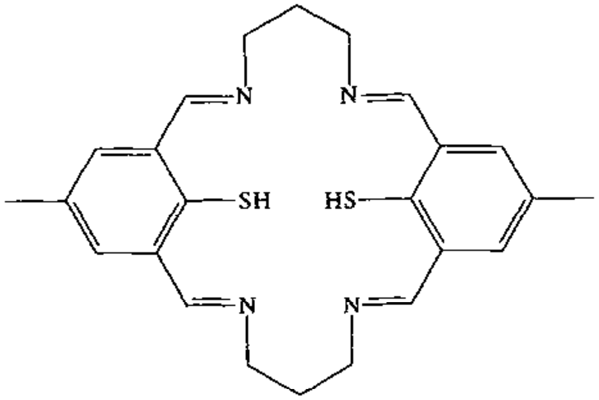


A combined electrochemical and structural study of Ni(II) complexes of the related ligands **(31)** and **(33)**–**(37)** has been published [115]. All complexes are square planar; Ni–S bond lengths vary surprisingly little, from 2.133(3) Å (a Ni–S(O)2R distance) to 2.211(3) Å (a Ni–thioether distance). All complexes show reversible Ni(I)/Ni(II) couples, and the Ni(I) species have been characterised by ESR spectroscopy. In CH_3CN, each substitution of a thioether for a thiolate donor gives a 700 mV positive shift in the Ni(I)/Ni(II) potential, and each substitution of a sulfinate for a thiolate gives a 300 mV positive shift. Thus, the Ni(I) complex of **(37)** is most readily accessed (–0.7 V). Interestingly, complexes of **(36)** and **(37)** exhibit reversible Ni(II)/Ni(III) couples *ca.* 2.0 V positive of the Ni(I)/Ni(II) processes. The ESR spectra of the Ni(III) complexes support a $(d_z2)^1$ geometry, which implies axial solvent coordination, surprising for such a sterically hindered system.



X = –SMe, Y = –S⁻ **(33)** X = Y = –SO_2 **(36)**
X = –SO_2, Y = –S⁻ **(34)** X = Y = –SMe **(37)**
X = –SO_2, Y = –SMe **(35)**

A novel dinucleating imine–thiolate macrocycle complex $[Ni_2(L)](PF_6)_2$ [H_2L = **(38)**] has been synthesised by template condensation of 2,6-diformyl-4-methylbenzenethiol with 1,3-propanediamine in the presence of $Ni(OAc)_2$ and NH_4PF_6 in CH_3CN [116]. The crystal structure

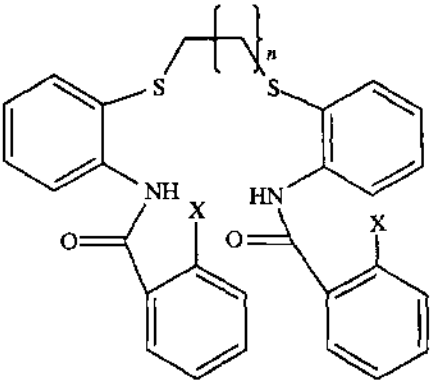


(38)

(of $[Ni_2(L)](PF_6)_2.2dmf$, recrystallised from dmf) shows the complex disposed about an inversion centre; the nickel(II) ions have square planar environments with two bridging thiolate ligands, and the macrocycle is bent to accommodate this. There is additional interaction between each nickel(II) ion and a dmf oxygen atom. The structure is thus different from that of the corresponding imine–phenolate ligand complex, which dimerises to give a tetrameric arrangement of pseudo-octahedral Ni(II) ions (*q.v.*).

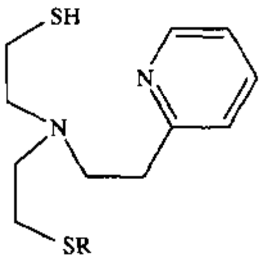
6.5.3 Nitrogen–thiolate–thioether donor sets

When the tetrathioether–bis–amides (**39**) were refluxed with $NiCl_2.6H_2O$ in isobutanol, the complexes [Ni(L)] formed [L = (**39A**)]. The spectroscopic evidence favours an octahedral geometry for these complexes, with four sulfur and two amide nitrogen donor atoms [117].



R = –S^{t}Bu; *n* = 1, 2 (**39**)

R = –S$^-$; *n* = 1, 2 (**39A**)



(**40**)

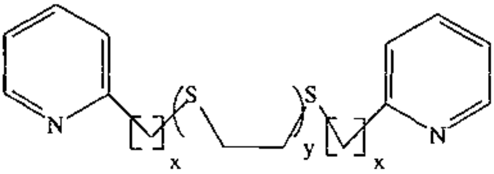
R = Me, Et

The ligands (**40**), with $Ni(ClO_4)_2.6H_20$ in MeOH, afforded black $[Ni_2(L)_2](ClO_4)_2.H_2O$, characterised by crystallography, X–ray Absorption Near–Edge Structure (XANES) and spectroscopic techniques [118]. When R = Me, the electronic spectrum of the complex suggests a pseudo-octahedral geometry. The magnetic data (μ_{eff} = 1.51 BM at room temperature, decreasing to 0.45 BM at 87 K) could not be rationalised simply in terms of antiferromagnetism. The crystal structure at room temperature, moreover, showed two distinct environments, one square planar

($N_2(\mu\text{–}SR)_2$) and the other distorted square pyramidal with a pendant thioether group acting as the fifth donor. The structure of a different crystal at 118 K showed planar environments for both Ni(II) ions. When R = Et, there is evidence for one Ni(II) being high–spin and the other low–spin; the magnetic behaviour varies with temperature in Curie–Weiss fashion.

6.5.4 Nitrogen–thioether donor sets

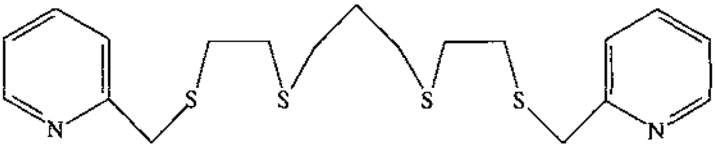
Pyridine–thioether multidentates have attracted some attention this year. The crystal structure of $[Ni(L)(NO_3)(H_2O)](NO_3)$ (L = (**41**)) shows pseudo-octahedral geometry, with the pyridyl donors mutually *trans* and the thioethers *cis* [119]. The Ni(II)–thioether bonds are quite long (2.453(1) and 2.411(1) Å), and hydrogen bonds link the two nitrate ions and the water molecule. Reaction of (**41**) with $Ni(ClO_4)_2.6H_20$ in EtOH afforded $[Ni(L)(H_2O)_2](ClO_4)_2$, which also has *trans*–disposed pyridine and *cis* thioether donors (Ni–S = 2.4073(8) and 2.4038(8) Å); H–bonds again link the perchlorate ions and the water ligands [120].



x = 2, y = 1 (**41**) x = y = 2 (**43**)

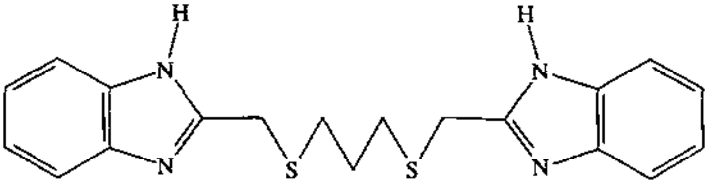
x = 1, y = 2 (**42**) x = 2, y = 3 (**44**)

A related series of ligands (**42**)–(**45**) has been prepared, and their coordination behaviour with $NiX_2.6H_20$ (X = ClO_4–, BF_4^-) examined [121]. All the ligands gave pseudo-octahedral monomeric complexes, with solvent molecules completing the coordination sphere where required. Crystals of all but the complex of (**45**) were obtained. For $[Ni(\mathbf{41})(CH_3CN)_2](ClO_4)_2$, the pyridine ligands are *trans*, but in $[Ni(\mathbf{43})(H_2O)](ClO_4)_2.CH_3OH$ and $[Ni(\mathbf{44})](ClO_4)_2$ they are *cis*. The solvent molecules are weakly bound in $[Ni(\mathbf{41})(CH_3CN)_2](ClO_4)_2$. All complexes showed poorly–reversible Ni(I)/Ni(II) couples at –0.6 – –0.8 V in acetonitrile.



(**45**)

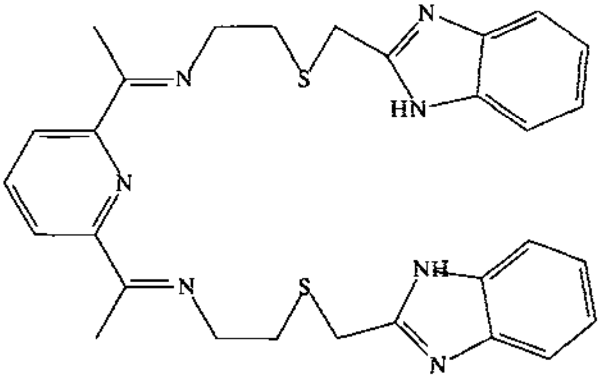
With $NiCl_2.6H_2O$ in EtOH, (**46**) forms $[Ni(L)(\mu\text{-}Cl)]_2Cl_2.5H_2O.2EtOH$. However, with $NiBr_2.3H_2O$ in EtOH/Bu^{t}OH, the product is $[Ni(L)Br_2].EtOH.0.5^tBuOH$ [122]. Both have been characterised crystallographically. They have pseudo-octahedral geometry, with *cis* halide ligands (bridging in the chloride), *trans* nitrogens and *cis* thioether coordination.



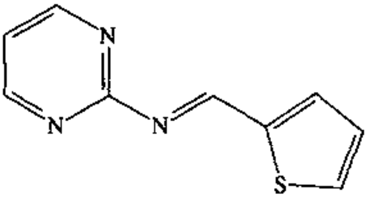
(46)

The nitrate and perchlorate salts were also prepared, and IR spectroscopy suggested a monodentate O–bound nitrate ligand, but no perchlorate coordination.

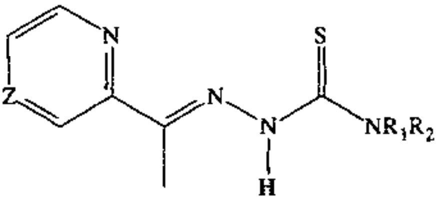
Attempts to make dinuclear nickel complexes with bridging benzimidazole ligands using the sacrificial anode method, and the potential compartmental ligand H_2L (**47**), have been described [123]. The insoluble complex [Ni(L)].4.5H_2O was isolated; IR spectroscopic evidence suggested that the ligand may be coordinating only *via* the five nitrogen donor sites.



(**47**)



(48)

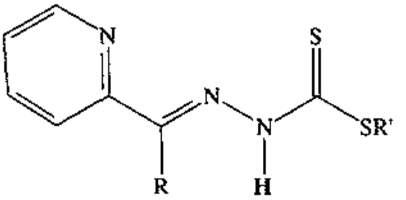


(49)

The complex [Ni(**48**)$_2$]Cl$_2$ has been reported. The ligand has bacteriocidal properties; these are greater, *in vitro*, for the complex [124]. On the basis of IR spectroscopic data, it is suggested that the complex is octahedral, and that the thiophene sulfur atoms are therefore coordinated.

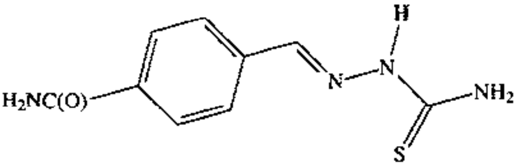
6.5.5 *Thiosemicarbazone and related ligands*

There is still extensive interest in thiosemicarbazones and related ligands, and their nickel complexes, partly stimulated by the question of whether complexation improves the bacteriocidal and, more importantly, the fungicidal properties these ligands exhibit. The structure of the complex [Ni(L)$_2$] (HL = (**49**): Z = N; R_1 = R_2 = Me) shows that a *mer* arrangement of ligands, with *cis* pyrazine and thiolate donors and *trans* imine donors, is favoured (the proton shown in bold is lost on complex formation). The complex is less fungicidal than the free ligand [125]. It has been shown that with more sterically demanding groups R_1 and R_2, the fungitoxicity of the free ligands HL increases. With NiX$_2$ in hot EtOH, complexes [Ni(L)X] (X = Cl, Br; Z = CH; R_1, R_2 = $(CH_2)_5$, $(CH_2)_6$) can be obtained [126], which have comparable fungitoxicity to the free ligands. Crystal structures of three examples have been obtained (X = Br; Z = CH; R_1, R_2 = $(CH_2)_6$ [126], X = Cl; Z = N; R_1 = H, R_2 = Me and R_1 = R_2 = Me [127]). All show square planar geometry, with the halide *trans* to the hydrazine nitrogen donor. Nickel(II) complexes of the related ligands HL (HL = (**50**)) have also been isolated. With one equivalent of ligand, square planar complexes [Ni(L)X] form. With two equivalents, complexes [Ni(L)$_2$] form, which are octahedral [128], with pyridine, hydrazino–*N* and thiolate donor atoms.



R = Me, Ph; R' = Me, CH$_2$Ph

(**50**)

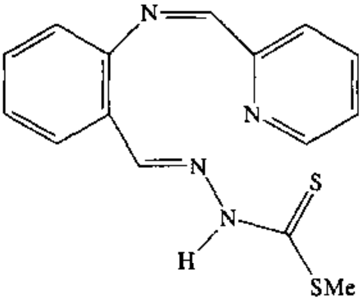


(**51**)

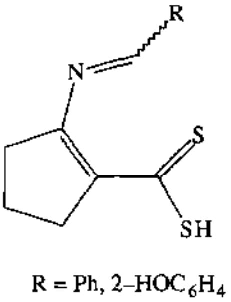
The bacteriocide HL [HL = (**51**)] forms octahedral complexes [Ni(HL)$_2$X$_2$] (X = Cl, Br, NO$_3$, NCS), with the ligand coordinated through hydrazine–*N* and carbothioamide–*S* donors. In the presence of aqueous NH$_3$, square planar [Ni(L)$_2$], with the ligand bound in the deprotonated (thiolate) form, could be isolated [129].

The effect of attaching extra potential donor sites in related thiosemicarbazones HL (HL = (**49**); Z = CH; R_1 = H, R_2 = $-CH_2$(2–pyridyl) or $-CH_2CH_2$(2–pyridyl); R_1 = Me, R_2 =

CH_2CH_2(2–pyridyl)) on their coordination chemistry with Ni(II) has been studied [130]. Complexes of stoichiometry [Ni(HL)X_2] were isolated. Although these have low conductivities in dmf, they are diamagnetic, suggesting that they are planar; IR spectroscopic data suggest thione–*S* coordination, but the additional pyridine ring is apparently not coordinated.



(52)

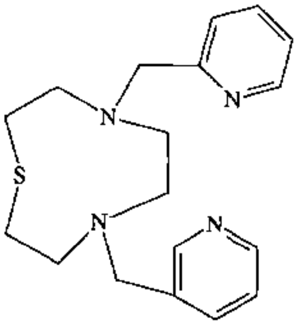


(53)

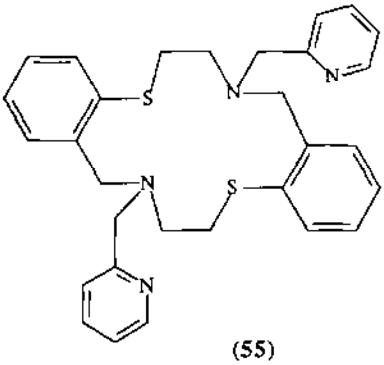
With the ligand HL (**52**), five–coordinate, paramagnetic [Ni(L)X] (X = Cl, NCS) and square planar, diamagnetic [Ni(L)]X (X = I, NO_3) were isolated; these were less fungitoxic than the free ligand [131]. With the ligands (**53**), $NiCl_2.6H_2O$ in refluxing acetone afford square planar $[Ni(L)_2]$, with the ligands in both cases acting as *N*, S^-–donors.

6.5.6 Macrocyclic N,S–donor ligands

Pendant arm macrocyclic ligands continue to attract interest. Whereas with Pd(II) and Pt(II), the ligand (**54**) forms square pyramidal $[M(L)]^{2+}$ (with the thioether in the apical site) with Ni(II) octahedral $[Ni(L)(H_2O)]^{2+}$ is obtained. This has *cis* pyridines, *cis* secondary amines and the thioether *trans* to a pyridine donor [132]. With $Ni(ClO_4)_2.6H_2O$ in MeOH, (**54**) gave distorted octahedral $[Ni(L)](ClO_4)_2$. The pendant 2–pyridyl groups are mutually *cis*, so that the macrocyclic ring is distorted, and the Ni(II) lies outside the cavity [133]. Although Ni–N bond lengths and

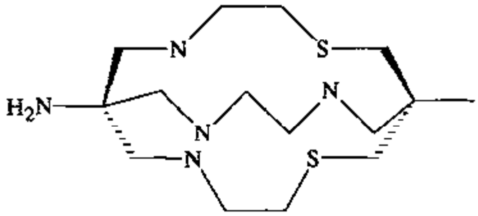


(54)



(55)

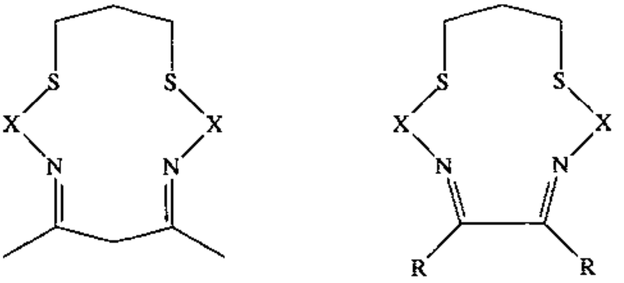
chelate ring angles suggest that Ni(II)–pyridine coordination is not optimal, electronic spectra suggest that the pendant arms remain coordinated down to low pH values in aqueous solution, whereupon the complex completely decomposes.



(Hydrogens of secondary amines omitted for clarity)

(56)

The Ni(II) complex of the encapsulating ligand (**56**) has been studied [134]. It is pseudo-octahedral, with Ni–N bond lengths closely similar to those in related hexaamine cage ligands, and quite short Ni–S bonds (2.398(5) Å). Detailed analysis of the single crystal electronic spectrum (obtained at 10 K and room temperature) is discussed in terms of the differential nephelauxetic effect, and the greater covalency of the Ni–S interaction for these mixed amine–thioether ligands. The synthesis and spectroscopic characterisation of a series of Ni(II) complexes of the macrocycles (**57**) has been reported [135]. These were made by template synthesis from the appropriate amine–thiol and dicarbonyl compound, 1,3–dibromopropane, and the Ni(II) salt in MeOH. They are diamagnetic and square planar.



X = -CH$_2$CH$_2$-, o–C$_6$H$_4$

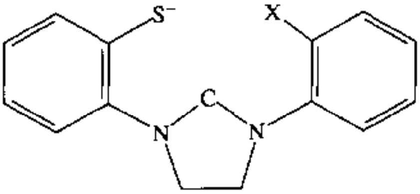
X = -CH$_2$CH$_2$-, R = H, Me, Ph

(57) X = o–C$_6$H$_4$, R = H, Me

6.6 COMPLEXES WITH MIXED C,S–, O,S– AND O,N,S–DONOR SETS

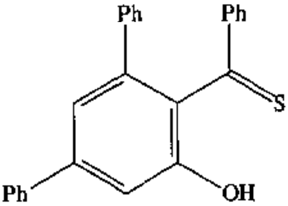
The reaction of [Ni(L)] (H$_2$L = *N,N'*–bis(2–mercaptophenyl)ethylenediamine) with CO, in biomimetic work aimed at modelling Ni CO dehydrogenases, unexpectedly gave the extraordinarily stable carbene complex [Ni(**58**)$_2$] [136]. Each Ni is coordinated to one non–bridged and two bridging thiolate donors and the carbene carbon, in a square planar arrangement. The reactions of this complex with donor ligands, H$^-$ and CH$_3^-$ reagents have been examined. With L (pyridine, PMe$_3$, PPh$_3$), or Et$_4$NCN, the thiolate bridge is cleaved to give [Ni(**58**)L] or Et$_4$N[Ni(**58**)(CN)].

The products of reaction with CO, and with $LiCH_3$, could not be characterised. With $LiBEt_3H$, an unexpected reaction to give [Ni(**59**)$_2$] and other products occurred, but [Ni(**58**)$_2$] was unaffected by concentrated aqueous HCl.



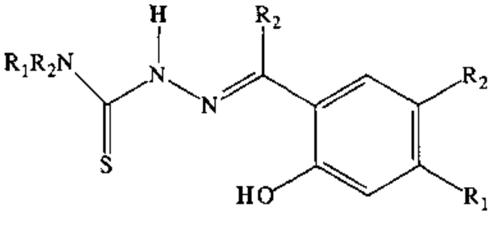
X = S⁻ (**58**)
X = H (**59**)

The ligand HL (**60**) reacts with $Ni(OAc)_2$ in the presence of base to afford a distorted square planar complex *cis*–[Ni(L)$_2$], with the ligand coordinated *via* the thione and the phenolate-oxygen donor [137].



(**60**)

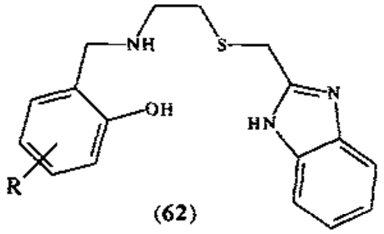
With the marked tendency for thiolates to act as bridging ligands in nickel chemistry, in the absence of steric effects, it is rather surprising that the ligands H_2L (**61**) react with $Ni(OAc)_2$ to afford dimeric, square planar [Ni(L)]$_2$ with hydrazino–*N*, bridging phenolate and non–bridging thiolate donors [138]. The reason may be the unusually low basicity of the S-lone pair *anti* to the C=N group, which would have to be donated to the second metal in a thiolate bridged form.



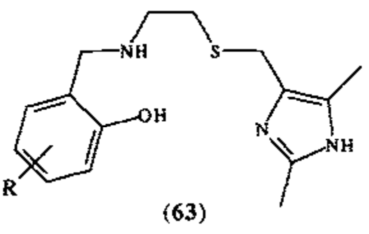
R_1 = H, R_2,R_3 = Me
R_1,R_2 = Me, R_3 = H
R_1,R_2,R_3 = H
(H's in **bold** lost on complexation)

(**61**)

The sacrificial anode technique has been employed to synthesise square planar, insoluble [Ni(L)$_2$] (HL = 1–hydroxypyridine–2–thione) [139]. With bpy or phen (L') in the electrolyte medium, octahedral [Ni(L)$_2$(L')] were the products. The formation of thione–amine oxide complexes with this ligand contrasts with earlier studies with pyridine–2–thione, which chelates as a pyridine–thiolate. Similarly, electro-oxidation of Ni metal in a solution of H_2L [H_2L = (62), (63)] gave insoluble complexes analysing as [Ni(L)]; these were assigned tetrahedral geometries on the basis of diffuse reflectance spectra [140].



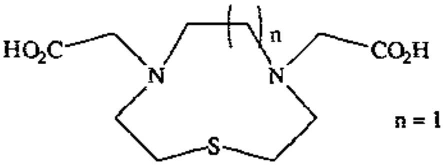
(62)



(63)

R = 4,6–OMe, 3–OEt, all–H

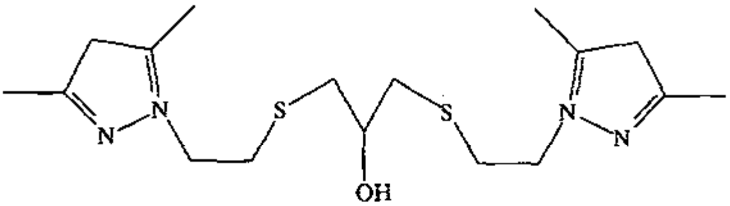
Stability constants for the formation of Ni(II) complexes with (64) in aqueous solution have been measured [141]. Complex formation with both ligands was stronger than with *N,N'*–dimethyl–*N,N'*–diacetic acid, in spite of the relatively weak interaction of hard Ni(II) with the lone thioether donor.



n = 1, 2

(64)

The stability constants for complex formation between Ni(II) and cysteine, D–penicillamine ($H_2NCH(CMe_2SH)COOH$, used as a therapeutic agent in Ni poisoning cases) or cysteic acid (primary ligands A) and his, histamine (hist) or imH (secondary ligands B) have been examined [142]. As well as binary complexes NiA and NiB, ternary complexes $NiABH_2$, NiABH, NiAB and $NiAB_2$ formed (the degree of protonation depending on pH). In these species, the imH, Hist and his secondary ligands are respectively mono–, di– and terdentate. For NiABH, the primary ligand was the site of protonation. (A = cysteine; B = any. A = penicillamine; B = imidazoleH). The primary ligand coordinates as an amine-thiolate, except cysteic acid, which binds like glycine.

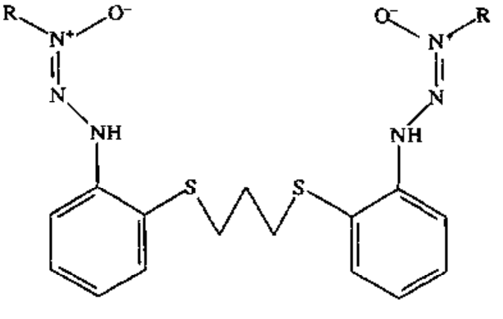


(65)

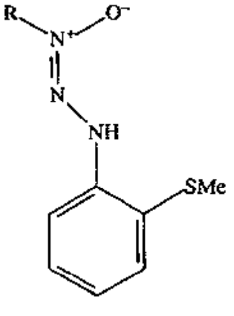
The reaction of $NiCl_2$ in EtOH with the ligand HL (65) afforded a dark green complex of formula $[Ni_3(L)(EtOH)Cl_5].3EtOH$. In acetonitrile, the product was $[Ni_2(L)Cl_3].MeCN$ [143].

X–Ray crystallography revealed that in the trinuclear complex, all 3 Ni atoms are bridged by the alkoxide group, and form an equilateral triangle. One chloride is μ_3, three bridge edges of the triangle, and one is terminal. Two Ni ions are almost equivalent, and have $NS(\mu_3–O)(\mu_2–Cl)_2(\mu_3–Cl)$ donor sets. The remaining Ni is coordinated in a $(\mu_3–Cl)(\mu_2–Cl)_2Cl(\mu_3–O)(EtOH)$ set. The dinuclear complex has both Ni(II) ions in a five–coordinate $NS(\mu_2–O)(\mu_2–Cl)Cl$ environment. With $NiBr_2$, only the corresponding dimeric complex could be isolated, presumably for steric reasons.

The thiosemicarbazones of methyl and ethyl acetoacetate (HL), with $Ni(OAc)_2$ in MeOH, afforded $[Ni(HL)_2]$, which spectroscopic data suggested were octahedral, presumably therefore with (thione S, hydrazino N, carbonyl $O)_2$ donor sets [144]. The ligands H_2L (**66**) (R = H, Me) form complexes [Ni(L)] [145]. With R = Me, X–ray crystallography revealed $Ni(N^-)_2O_2S_2$ coordination. The Ni–S bonds were very long (2.494(4), 2.526(3) Å), and this is probably responsible for the particularly large splitting observed in the υ_1 and υ_2 bands in the electronic spectra. The CV shows a single oxidative process at + 0.75 V, and this is assigned to Ni(II)/Ni(III) since the ESR spectrum of the electrogenerated product is consistent with a Ni(III), $(d_{z^2})^1$ ion. With HL (**67**), similar complexes $[Ni(L)_2]$ were obtained, with even longer Ni–S bonds (2.519(2), 2.549(2) Å). These could also be electro-oxidised (E + 0.74 V) to transient Ni(III) $(d_{z^2})^1$ species [146].



(66)



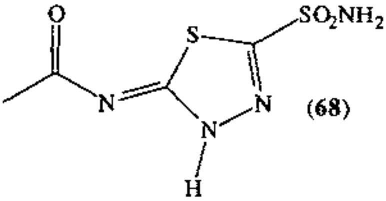
(67)

6.7 COMPLEXES WITH NON-MACROCYCLIC NITROGEN DONOR LIGANDS

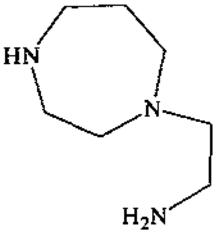
6.7.1 Complexes of monodentate amine and related ligands

The pharmacologically active methazolamide HL (**68**) acts as a monodentate, binding through the deprotonated sulfonamide N in *trans*–$[Ni(L)_2(NH_3)_4]$ [147].

The first square planar Ni(II) complex with an ammine ligand has been described this year. When the pseudo-octahedral $[Ni(\textbf{69})(H_2O)_3](ClO_4)_2$ reacts with aqueous ammonia, the product is planar, diamagnetic $[Ni(\textbf{69})(NH_3)]$ [148]. The binding constant log K was 3.3±0.1; interestingly, the Ni–N bond lengths were very similar (Ni–NH_3 1.913(5) Å). The crystal structure of *trans*–$[Ni(NCS)_2(NH_3)_4]$ has been re–determined (Ni–NCS = 2.079(3) Å, Ni–NH_3 = 2.103(2) Å) [149].



(68)

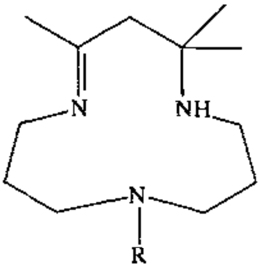


(69)

6.7.2 *Complexes of di– and multidentate amines and related ligands*

Bromine oxidation of $[Ni(en)_2Br_2]$ affords $[Ni^{III}(en)_2Br_2]Br$, whereas with $[Ni(R,R'–1,2–(H_2N)_2C_6H_{10})_2Br_2]$, the product is an unusual 1–dimensional Ni(III) complex $\{Ni(L)_2Br\}_nBr_{2n}$. The crystal structure of $[Ni(en)_2Br_2]Br$ has now been reported [150]. The cation is centrosymmetric, with the long Ni–Br bond (2.635(1) Å) expected for this d^7 $(d_{z^2})^1$ complex. The Ni–N bonds shorten considerably on oxidation. Since both Ni(II) complexes, in MeOH solution, exhibit virtually identical CVs, it is proposed that the different solid state structures for the two complexes are caused purely by strong NH...Br...HN bonding in the 1–D complex.

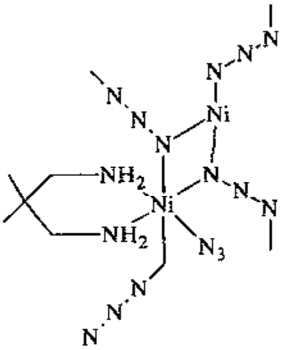
The oxidation of $[Ni(L)]^{2+}$ by $[S_2O_8]^{2-}$ has been investigated, and the crystal structure of the Ni(II) complex reported (L = $CH_3C(CH_2NHCH_2CH_2NH_2)_3$) [151]. Compared with analogous sarcophogane ligands, the Ni(II) complex of L is less rigidly symmetric, showing some tetragonal distortion. ESR and electronic spectroscopies have been used to investigate the formation of $[Ni(L)]^{3+}$ and its decay, apparently to axial $[Ni(L)X_2]^+$ complexes with coordinated sulfate ions.



a: R = H

b: R = Me

(70)



(71)

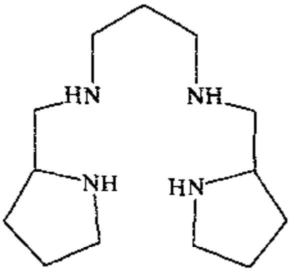
With the aim of establishing magnetostructural correlations, a variety of azide–bridged Ni(II)–amine complexes has been made and characterised crystallographically. The dimeric complexes $(\mu_{1,3}\text{–}N_3)_2[Ni(L\text{–}L)_2]X_2$ (L–L = en, 1,2–propanediamine, X = PF_6; L–L = 1,3–propanediamine, X = BPh_4) have been isolated by reaction of nickel nitrate, the diamine, NaN_3 and NaX in water. The crystal structure of the en and 1,3–propanediamine complexes have been determined. These have *cis*–, end–to–end bridging azide ligands, and are antiferromagnetic; extended Hückel calculations indicate that the smaller the dihedral angle between the N–Ni–N plane and the plane formed by the two N_3^- bridging ligands, the stronger is the antiferromagnetism. Thus, for the en complex this angle is 45° and $J = -4.6$ cm^{-1}, whereas for the 1,3–propanediamine complex, it is 3° and $J = -114.5$ cm^{-1} [152]. The reaction between *N,N'*–bis(2–aminoethyl)–1,3–propanediamine (2,3,2–tet), $Ni(ClO_4)_2.6H_2O$ and NaN_3 in water afforded two products as separable crystals. One, the dimeric $(\mu\text{–}N_3)_2[Ni(2,3,2\text{–tet})]_2(ClO_4)_2$, had end–on bridging azide ions and was strongly ferromagnetic ($J = +33.8$ cm^{-1}) [153]. The other, *catena*–$(\mu\text{–}N_3)[Ni(2,3,2\text{–tet})](ClO_4)$, had a polymeric zig–zag structure with end–to–end azide bridges, and was antiferromagnetic ($J = -26.9$ cm^{-1}) [154]. With *N,N'*–bis(3–aminopropyl)–1,2–ethanediamine (3,2,3–tet), only the polymeric antiferromagnetic complex could be isolated. Although macrocyclic ligands are dealt with later, mention is appropriate here of complexes of (**70**). By making five–coordinate ferromagnetic complexes $(\mu\text{–}N_3)_2[Ni(L)]_2(ClO_4)_2$, with end–on azide bridges, [L = (**70**)], it was hoped that stronger Ni–N_3 bonds would result, giving a larger interaction [153]. This was realised for (**70a**) ($J = +43.9$ cm^{-1}) but not for (**70b**), which gave antiferromagnetic $(\mu\text{–}N_3)_2[Ni(L)]_2(ClO_4)_2.H_2O$ ($J = -84.4$ cm^{-1}). However, crystal structure data could not be obtained for the latter. A particularly unusual complex was obtained using the ligand 2,2–dimethyl–1,3–diaminopropane (L). This gave a 2–D layer structure, where each Ni was coordinated to a didentate amine, a terminal azide ligand, and to three azide bridges [see (**71**)] [155]. The behaviour of the magnetic moment as a function of temperature showed a discontinuity at *ca.* 60 K, perhaps indicative of a solid–state structural change.

There is increasing interest in amphiphilic metal complexes. Nickel(II) complexes of 6–R–2,3,2–tet (L) (and also of 2–R–1,3–propanediaminetetraacetic acid, H_4L') have been prepared (R = *n*–decyl or *n*–dodecyl) [156]. The electronic spectra of the complexes $[NiCl_2(L)]$ (and $[Ni(H_2L')(H_2O)]$) in water did not differ from the spectra recorded in MeOH, suggesting that micelle formation did not affect the coordination environment (dissociation to planar, yellow $[Ni(L)]^{2+}$ occurred). However, $CHCl_3$ solutions were violet. Surface tension measurements are reported. Nickel(II) complexes of *N,N'*–dimethyl–*N'*–R–1,2–ethanediamine in water showed activity for the stereospecific epimerisation of aldoses only when R ≥ octyl, suggesting that catalysis only occurred in the micelle environment [157].

Zerovalent complexes of nickel with tmen catalyse the electroreduction of CO_2, and also its catalytic activation by incorporation into organics, for example in cyclo-oligomerisation of alkynes to give unsaturated cyclic esters. Competing reactions include reductive disproportionation giving CO and $[Ni(tmen)(CO_3)]$. Two other products have now been isolated from the reaction with $EtC{\equiv}CEt$, and crystallographically characterised [158]. One is an organometallic complex of Ni(II) with diethylmaleic anhydride. The other is $[Ni_3(tmen)_3(\mu_2\text{–}CO_3)_2(\mu_2\text{–}O_2CC(Et)C(Et)CO_2]$. This has a cyclic structure. One of the Ni(II) ions has a chelating tmen ligand, and has two bridging didentate CO_3^{2-} ions linking it to the other Ni(II) ions. A second Ni(II) has a chelating tmen ligand and is linked to the first Ni(II) *via* a $[CO_3]^{2-}$ ion, but to the third Ni(II) *via* the bridging carboxyl group. The third Ni(II) ion also has a chelating tmen ligand and is coordinated to both carboxyl groups of the $O_2CC(Et)C(Et)CO_2$ moiety, and to the bridging CO_3^{2-} linking it to the first Ni(II) ion. On treatment of [Ni(acac)(tmen)]BPh_4 with oxamide and KOH in $MeOH/H_2O/CH_3CN$, followed by recrystallisation from MeOH, crystals were obtained which X–ray crystallography revealed to be co-crystallised [(acac)(tmen)Ni(μ–CO_3)Ni(tmen)(acac)] and [Ni(acac)(tmen)(H_2O)(CH_3OH)]BPh_4 (one molecule of each per unit cell) [159]. Complexes [Ni(dike)(tmen)]$^+$ (dike = β–diketonate) are solvatochromic owing to equilibria with 6–coordinate species in polar solvents. The five–coordinate analogues [Ni(dike)(L)]BPh_4 (dike = acac, benzoylacetonate; L = *N,N,N',N'',N''*–pentamethyl-diethylenetriamine) have been characterised, and their interaction with solvent molecules studied [160]. The complexes are five–coordinate and high–spin, in contrast to [Ni(dike)(tmen)]$^+$ which are square planar. The equilibrium constants for coordination of solvent molecules in a range of solvents have been measured.

Dinuclear complexes [Ni_2(dike)$_4$(hmtt)] (hmtt is *N,N,N',N'',N''',N'''*–hexamethyl-triethylenetetramine) have been described [161]. Attempts to isolate mononuclear complexes failed, except in the case where dike = dipivaloylmethanoate, where [Ni(dike)(hmtt)]$^+$ was isolated.

The square planar complex [Ni(*S,S*–L)]$^{2+}$ [*S,S*–L = (72)] shows diastereoselectivity in binding racemic amino acids, and the determination of stability constants has been demonstrated to provide a quick method of elucidating the chiral recognition process [162]. Molecular mechanics calculations to shed more light on this were aided by a crystal structure determination of the complex, which is also reported.



(72)

Two crystal structures, of [Ni(2,5,9,13,16–pentaazaheptadecane)($OClO_3$)]ClO_4 (distorted octahedral) [163] and *cis*–[Ni(tren)Cl(H_2O)]Cl [164] (also distorted octahedral) have been reported. The latter has been used to bind nucleobases in DNA. The interaction of the series of methyl–terminated long–chain multidentate polyazaalkanes from 1,14–bis(methylamino)-3,6,9,12–tetraazatetradecane to 1,23–bis(methylamino)3,6,9,12,15,18,21–heptaazatricosane with Ni(II) ions in aqueous solution has been studied [165]. All form mononuclear NiL^{2+} species. The two longest–chain ligands also form dinuclear Ni_2L^{4+} species. Only for 1,3,6,9,12,15–hexaaza–cyclooctadecane was there evidence of a significant macrocyclic effect with respect to its linear polyaza-analogue on complexation with Ni(II).

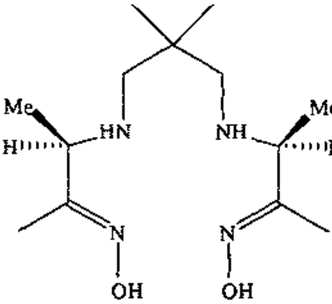
Complexes of en, diethylenetriamine and tien accelerate the rate of hydrolysis of amino acid esters by 10 – to 30 – fold compared with Ni(II) ions alone [166]. Scaled particle theory has been used to estimate partial molar volumes at infinite dilution for $[NiL_n]^{x+}$ (L = NH_3, n = 6; L = en, 1,3–

propanediamine, cyclohexane–1,2–diamine, bpy, phen, n = 3; x = 2,3). As the oxidation state increases, the partial molar volumes at infinite dilution decrease by up to 25 cm^3 mol^{-1} [167].

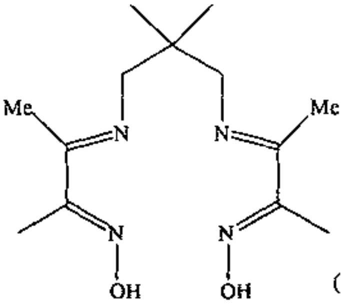
Finally, a combination of molecular mechanics and angular overlap model calculations has been applied to predict d–d spectra for first–row transition metal ions with amine ligands [168]. In the absence of significant spin–orbit coupling and π–bonding, this simple approach predicts σ–donor strength and the electronic spectra well.

6.7.3 *Imines, oximes and related ligands*

Complexes of Ni(II) with dimethylglyoxime have been tested in a silverless photographic process [169]. When the ligand H_2L (**73**) reacts with $Ni(ClO_4)_2.6H_2O$ in MeOH, $[Ni(HL)]ClO_4$ precipitates. There is a very strong intramolecular H–bond C=N–O–H...O$^-$–N=C in the complex cation [170]. The latter is also found in the complex $[Ni(HL')]ClO_4$ [H_2L' = (**74**)], the crystal structure of which shows square planar Ni(II), with quite similar Ni–N bond distances (1.867(3) Å (HL), 1.886(3) Å (HL') respectively) [171].



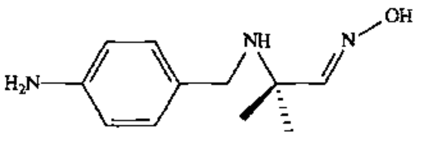
(73)



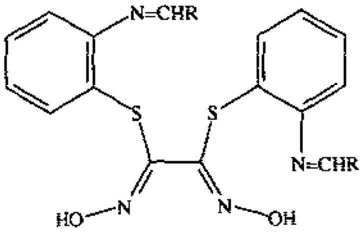
(74)

Metal complexes of suitably functionalised amine–oxime mixed donor ligands have been proposed as agents for radiotherapy. The synthesis and X–ray structure of the complex, $[Ni(L)(HL)]ClO_4$, of one such ligand [HL = (**75**)] has been reported. The geometry is distorted square planar, with the Ni(II) coordinated to the aliphatic amines and oxime nitrogens [172]. Some crown ether–functionalised *vic*–dioximes H_2L (**76**) have been synthesised and their coordination behaviour with Ni(II) examined. Binding to the glyoxime functions was proposed as the pH of the solution fell on complexation; the product was square planar $[Ni(HL)_2]$.

The *cis–trans* equilibria for complexes $[Ni(HL)_2]$ (H_2L = MeC(=NOH)C(=NOH)R; R = Et, Pr, Bu, Ph, p–MeC_6H_4, p–$MeOC_6H_4$, p–ClC_6H_4) in pyridine-d_5 and $CDCl_3$ have been examined by ^1H NMR spectroscopy [173]. The *trans*–isomer predominated in pyridine-d_5 for R = alkyl. For the aryl compounds, the equilibrium constant for the *trans–cis* reaction increased with the Hammett σ–constant of the substituent.

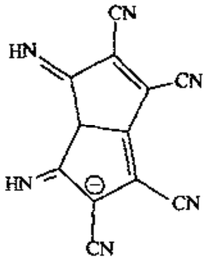


(75)

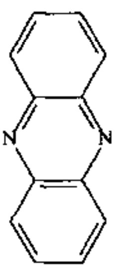


R = benzo–15–crown–5

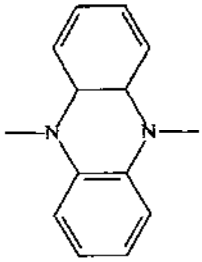
(76)



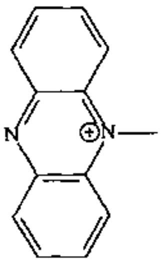
(77)



(78)



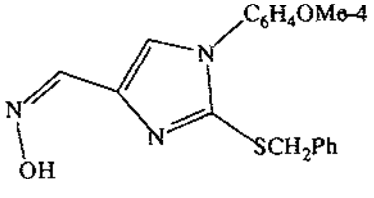
(79)



(80)

Nickel complexes of the ligand (**77**) have been employed as electron acceptors in donor–acceptor stacked compounds with phenazine (phz) (**78**), 5,10–dimethyl–5,10–dihydrophenazine (dmphz) (**79**) and *N*–methylphenazinium cation (mphz$^+$) (**80**) [174]. Compounds of stoichiometry $[Ni(L)_2]$.2phz.2CH_3CN and $[Ni(L)_2]$.dmphz.2CH_3CN were precipitated from comproportionation reactions between $[Ni(L)_2]$ and the donor. Their crystal structures both show donor and acceptor molecules alternating along the crystallographic *c* axis. The low–bandgap semiconductor compound $[Ni(L)_2^{\cdot -}]$mphz.2MeOH was made by electrocrystallisation.

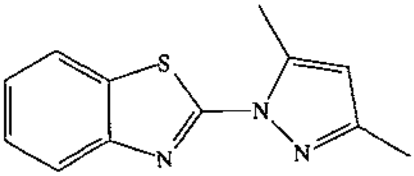
With $NiCl_2$ in EtOH, the potential antitumor drug L (**81**) affords a complex $[NiCl_2(L)_2]$, which was thought to have *trans*-pseudo-octahedral geometry with L bound *via* imine oxygen and imidazole nitrogen on the basis of IR spectroscopic data [175].



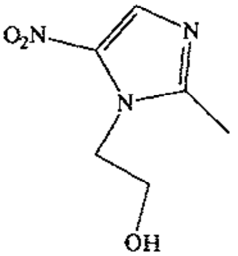
(81)

6.7.4 Heterocyclic nitrogen donor ligands

The complex $[Ni(L)_2](NO_3)_2$ (L = tris(pyrazol-1-yl)methane) is centrosymmetric, with a slight trigonal distortion caused by the N–M–N bite angle of the ligand (84.6°-86.2°) [176]. Electronic spectra of the complex suggest that this ligand is a moderately strong σ–donor and a weak π–acceptor. With the ligand (**82**), Ni(II) salts in EtOH afforded green paramagnetic complexes assigned as six–coordinate $[Ni(L)X_2(H_2O)_2]$ (X = Cl, Br, NO_3, ClO_4) on the basis of conductivity measurements in dmf [177]. The compound (**83**) is a radiosensitiser of hypoxic cells and has been investigated in photodynamic cancer therapy. The complex '$Ni(L)SO_4$' [L = (**83**)] has been investigated by pulse radiolysis and flash photolysis methods [178].



(**82**)

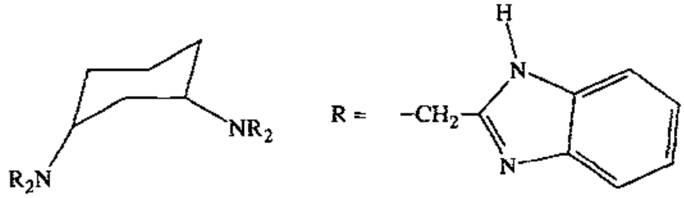


(**83**)

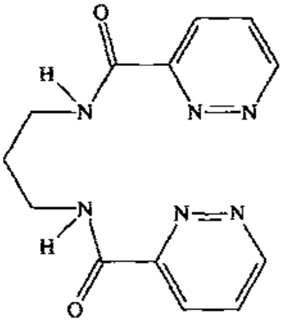
The reaction of $[Ni(acac)_2]$ with sodium 3,5–dimethylpyrazolate in thf in the presence of Et_3Al afforded, after one month, orange crystals of a trinuclear complex characterised crystallographically [179]. All three Ni(II) sites are square planar. The peripheral Ni(II) ions are coordinated to an $acac^-$ ligand and two bridging pyrazolate ions. The central Ni(II) is therefore coordinated to four pyrazolate nitrogens. The terminal coordination planes are almost perpendicular to the central plane. The ligand L (**84**) has been designed to simulate the kind of donors, and low–symmetry strained environment, that metal ions may experience in binding to proteins. With hydrated $NiCl_2$ in EtOH, one equivalent of L gave $[Ni(L)]Cl_2.H_2O$, and with $Ni(ClO_4)_2.6H_2O$, $[Ni(L)](ClO4)_2.CH_3CN$ (after recrystallisation) [180]. Both were monomeric and pseudo-octahedral.

The isomerism of complexes of general formula $NiBr_2(L)_4.nS$ (L = benzimidazole) has been investigated by thermoanalytical and spectroscopic methods [181]. Octahedral $[NiBr_2(L)_4]$.2acetone, when heated at 115 °C, lost 1.5 mol of acetone to give another octahedral species, and at 175 °C gave a green compound formulated $[Ni_2Br_2(\mu\text{–}Br)L_8]Br$. When left under $CHCl_3$ for extended periods, $[NiBr_2(L)_4]$.2acetone gave orange $[NiBr_2(L)_4].3CHCl_3$; the $CHCl_3$ could be driven off by heating to give orange, planar $[Ni(L)_4]Br_2$.

The square planar, diamagnetic complex $[Ni(L)].2H_2O$ (H_2L = (**85**); amide protons lost on complex formation) reacts with square planar [Ni(dithiophosphate)$_2$] to afford a dinuclear complex [Ni(μ–L)Ni(dithiophosphate)$_2$] in which the two pyrazine moieties bridge the metal centres and the dithiophosphate complex is six–coordinate and paramagnetic [182].



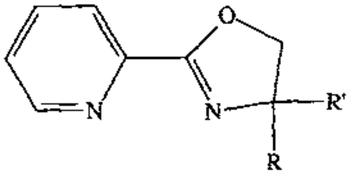
(84)



(85)

Complexes of pyridine and functionalised pyridines continue to attract interest. A range of complexes of stoichiometry $[Ni(L)_6]X_2$, $[NiX_2(L)_4]$ and NiX_2L_2 (L = 2–,3– or 4–methylpyridine; X = F, Cl, Br, I) has been investigated by thermoanalytical techniques [183]. With 3–hydroxypyridine (L), $NiCl_2$ in EtOH afforded octahedral, blue $[NiCl_2(L)_4]$. On treatment with Cl_2/EtOH, this afforded a yellow–brown complex, and 3–hydroxy–4–chloropyridine [184]. The thermal decomposition reactions of Werner clathrates $[Ni(NCS)_2$(4–methylpyridine)$_4]$.2G (G = naphthylene derivative) have been studied [185]. Another, extensive, study of Werner clathrates with the host complex $[Ni(NCS)_2(L)_4]$ (L = 4-vinylpyridine), including six crystal structures, has appeared [186]. Attempts to vary systematically the included guest by recrystallising from different solvent mixtures in a controlled manner were not wholly successful, and the conclusion from structural studies was that there are no significant host–guest Wan der Waals interactions, nor is the degree of freedom of the ligand the primary reason for the clathrating ability of the complex.

The behaviour of polymers and polymer blends of 4–vinylpyridine when complexed with $Ni(OAc)_2$ has been examined [187]. Complex formation raised the glass transition temperature of binary and ternary blends, and enhanced miscibility of otherwise immiscible copolymers, for example poly–4–vinylpyridine and poly–4–vinylpyridine–polybutylmethacrylate.



R = R' = Me

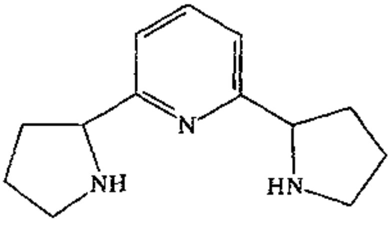
R = Me, R' = CH_2OH

R = R' = CH_2OH

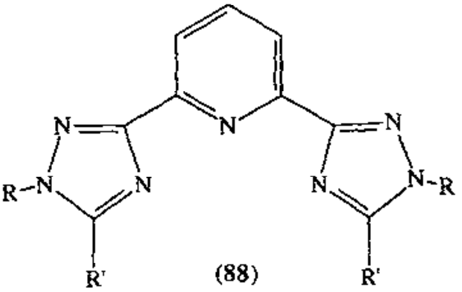
(86)

Metal–catalysed nucleophilic addition to nitriles is of interest in organic synthesis. Reaction between pyridine–2–carbonitrile, Ni(II) salts and $HOCH_2C(RR')NH_2$ (R = R' = CH_2OH; R = CH_2OH, R' = Me; R = R' = Me) afforded Ni(II) complexes $[NiX_2(L)_2]$ (L = (**86**); X = Cl, Br, NCS) or $[Ni(H_2O)_2(L)_2](ClO_4)_2$ [188]. With $NiBr_2$ and $HOCH_2C(Me)(CH_2OH)NH_2$ the reaction could be made catalytic to afford the free oxazoline. Transmetallation of the very sterically–crowded lithium 2–(bistrimethylsilyl)methylpyridine with $NiCl_2$ afforded, in low yield, the surprisingly air–stable square planar [Ni(2–{bis(trimethylsilyl)}methylpyridine)$_2$] [189].

The coordination of racemic (±L) (**87**) by Ni(II) has been shown to be highly stereoselective; 99% of the product is $[Ni(+L)(-L)]^{2+}$, with the S_4 point group [190]. The perchlorate salt was characterised crystallographically. In solution, the 1:1 complex shows a pH–dependant six coordinate–square planar equilibrium between $[Ni(L)(H_2O)_3]^{2+}$ and $[Ni(L)(OH)]^+$. The related ligand 2,6–bis(aminomethyl)pyridine (L) with $NiCl_2$ in EtOH forms $[Ni(L)_2]Cl_2.H_2O$, the crystal structure of which has been determined [191]. It shows rather short Ni–(pyridine N) and long Ni–(amine N) bonds.



(**87**)

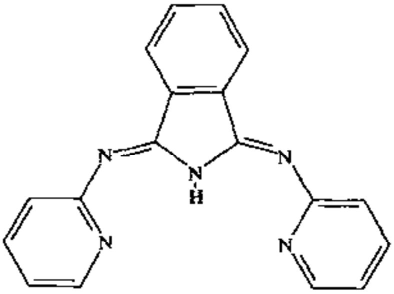


(**88**)

The syntheses of $[Ni(L)_2]X_2.nH_2O$ (L = (**88**); R = R' = H, X = Cl, ClO_4, n = 3; R = Me, R' = H, X = ClO_4, n = 0; R = H, R' = Me, X = ClO_4, n = 2; R = R' = Me, X = ClO_4, n = 0) have been reported, and the crystal structure of *mer*–$[Ni(L)_2]Cl_2.3H_2O$ (R = R' = H) was determined, as part of a wider study of the (isomorphous) spin–crossover Fe(II) complexes with these ligands [192]. There is significant tetragonal distortion, due to the rather rigid five–membered chelate rings. The electronic spectrum of the Ni(II) complexes was consistent with the ligands being weaker–field than terpy.

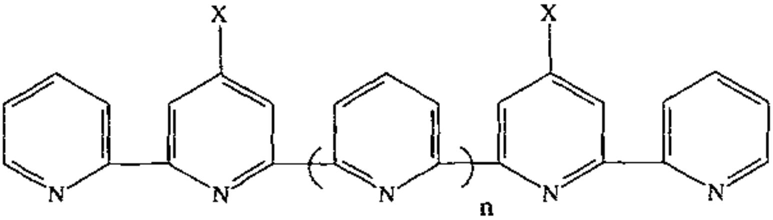
There has been a resurgence of interest in cyanamide ligands. Complexes of formula [Ni(L)X] (HL = (**89**), X = Cl, Br, NCS, $Ar{-}N{=}C{=}N^-$; Ar = 2–ClC_6H_4, 4–ClC_6H_4, 2,6–$Cl_2C_6H_3$, 2,3,5,6–Cl_4C_6H) have been described, and the crystal structure of [Ni(L)(2–ClC_6H_4NCN)] determined [193]. The complex is distorted square planar with the cyanamido ligand coordinated *via* the terminal nitrogen, with a Ni–N bond length of 1.874(10) Å, and C=N–Ni angle of 161.8(10)°. The complexes were solvatochromic, forming six–coordinate species in donor solvents. A related paper describes benzimidazole and related complexes of $Ni(N\{CN\}_2)_2$. These were pseudo-octahedral, of formula $[Ni(N\{CN\}_2L_2]$, and are probably polymeric with the cyanamide ligands bridging *via* both central and terminal nitrogens [194]. A pseudo-octahedral complex,

$[Ni(L)Cl_2]$, where L is the condensation product of 2–pyridinecarboxaldehyde with *o*–phenylenediamine, has been described [195].



(89)

The electrochemistry of $[Ni(bpy)_3](ClO_4)_2$ in CH_3CN has been re–investigated using CV, ring–disk and rotating ring–disk techniques [196]. The Ni(II) complex undergoes a quasi-reversible one electron oxidation to Ni(III) at +1.5 V, and a two–electron reduction followed by a fast chemical step at −1.65 V, affording $[Ni(bpy)_2]$ and bpy. No evidence for Ni(I) intermediates was found. The products of the reduction could be detected by re–oxidation at the ring; it was possible to observe the formation of $Ni^{(II)}(bpy)_2$ and $Ni^{(III)}(bpy)_2$ species, the latter at more positive potentials than for the formation of $[Ni(bpy)_3]^{3+}$.



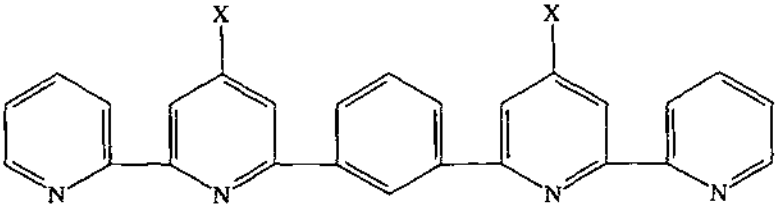
n = 1; X = SMe, 4–Z–C_6H_4 (Z = HO, Me_2N, Me, Cl, H) **(90)**

n = 2; X = SMe, S^nPr **(91)**

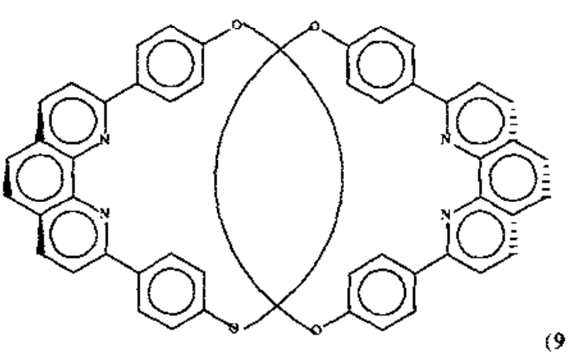
The coordination chemistry of oligopyridine ligands continues its development. Two papers report the preparation of Ni(II) complexes with 4′,4‴–substituted quinquepyridines **(90)** [197,198], and both include descriptions of the crystal structure of one of them, $[Ni_2(L)_2(OAc)](PF_6)_3$ [**(90)**; X = SMe]. The complex has a double helicate arrangement of intertwining ligands. Both enantiomers (that is, both right– and left–handed helices) are present in the crystal lattice. Both Ni(II) ions have distorted octahedral coordination. One is coordinated by a terpy fragment from each ligand, the other by a bpy fragment from each ligand and a chelating acetate ligand. The distortions dictate a wide range of Ni–N bond lengths (1.972(12)–2.221(12) Å). The other ligands all form similar complexes with $Ni(OAc)_2$, and the substituents have a very limited effect on their coordination chemistry, the only exception being [(**90**); X = $Me_2NC_6H_4$] which forms $[Ni_2(L)_2(H_2O)_2]^{4+}$ rather than $[Ni_2(L)_2(OAc)](PF_6)_3$. The CV's showed no accessible Ni(II)/Ni(III) process, and four quasi–reversible reductions. The first reduction was assigned either as a ligand–based process [198] or, on the basis of coulometry, as a 2–electron Ni(II)/Ni(I) wave [197]. The other three reductions are all ligand–based.

The corresponding sexipyridine ligands (**91**) gave symmetrical, octahedral $[Ni_2(L)_2](PF_6)_4$, with both Ni(II) centres octahedrally coordinated by a terpy fragment from each ligand [197] and similar electrochemistry to the quinquepyridine complexes. The coordination chemistry of the related ligands (**92**) with Ni(II) has also been described [199]. With $Ni(OAc)_2/NH_4PF_6$ in MeOH, this afforded $[Ni_2(L)_2(OAC)_2](PF_6)_2$. The crystal structure (X = SMe) showed both Ni(II) ions coordinated by a bpy unit from each ligand and a didentate acetate. Nuclear magnetic resonance spectroscopic data suggest that the helical structure is preserved in solution. An interesting feature of the structure is the lack of significant intramolecular inter–strand pyridine π–stacking interaction.

The ligand L (**93**) forms tetrahedral $[Ni(L)]^{2+}$, the geometry being imposed by the catenand structure of the ligand [200]. The photophysical properties of the free ligand and its complexes [including Ni(II)] have been studied. Coordination to Ni(II) supresses the luminescense because the partially–occupied d–orbitals provide a path for radiationless decay from the ligand excited state.



X = SMe, H (**92**)

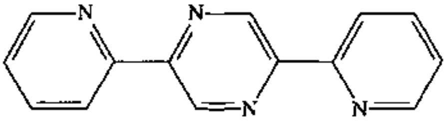


(**93**)

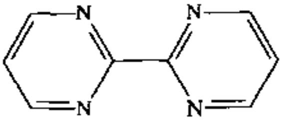
Linking group is $-O(CH_2CH_2O)_4CH_2CH_2O-$

The ligand L (**94**) has been employed extensively in photophysical studies of dinuclear complexes. The complex $[\{Ni(hexafluoroacac)_2\}_2(\mu\text{-}L)]$ has been investigated [201]. Magnetic measurements show that the metal centres are not significantly coupled *via* L, presumably since H...H interactions twist the donor sites out of plane. The dinucleating ligand (**95**) formed octahedral $[Ni_2(H_2O)_8(\mu\text{–}L)]^{4+}$, isolated as sulfate and nitrate salts [202]; crystal structures of both were determined. The cations were essentially isostructural, centrosymmetric, with slightly distorted six–coordinate N_2O_4 sites. Weak antiferromagnetic exchange was observed [$J = -14$ cm^{-1} (nitrate), -12 cm^{-1} (sulfate)].

The effect of axial–equatorial interactions on the geometry of five–coordinate nickel(II) complexes of piperidine, glyoxime and related ligands has been explored. Several apparent correlations in structural parameters are noted [203]



(**94**)



(**95**)

6.7.5 Jack bean urease, and related complexes

Jack bean urease (JBU) is a hexameric protein with two Ni(II) sites (with $Ni(N/O)_6$ coordination) per subunit. In contrast to an earlier study, which found evidence of weak antiferromagnetic coupling between these Ni(II) sites, saturation magnetisation data at four field strengths show there to be no antiferromagnetism [204]. The magnetic properties can be accounted for by a population of high– and low–spin Ni(II) ions, the proportions of which changes with pH. To model the active site in JBU, two Ni(II) complexes of urea have been synthesised [205]. On treatment of the dimer $[(tmen)(AcO)Ni(\mu\text{–}H_2O)(\mu\text{–}OAc)_2Ni(OAc)(tmen)]$ in CH_2Cl_2 with, successively, $[Me_3Si]O_3SCF_3$ (Me_3SiOTf) and urea, two products form. One is green $[Ni(OAc)(urea)_2(tmen)(OTf)$, the other is the blue–green dimer $[Ni_2(OAc)_3(urea)(tmen)_2](OTf)$. X–Ray crystallography establishes that the coordination sphere of the former has two *cis* O–bound urea ligands, a chelating tmen ligand with one of its donors *trans* to one urea, and a chelating acetate ion. In the dimer, two symmetrically–bridging acetate ions link the Ni(II) sites. One of the Ni(II) ions is additionally coordinated to a chelating tmen, and to a chelating acetate ion. One of the oxygen atoms of the latter additionally bridges to the second Ni(II) ion, which additionally has a chelate tmen ligand and a unidentate, *O*–bound urea ligand. The dimer shows weak antiferromagnetism.

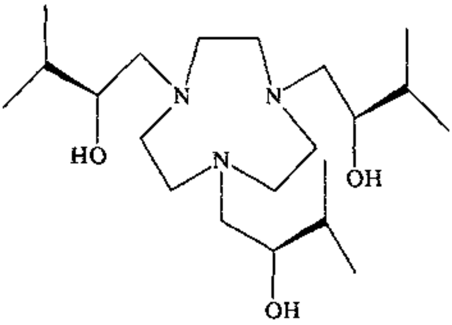
Small–angle X–ray scattering has been used to probe the structure of aqueous surfactant solutions of JBU, and the activity of these solutions for urea hydrolysis has been studied. Interestingly, the results suggest that an anionic surfactant breaks up the protein into its subunits, and that these are still active [206].

6.8 COMPLEXES WITH MACROCYCLIC NITROGEN DONOR LIGANDS

6.8.1 *Triazamacrocyclic ligands*

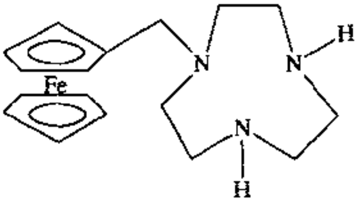
The volume of activation for $[S_2O_8]^{2-}$ oxidation of $[Ni(tacn)_2]^{2+}$ has been determined (-25.8 ± 2.3 cm^3 mol^{-1}) [207]. Another study reports the kinetics of this reaction as a function of $[S_2O_8]^{2-}$ concentration and temperature [208]. The reaction is first–order in both reagents (second-order rate constant 1.13 mol dm^{-3} s^{-1} at 298 K), and the activation energy is 38±1.8 kJ mol^{-1}. In mixed solvents, the rate was slower.

As part of a wide study of magnetically coupled di– and polynuclear ligand–bridged Ni(II) complexes, a complex was isolated by reaction of $[Ni(L)(H_2O)_2](ClO_4)_2$ (L = 2,4,4–trimethyl–1,5,9–triazacyclododec–1–ene (**70**)) with $NaNO_2$. Surprisingly, the crystal structure revealed that the product was mononuclear $[Ni(O_2N)(L)(H_2O)]ClO_4.2H_2O$, which is six–coordinate, with a didentate nitrito ligand, and the triazamacrocycle arranged facially with N_5 *trans* to the water ligand [209]. This contrasts with the reaction with azide, described in section 6.7.2.



(**96**)

The pendant arm macrocycle (**96**) has been synthesised and some of its coordination chemistry examined [210]. With Ni(II), mononuclear $[Ni(L)](NO_3)(PF_6)$ was isolated, the X–ray crystal structure of which showed Ni(II) coordinated by the three amines and three alcohol oxygens. The complex has C_3 symmetry, with a twist from octahedral geometry of 18°. The electronic and CD spectra were consistent with strong trigonal distortion, which mixes the three metal–centred transitions.



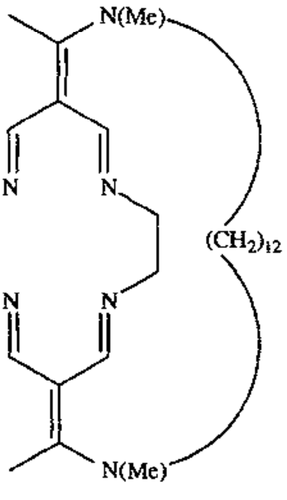
(**97**)

The ligand tacn has also been modified with a ferrocene pendant group; the Ni(II) complex of L (97), $[Ni(L)_2](ClO_4)_2$, has been isolated [211]. It underwent a single, two–electron oxidation at *ca.* +0.5 V, due to the simultaneous oxidation of both ferrocenes. The one–electron Ni(II)/Ni(III) oxidation, which occurred at a much more positive potential, was shifted 0.43 V more positive than that observed for $[Ni(tacn)_2]^{2+}$ itself, owing to the electrostatic repulsions inherent in the $[Ni(L)]^{4+/5+}$ moieties.

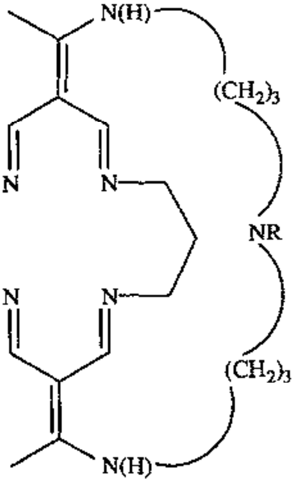
6.8.2 Tetraazamacrocyclic ligands

6.8.2.1 Cyclidene macrocycles and related ligands

A novel 14–membered ring cyclidene ligand L (98) has been synthesised using Ni(II) as a template [212]. The cavity enclosed by the C_{12} strap is wide and very low compared with those found for the 16–membered ring analogues, as determined by X–ray crystallography for the complex $[Ni(L)](PF_6)_2$. Again in contrast to the more common 16–membered ring analogues, the ring methyl groups occupy mutually *trans*–positions. Some examples of Ni(II)–cyclidene complexes with the strap incorporating an additional secondary or tertiary amine donor, (99), have been described [213].



(98)



(99)

6.8.2.2 Complexes of cyclam and substituted cyclam ligands

The complex *catena*–$(\mu-N_3)[Ni(cyclam)](ClO_4).H_2O$ has been prepared from the perchlorate salt and NaN_3 in concentrated aqueous solution [214]. The crystal structure shows 1–D $Ni-N_3$ chains, isolated by ClO_4^- and water molecules in the interchain spaces. The $Ni-N_3-Ni$ units are strongly asymmetric. Magnetic data indicates strong antiferromagnetism; $J = -39.2\ cm^{-1}$. With the related ligands L = *meso*–5,7,7,12,14,14–hexamethylcyclam and L′ = 2,3–dimethyl–1,4,8,11–tetraazacyclotetradeca–1,3–diene, X–ray crystal structures of the complexes *catena*–(μ–N_3)[Ni(L)](ClO_4) show related arrangements, but with L there are two different chains in the unit cell, in the ratio 2:1, showing different symmetry and different antiferromagnetic couplings [215]. With L′, there is a C_2 axis at Ni and alternating inequivalent azide bridges with C_2 symmetry at the central N; thus, two different values of J are required to describe the magnetic properties of the system. In other attempts to prepare magnetically coupled systems, complexes [Ni(L)]X_2] (L = *meso*–5,7,7,12,14,14–hexamethylcyclam; X = N_3, NCO, NCS, I, OAc) have been prepared, and one crystal structure (X = I) determined [216]. The latter complex is square planar, with uncoordinated axial iodide ions. In the solid state, the other complexes were six–coordinate and paramagnetic. Electrochemical data were obtained for the Ni(II)/Ni(III) process. The complexes were monomeric.

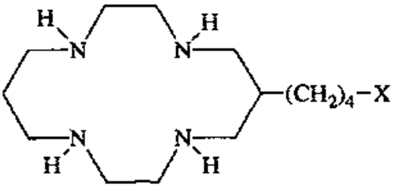
Co–crystallisation of $[Ni(cyclam)]^{2+}$ and $Bu_4N[Ni(dmit)_2]$ [dmit = (**20**)] from CH_3CN gave a compound, $[Ni^{II}(cyclam)(CH_3CN)_2][Ni(dmit)_2]_2$ [217]. X–Ray crystallography and temperature–dependant magnetic measurements showed that the complex cations were independent of the radical anions, which formed antiferromagnetically–coupled dimers ($J = -125.3(9)$ cm^{-1}).

The crystal structure of a Ni(III)–nitrate complex, *trans*–$[Ni(NO_3)_2(cyclam)]ClO_4$ (isolated from a saturated solution of the Ni(II) perchlorate salt in 1.5M HNO_3) has been determined. The unit cell contained two independent, centrosymmetric cations with *O*–bound nitrate ligands. Using the structural data, and electron transfer data from the reactions of both $[Ni(cyclam)]^{2+}$,and the Ni(III) complex with known outer–sphere redox reagents, an estimate of the self–exchange rate for the Ni(II)/Ni(III) couple (10^8 M^{-1} s^{-1}) was obtained [218]. The kinetics of the reaction of $[Ni(cyclam)]^{2+}$ in acidic aqueous solution with alkyl hydroperoxides have also been studied [219]. The kinetics of reduction of $[Ni(cyclam)(H_2O)_2]^{3+}$ and species $[Ni(cyclam)X(H_2O)]^{2+}$ (X = Cl, Br) by SO_2 in acid media have been investigated [220]. Only $SO_3{}^{2-}$ and $HSO_4{}^-$ were detected; no evidence was found for $S_2O_6{}^{2-}$, which would be expected if $SO_3{}^-$ were an important intermediate. Halide ions accelerated the reaction. A mechanism involving insertion of S(IV) into Ni^{III}–X bonds was proposed.

The complex $[Ni(tmc)]^{2+}$ (tmc = *R,S,R,S*–1,4,8,11–tetramethylcyclam) has been employed as a probe for the change in polarisation of water in reverse micelles of water and sodium bis(2–ethyl–1–hexyl)sulfosuccinate in heptane, as a function of composition [221]. With large micelles ([water]/[surfactant] > 10) the spectrum resembled that of the complex in bulk water (*i.e.* square planar $[Ni(tmc)]^{2+}$), but smaller micelles gave spectra resembling that of 5–coordinate $[Ni(tmc)(OH)]^+$. The axial coordination of py, 2–Mepy , 4–Mepy and water to $[Ni(tmc)]^{2+}$ in nitrobenzene has been examined [222]. Unusually, although none of the pyridines complexed appreciably, water did do so, and the complexation was stronger in the presence of the pyridines as a result of H–bonding between the coordinated water and the pyridine nitrogen.

6.8.2.3 Tetraamine macrocycles with pendant groups

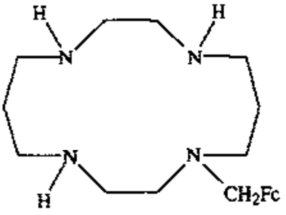
This section will consider firstly ligands functionalised with exocyclic redox and other groups, then ligands functionalised at C with additional potential donors and finally ligands functionalised at N with additional potential donors. The electrochemistry of $[Ni(L)](ClO_4)_2$ [L = cyclam and (**100**)] has been explored [223]. In the presence of Cl^- co-ligands in pure CH_3CN, the Ni(II)/Ni(III) redox process (involving $[Ni(L)Cl_2]$) was shifted to less positive potentials; this effect disappeared on addition of sufficient water as water displaced halide ions from the coordination sphere. The pendant group had a small stabilising effect on Ni(III) in pure CH_3CN.

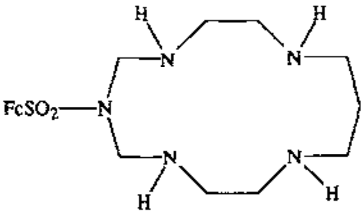


X = SMe

X = $CONH_2$

(**100**)

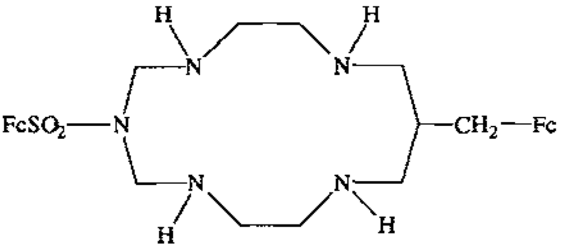




(Fc = ferrocenyl)

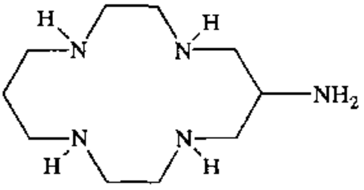
(**101**) (**102**)

There has been much interest lately in building polymetallic redox systems. Ferrocene–appended macrocycles afford good opportunities here, and Ni(II) complexes of the ligands L, $[Ni(L)]^{2+}$, [L = (**101**) and (**102**)] have been described [211], and their oxidative electrochemistry examined in different media. The ferrocene (Fc) moiety is oxidised at *ca*. +0.5 V, and the Ni(II)/Ni(III) wave occurs at more positive potentials. Since these systems consist of a coordinatively saturated fragment (Fc) linked to a coordinatively unsaturated one [Ni(II)], the difference in redox potentials between the two sites varies with the donor power of the solvent, or the electrolyte anion. A note from the same group [224] describes the preparation of the complex $[Ni(L)]^{2+}$; L = (**103**), made by template synthesis. Although, as desired, the two ferrocene moieties oxidise at different potentials, in this case the Ni(II)/Ni(III) redox process was irreversible.

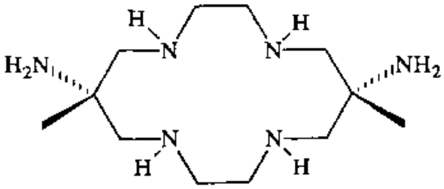


(**103**)

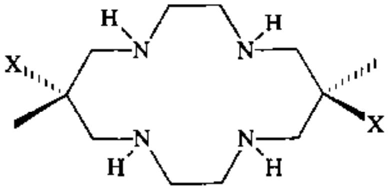
Turning now to tetraazamacrocycles C–functionalised with additional donors, the ligand L (**104**) has been synthesised by a non–template method. Reaction of L with $Ni(ClO_4)_2.6H_2O$ at pH 8.5 gave $[Ni(L)(H_2O)](ClO_4)_2.H_2O$, the crystal structure of which shows the pendant amine coordinated to the metal and *trans* to a coordinated water [225]. The strain inherent here is illustrated by the H_2N–Ni–OH_2 angle (170.1(3)°) and the rather long Ni–NH_2 bond (2.141(7) Å). The ligand adopts the *trans* I configuration. In acid, the pendant amine de-coordinates and is protonated (log $K = 3.8$; $I = 0.1M$). The intermediate 4-coordinated *trans*–I complex rearranges (0.4 h^{-1}, 60°C, pH 3) to a more stable *trans*–III configuration, as revealed by X–ray crystallographic study of the isolated $[Ni(LH)](ClO_4)_3.1.5H_2O$. The latter, on deprotonation, gives an intermediate square planar $[Ni(L)](ClO_4)_2$, which rearranges again to 6–coordinate *trans*–I $[Ni(L)(H_2O)](ClO_4)_2$. Electrochemical studies showed that the pendant amine stabilises the Ni(III) state better than cyclam for the *trans*–I complex; no Ni(I)/Ni(II) process could be detected. As an electrocatalyst for CO_2 reduction, $[Ni(LH)](ClO_4)_3$, however, proved more effective than $[Ni(cyclam)]^{2+}$.



(**104**)



(**105**)



X = -NO_2

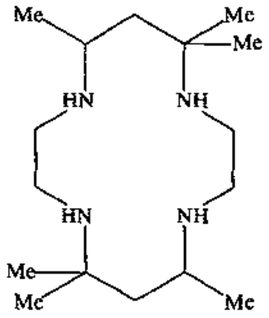
X = NH_2

(**106**)

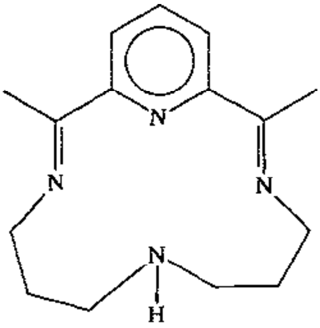
Complexes of the ligand *cis*–diammac (**105**) have been prepared, and their properties compared with complexes of the *trans* isomer (**106**) (X = NH_2) [226]. While the latter displayed unusually short Ni–N bonds, high energy d–d transitions and negative Ni(II)/Ni(III) potentials, the *cis*–diammac complexes do not. A detailed study of Ni(II) coordination by (**106**) (X = NH_2) has also appeared [227]. Two isomers of Raney nickel–catalysed hydrogenation of the Ni(II) complex of (**106**) (X = NO_2). One, designated α, was metastable. Triplet complexes of Ni(II) with the ligand in this arrangement had (**106**) pentadentate, with the remaining pendant amine protonated (as in $[Ni(LH)Cl](ClO_4)_2$) or neutral (as in $[Ni(L)(H_2O)]Cl_2$). In this form, the ligand adopts a configuration with all four NH groups on the same side of the macrocycle ring. The stable β form has the 'two up, two down' configuration (*R,R,S,S*) common in cyclam coordination chemistry, and forms triplet complexes such as $[Ni(L)]Cl_2$ (all amines coordinated), $[Ni(L)(NCS)_2]$ with primary amines neutral and uncoordinated, and $[Ni(LH_2)(NCS)_2](CNS)_2$. Square planar $[Ni(LH_2)]^{4+}$ were also isolated, for both α and β forms.

6.8.2.4 Nickel–tetraazamacrocycle complexes in electrocatalysis

The complex $[Ni(L)]^{2+}$ [L = (**107**)] has been employed as an electrocatalyst for the reductive coupling of alkyl bromides to olefins activated by electron–withdrawing groups. CV evidence suggested that the Ni(I) complex reacts catalytically with R–Br affording R· and Br^-; the R· then react with the double bond [228]. Similar electroreduction of *N*–allylic and *N*–propargyl–α–bromoamides using $[Ni(L)]^{2+}$ [L = (**107**), (**108**)] gave, under the correct conditions, 5–membered lactones *via* intramolecular radical addition [229]. Other products were detected and a rationale offered for the product distribution; the presence of an H–atom donor (*e.g.* Ph_2PH) was useful in optimising the yield of lactone.

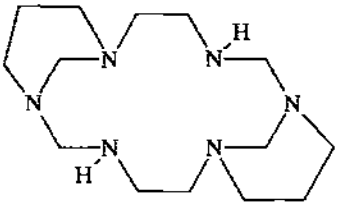


(**107**)

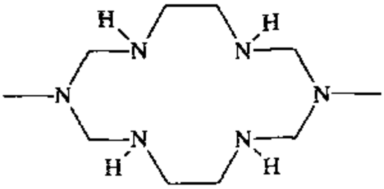


(**108**)

The reduction of CO_2 electrocatalysed by Ni(II) complexes of ligands (**109**) and (**110**) at Hg and Cu electrodes has been studied, in the hope that the less negative Ni(I)/Ni(II) waves seen for these complexes would result in greater efficiency. For the complex of (**109**) the catalytic current for CO_2 reduction was smaller than that for $[Ni(cyclam)]^{2+}$, but the peak potential was more positive by 280 mV. For (**110**), the complex was more active for CO_2 reduction [230].



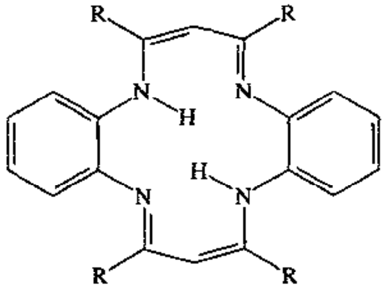
(**109**)



(**110**)

The electroreduction of CO_2 using Hg–adsorbed $[Ni(cyclam)]^{2+}$ as electrocatalyst has been studied further [231]. With added CO, the product of the reaction, the catalytic activity decreased. Formation of an insoluble Ni(0) complex, '[Ni(cyclam)(CO)]', adsorbed on the electrode surface, was proposed as the reason for this inhibition.

Nickel–tetraazaannulene complexes adsorbed on carbon are good electrocatalysts for O_2 reduction, an important reaction in fuel cell technology. A theoretical study of the interaction of [Ni(L)] [H_2L = (**111**)] with graphite, using a computer model based on MM but with additional terms to account for π–π interactions, has been published [232]. The planar complex (R = H) adsorbs parallel to the C surface but electrostatic π–π interactions are repulsive; the London dispersion energy is responsible for the nett attractive interaction. The saddle–shaped complex (R = Me) orients with the Me groups next to the surface, with the molecule centre above a graphite ring centre.

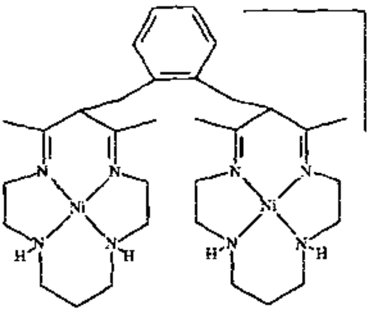


(**111**)

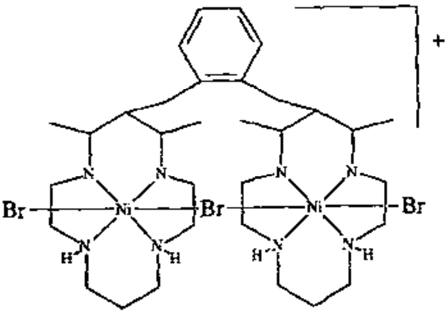
6.8.2.5 Other novel tetradentate N–donor macrocycles

Some coordination chemistry of the macrocycle–catechol ligand H_2L (**112**) with Ni(II) has been reported [233, 234]. The complex [Ni(L)] [H_2L = (**112**)] was made either by direct reaction of H_2L with $Ni(OAc)_2$, or by Ni(II)–templated condensation of 2,2'–(ethane–1,2–diyldiimino)bis(5'–*R*–benzaldehyde) and 1,2–diamino–4,5–dimethoxybenzene, followed by base–catalysed demethylation [233]. Treatment of square planar [Ni(L)] with ferrocinium ion in dmf afforded, in the presence of NEt_3, the neutral semiquinone. The crystal structure of the latter showed two square planar Ni(II) complexes in a centrosymmetric dimer with strong intermolecular H–bonding between semiquinone units. In the solid state, this complex showed antiferromagnetic behaviour and was ESR–active, but in dmf it was ESR–silent and diamagnetic, suggesting that disproportionation to catechol–quinone dimers may have occurred. The catechol units in [Ni(L)] may themselves be employed as ligands in construction of supramolecular complexes, and reaction with base and $[Mo_2O_2S_2(S_2)(dmf)_3]$ in dmf or thf afforded $[Ni(L)\{Mo_2O_2S_2(S_2)\}]^{2-}$ [234], with one of the Mo(V) ions coordinated to the catechol oxygens.

Reaction of [Ni(L)] (H_2L = (**111**); R = Me) with $CH_3(CH_2)_{14}COCl/NEt_3$ afforded the amphiphilic complex [Ni(6,13–bis{hexadecanoyl}–5,7,12,14–tetramethyldibenzo[*b*,*i*]–tetraaza[14]annulene)] [235]. This formed ordered monolayers on water (the complex probably lying edge–on), which could be transferred to silanised quartz plates. Optical measurements suggested that the macrocycle rings lie coplanar with the surface on the latter.



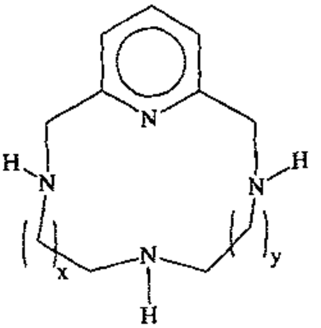
(112)



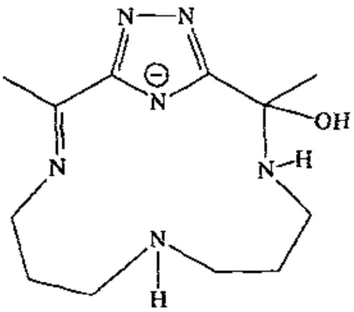
(113)

On treatment of $[Ni(L)](NO_3)$ (HL = 5,7–Me_2–[14]–4,7–diene–N_4) with 1,2–$(XCH_2)_2C_6H_4$ (X = Cl, Br), the complex (**112**) formed, which on treatment with $NaBH_4$, followed by anion exchange chromatography, yielded the unusual complex (**113**), ≥80% of which had the *meso* arrangement of the new chiral centres, with the macrocycles adopting the '*trans*–III' (*R,R,S,S*) arrangement [236]. Two methyl groups are equatorial with respect to the chair–form six–membered ring, and the *o*–xylylene group is axial, giving the face–to–face geometry observed.

The ligands (**114**) have been prepared, and their complexation equilibria with Ni(II) studied using potentiometry and ^1H NMR spectroscopy. The log *K* values decreased slightly with increasing ring size [237]. In aqueous solution, the $Ni(NO_3)_2$ complexes of the 12– and 13–membered ring ligands exhibit square planar ⇌ six coordinate equilibria (with the 12–membered macrocycle probably folded and *cis*), while with the 14–membered ring the complex is five–coordinate and paramagnetic.



(114)

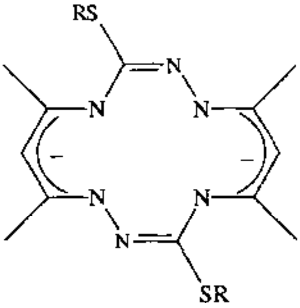


(115)

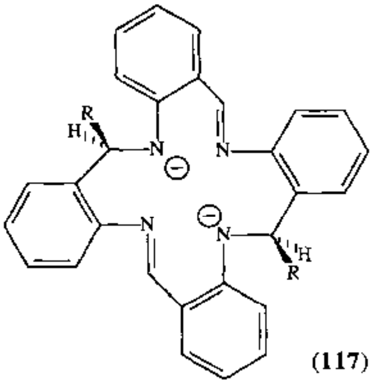
Template condensation of 3,5–diacetyl– or 3,5–diformyl–1,2,4–triazole with bis(3–aminopropyl)amine, $Ni(ClO_4)_2$ and LiOH gave $[Ni(L)]ClO_4$ [L^- = (**115**)]. Reduction of the complex with $NaBH_4$ gave the corresponding saturated tetraazamacrocycle complexes. Laser–

assisted secondary ion mass spectrometry was employed to characterise the products, which were square planar in the solid state, but paramagnetic in solution in polar solvents [238].

The complex [Ni(L)] [L = (**116**)], previously prepared by template condensation of 2,4–pentanedionebis(*S*–methylisothiosemicarbazonato)nickel(II) with acacH and $HC(OEt)_3$, also forms when [Ni(2,4–pentanedione–*S*–methylisothiosemicarbazonate)(NH_3)].$2H_2O$ is treated with acacH and $HC(OEt)_3$ [239]. The reactions of [Ni(TAAB)] (TAAB = cyclotetrameric Schiff base of *o*–aminobenzaldehyde) with Grignard and organolithium reagents yielded complexes [Ni(R_2TAAB)] [R_2TAAB = (**117**)] regio– and stereospecifically (RMgX with R = Me, ^{n}Pr, ^{n}Bu, Ph, CH_2Ph; RLi with R = Me, Et, tBu, Ph) [240]. When the TAAB precursor compound was treated with Grignard reagents, followed by workup, the free ligands H_2R_2TAAB were obtained, from which the Ni(II) complexes could be isolated in better overall yield.

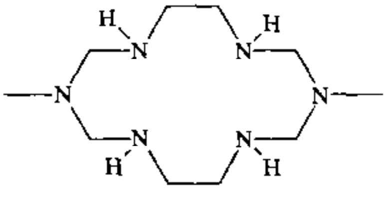


(**116**)

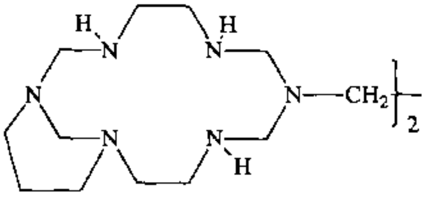


(**117**)

There has been much recent interest in the synthesis of macrocycles employing the condensation reaction between diamine complexes [of Ni(II)], RNH_2 and HCHO. The archetypal ligand of this type is (**118**), and the stabilisation of Ni(III) complexes of this ligand in neutral and alkaline solution by coordination of axial anions has been studied by CV and spectrophotometry [241]. Dianions (SO_4^{2-}, HPO_4^{2-}) were more effective in this respect than monoanions (F^-, RCO_2^-).

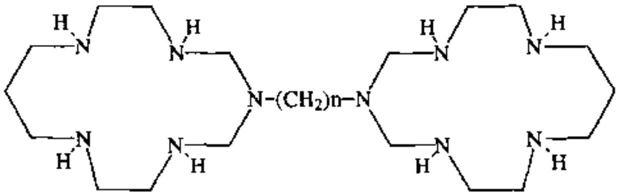


(**118**)



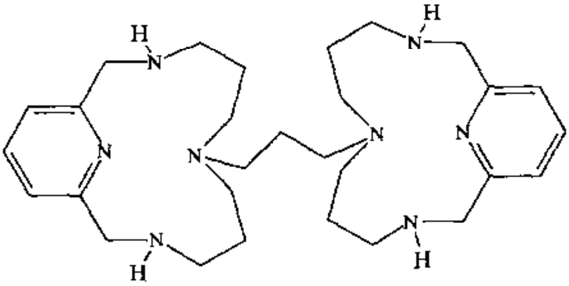
(**119**)

Attempts to use condensation reactions between HCHO, Ni(II)–multidentate amine complexes and α,ω–diamines to make dinuclear macrocycle complexes have been described. For example, a one–pot reaction between 1,4,8–triazaoctane, en and HCHO in the presence of Ni(II) gave the complex $[Ni_2(L)][ClO_4)_4$ [L = (**119**)] in 20% yield after repeated recrystallisation [242]. Electronic spectra and CV data indicate negligible interaction between metal centres. Similarly, template condensation of $[Ni(1,4,8,11\text{–tetraazadodecane})](ClO_4)_2$ with HCHO and α,ω–diamines $H_2N(CH_2)_nNH_2$ (n = 2–5) afforded complexes $[Ni_2(L)][ClO_4)_4$ [L = (**120**)]; again, these did not differ in their chemical, redox or spectroscopic properties from the corresponding mononuclear complexes [243]. The complex $[Ni(L)]^{2+}$, formed by template condensation of ammonia, HCHO, Ni(II) and en, has been employed in further condensations with HCHO and H_2NRNH_2 (R = $(CH_2)_2$, $(CH_2)_4$, p–$H_2CC_6H_4CH_2$) to give complexes of the corresponding dinuclear ligands [244].



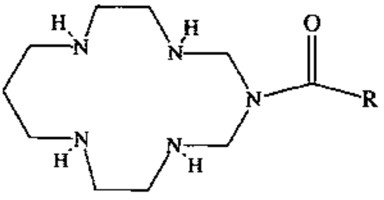
(**120**)

The uncoordinated secondary amine functions in the 'lariat' complex $[Ni(L)]^{2+}$ [L = the dinucleating macrocycle (**121**)] react with $CH_2{=}CHCN$ to afford the asymmetrical 'lariat' analogue with pendant $-CH_2CH_2CN$ groups. On reaction with $Ni(ClO_4)_2.6H_2O$, followed by chromatography on Sephadex resin (Cl^- form), this afforded $[Ni_2(L)Cl](ClO_4)_3.2H_2O$. The –CN groups remain uncoordinated, but the weaker donor strength of the tertiary amine groups in the second macrocycle gives rise to a high–spin, 5–coordinate Ni(II) environment here; the other Ni(II) remains square planar [245].

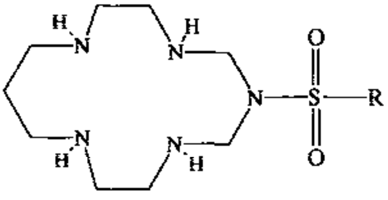


(**121**)

It was found recently that amides and sulfonamides could be employed in the place of secondary amines in these HCHO condensation reactions; examples of ferrocene–appended macrocycles made in this way have already been described. The cyclisation of 1,3,7,9–tetraazaundecane with HCHO and $H_2NC(O)R$ (R = Me, Ph) or H_2NSO_2R (R = Me, Ph, p–MeC_6H_4, p–$HOOCC_6H_4$, naphthyl) templated by $NiCl_2$ afforded $[NiCl_2(L)]$ or (after precipitation with excess $HClO_4$) $[Ni(L)](ClO_4)_2$ [L = (**122**)] [246]. The reaction has been used to construct macrocycles functionalised with exocyclic pyridines [(**122a**); R = 3–pyridyl, 4–pyridyl] [247]. The crystal structure of $[Ni(L)](ClO_4)_2.HClO_4$ (L = (**122a**); R = 4–pyridyl) shows the Ni(II) in a square planar environment; the pyridyl nitrogen is protonated. The amide nitrogen has bond lengths and angles suggestive of sp^2 hybridisation. The pyridyl moieties could be complexed to other metal centres affording supramolecular polymetallic complexes. For example, reaction of the nickel complex (L') with $PtCl_4^{2-}$ or $[RuCl_2(bpy)_2]$ afforded trimetallic complexes $[PtCl_2(L')]$ and $[Ru(bpy)_2(L')_2]^{2+}$ respectively.



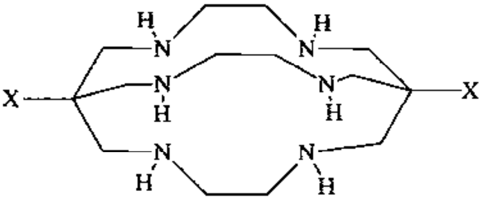
(**122a**)



(**122b**)

6.8.3 Azamacrocycles with more than four ring donor atoms

The complexation of the ligands [18]–ane–N_6 (1,4,7,10,13,16–hexaazacyclooctadecane) and 1,4,7,13–tetramethyl–1,4,7,10,13,16–hexaazacyclooctadecane with Ni(II) in aqueous solution has been investigated potentiometrically [248]. The tetramethylated ligand complexes more weakly (log $K = 16.24(6)$) than [18]–ane–N_6 (log $K = 21.1$) owing to a much lower enthalpic contribution ($-\Delta H = 8.9(5)$, $21.1(5)$ kcal mol^{-1} respectively).

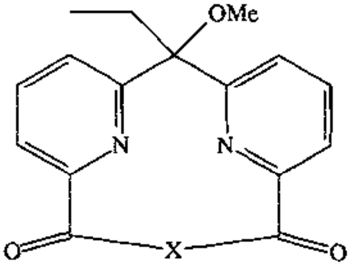


(**123**) X = H
(**124**) X = $-NH_3^+$

The syntheses, redox chemistry and spectroscopic properties of complexes of Ni(II) and Ni(III) with sarcophagine ligands (**123**) (L) and (**124**) (L') has been the subject of a comprehensive investigation [249, 250]. The complexes $[Ni(L)]^{2+}$ and $[Ni(L')]^{4+}$ were synthesised by reaction of Ni(II) salts with the free ligands. Oxidation to Ni(III) cations was achieved by controlled potential coulometry in acetonitrile, or Ce(IV) oxidation in aqueous solution; only $[Ni(L)](CF_3SO_3)_3$ could be isolated as a pure solid. The Ni(II) complexes were all octahedral, with all six cage amine donors coordinated, although an orange and presumably planar form of $[Ni(L)]^{2+}$ was observed but not fully characterised. The Ni(II) complexes could be resolved into their enantiomers by fractional crystallisation as bis((+)–tartrato)diantimonate salts, and the optically pure Ni(III) cations obtained from these. The electron self–exchange rate between enantiomeric forms in the two oxidation states was measured using a novel stopped flow circular dichroism technique ($k$ct = 5300 ± 300 dm^3 mol^{-1} s^{-1} at 298 K, I = 0.2 M). The rate constant, and the activation parameters, were consistent with only minor rearrangements of the coordination spheres on electron transfer. The structures of $[Ni(L')](NO_3)_4.H_2O$ and of $[Ni(L')]Cl_4.H_2O$ have been determined. The former crystallised in the non–centrosymmetric $P2_12_12_1$ space group, as a mixture of optically–pure crystals. The latter crystallised in the $P2_1$ space group. Whereas the nitrate salt adopted the conventional *lel*$_3$ arrangement of its $-HNCH_2CH_2NH-$ chelate rings, the chloride salt is unusual in having the *lel*$_2$*ob* configuration.

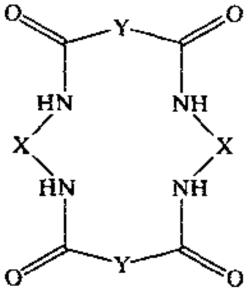
6.8.4 *Macrocycles incorporating amide donor groups*

Complexes [Ni(L)] of the hybrid ligands H_2L [H_2L = (**125**)] have been described [251]. All the complexes have square planar coordination; this was established crystallographically for [Ni(L)] (H_2L = (**125**); X = 1,2-$(HN)_2C_6H_4$); average Ni–N(pyridyl) = 1.848 Å, Ni–N(amide) = 1.820 Å). Competition experiments established that complexation was much faster for the 13-membered ring ligands. Template condensation of dicarboxylic acids with diprimary amines in the presence of $NiCl_2.6H_2O$ afforded complexes assigned as square planar $[Ni(H_4L)]Cl_2$ (H_4L = (**126**)) [252], on the basis of electronic spectra, ^{1}H NMR spectra, magnetic moments and conductivities. In view of the ease with which related amine–amide macrocycles deprotonate on complexation, this is unusual.



X = $HN(CH_2)_nNH$ (n = 2,3),
X = 1,8–$(HN)_2C_{10}H_6$
X = 1,2–$(HN)_2C_6H_4$
X = 1,2–$(HN)_2C_6H_{10}$

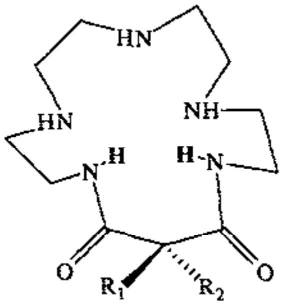
(**125**)



X = $(CH_2)_2$; Y = $(CH_2)_n$ (n = 1,2,3), 1,2–C_6H_4
X = $(CH_2)_3$; Y = $(CH_2)_n$ (n = 1,2,3), 1,2–C_6H_4

(**126**)

The crystal structure of the phenyl dioxocyclam complex [Ni(3–phenyl–1,5,8,12–tetraazacyclotetradecane–2,4–dionato–*N,N′,N″,N‴*)] has been determined [253]. The complex is square planar and has near–mirror symmetry, with the two amine N–H bonds directed to the same side of the coordination plane (average Ni–N(amine) = 1.937(2) Å, average Ni–N(amide) = 1.880(2) Å). The ligand 5,7–dioxo–cyclam reacts with acrylonitrile to afford the pendant arm derivative *N,N′–bis*(2–cyanoethyl)–5,7–dioxo–cyclam H_2L [254]. This reacts with $Ni(ClO_4)_2.6H_2O$ (log K for complexation = –14.45) to afford a complex of stoichiometry $[Ni(L)].Ni(H_2O)_2(ClO_4)_2$, of uncertain structure. Finally, the unusual reactivity of the five–coordinate low spin complexes [Ni(L)] [H_2L = (**127**)] towards O_2 (they form brown six-coordinate $[Ni(L)(O_2^-)]$ enables them to act as catalysts in non-specific cleavage reactions of DNA with ambient oxygen [255].



$R_1 = R_2 = H$

$R_1 = CH_2C_6H_5, R_2 = H$

$R_1 = F, R_2 = H$

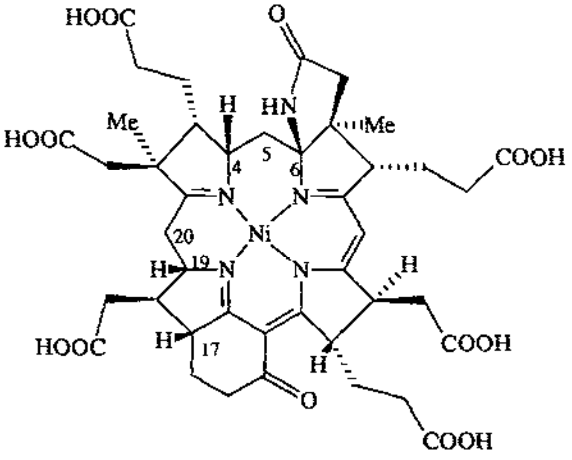
$R_1 = F, R_2 = CH_2C_6H_5$

$R_1 = R_2 = CH_3$

(**127**)

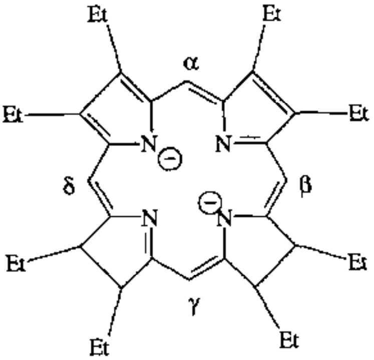
6.8.5 Porphyrins and related ligands

Nickel–porphyrin chemistry has been given fresh impetus by the discovery of the role of F_{430} (**128**) in the final step in methanogenesis from CO_2, namely reductive cleavage of methyl coenzyme M to CH_4 and coenzyme M. The Ni(I) state is thought to be important in this process. A quantitative ESR analysis of the reduced factor F_{430} pentacarboxylic acid and of the 12,13 epimer

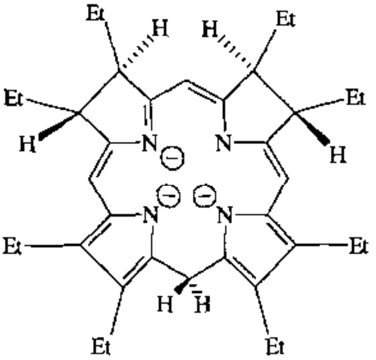


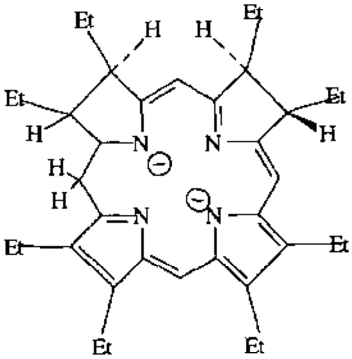
(**128**)

(isolated from cell extracts) has been performed, and the results compared with those for the pentamethyl ester, whole cells of *thermoautotrophicum* and of purified methyl coenzyme M reductase [256]. Titanium(III) citrate quantitatively reduces the Ni(II) form to the d^9 Ni(I) form, a tetragonally–distorted octahedral system with the vacancy in the $d_{x^2-y^2}$ orbital ($g_\perp = 2.061$, $g_\parallel = 2.244$; $g_\perp = 2.057$, $g_\parallel = 2.238$ (di–epimer)). The spectra differ from those earlier reported for the product of dithionite reduction of F_{430}, but in the latter, the signal strength corresponded to 1% of total Ni, so might not have been true Ni(I)–F_{430}. Moreover, the spectra were very similar to those of the whole cells in the reduced form.



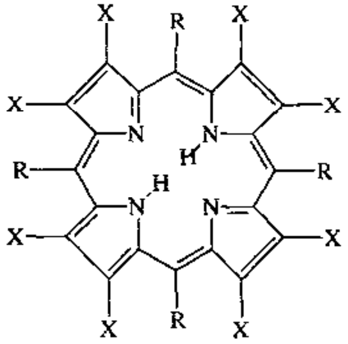
(129)



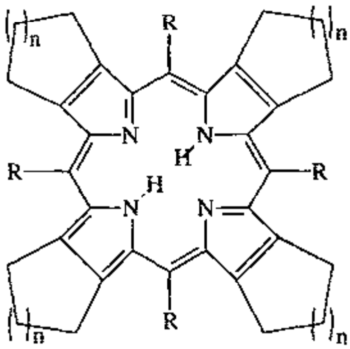


(130) **(131)**

Complexes of isobacteriochlorins are frequently used as F_{430} mimics because they, too, can be reduced to isolable Ni(I) complexes. The reactions of $[Ni^I(L)]^-$ [L^{2-} = (**129**)] with alkyl and aryl halides have been studied [257]. The organic products resulted from reduction or dehydrohalogenation; alkene formation was favoured by polar solvents, and isomerisation of alkenes occurred during reaction. This implies the intermediacy of Ni–H and Ni–R species in the reactions. Resonance Raman (RR) spectra of a series of complexes of (**129**), including Ni(II) (high– and low–spin forms) and Ni(I), and of the α,β,γ–deuterated isotopomer, have been studied [258]. Reduction of the metal perturbs the macrocycle conformation, although the change is smaller than that observed on going from low to high spin on axial ligation; the latter form requires a more planar macrocycle for optimum Ni(II)–axial ligand interaction. There is evidence of significant metal d_{π}–ligand back–bonding in the Ni(I) complex. The subtlety of macrocycle conformation and its effect on axial ligation is further illustrated by the fact that the Ni(II) complexes of the two configurational isomers of (**129**), which differ only in the stereochemistry of the ethyl groups on the saturated rings and which are usually employed as a mixture, have been shown to have different binding constants for pyridine and piperidine ligation [259]. Although the Ni(I) complex of (**129**) is very resistant to further reduction, in the presence of proton donors reduction of the macrocycle ring occurs [260], affording initially the Ni(I) complex of (**130**), the first complex of this precorrin to be identified. On treatment of this with Bu_3HNClO_4, the Ni(II) complex of the known hexahydroporphyrin (**131**) formed.



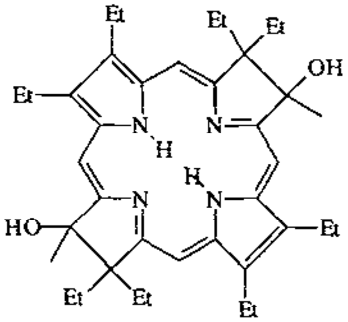
(**132**)



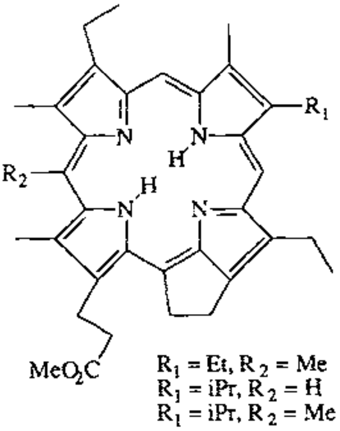
(**133**)

Highly substituted porphyrins and related reduced systems, and their nickel complexes, are currently being intensively investigated. Interest here focuses on the degree to which steric interactions between substituents distorts the macrocycle ring into a saddle conformation; non-planar porphyrins occur in metalloenzymes. Two groups have employed RR spectroscopy in combination with isotopic substitution and normal coordinate analysis to investigate the Ni(II) complex of octaethyltetraphenylporphyrin (**132**; X = Et, R = Ph). Comparison with data for octaethylporphyrin and tetraphenylporphyrin complexes, in particular large downfield shifts in a number of porphyrin skeletal modes, suggests a highly non-planar conformation [261, 262]. At room temperature, in solution, both planar and non-planar conformers were found for [Ni(L)] (L = octaethylporphyrin dianion) using RR spectroscopy [263]. Substitution of a single nitro–group at a methine bridge carbon shifts this equilibrium in favour of the non-planar conformer. Further, use of larger metal ions (Cu(II), Zn(II)) favours the planar conformer, an observation also made for octaethyltetranitroporphyrin (**132**; X = Et, R = NO_2) [264]. Here, while X–ray crystallography revealed the Ni(II) complex to be severely non-planar, the Tl(III) complex [Tl(L)Cl] was only moderately distorted from planarity. Similar results have been found in the coordination chemistry of the porphyrin (**133**; n = 1, R = 3,4,5$(MeO)_3C_6H_2$). While the Ni(II) complex is moderately distorted from planarity, the Cu(II) complex is planar [265]. In the latter example, an otherwise reliable molecular mechanics method incorrectly predicted a planar conformation for the Ni(II) complex, and possible reasons for this are discussed. In another paper, RR spectra of CS_2 solutions of the parent complex [Ni(L)] (H_2L = (**132**: X = R = H) have been interpreted in terms of two conformers in solution, but the spectra are not simply interpretable in terms of one of the conformers being ruffled, and the structure of the minor conformer remains a mystery [266].

A series of square planar Ni(II) complexes of porphyrins with varying substituents has been investigated using X–ray crystallography (solid state) and EXAFS (solid, solution), to see whether the structure in the solid state is maintained in solution [267]. In the solid state, for complexes of (**132**: X = Et, Pr, R = Ph) and (**133**: n = 2; R = Ph) saddle–shaped macrocycle rings were found. EXAFS data on these complexes showed that the conformation was unchanged in solution. While X–Ray data could not be obtained for the complex of (**132**: X = R = Ph), EXAFS data also indicated the same (distorted) structure in the solid as in solution. EXAFS data for complexes of (**133**: n = 1, R = Ph) and (**133**; n = 1, R = 3,4,5$(MeO)_3C_6H_2$), however, were interpreted in terms of a planar macrocycle configuration in both solid and solution phases. The structure of [Ni(L)] (H_2L = (**132**: X = Br, R = C_6F_5) has been determined. The Br atoms deviate from the plane defined by the ring nitrogens by up to 2.36 Å , leading to a pronounced tetrahedral distortion at Ni(II) [268].



(134)

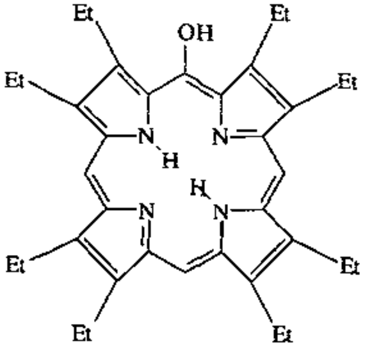


R_1 = Et, R_2 = Me
R_1 = iPr, R_2 = H
R_1 = iPr, R_2 = Me

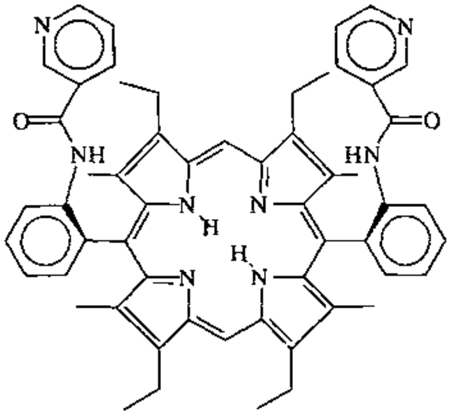
(**135**)

Resonance Raman and FT-IR spectra have been determined for [Ni(L)] [H_2L = (**134**)], of interest because of its structural similarity to bacteriochlorophyll, and insight was thus gained into the vibrational characteristics of metallobacteriochlorins [269]. The crystal structures of a series of Ni(II) complexes of bacteriopetroporphyrins (**135**), derived from bacteriochlorophylls, have been determined [270]. The presence or absence of the methine Me group modulates the absorption spectrum of these systems, and is therefore important in light harvesting. The structures show a greater degree of non-planarity in the two methyl–substituted ligand complexes. A series of porphyrins has been isolated from coral sponges, and the reactivity of their Ni(II) complexes towards formylating agents examined [271].

The crystal structure of *trans*–1,2–bis(*meso*–[octaethylporphyrinylnickel(II)])ethene showed that the molecule was non-coplanar; the Ni(II) coordination planes were almost perpendicular to the plane of the central double bond. The porphyrin rings are distorted from planarity [272]. The reactions of oxidised complexes of the porphyrin (**132**: X = H; R = 3,5–(tBu)$_2$–4–(HO)C_6H_2) with *p*–cresol (a peroxidase substrate) have been studied [273]. In $CHCl_3$, the rate is second order in substrate, attributed to a pre–equilibrium rate–determining formation of a *p*–cresol dimer.



(136)

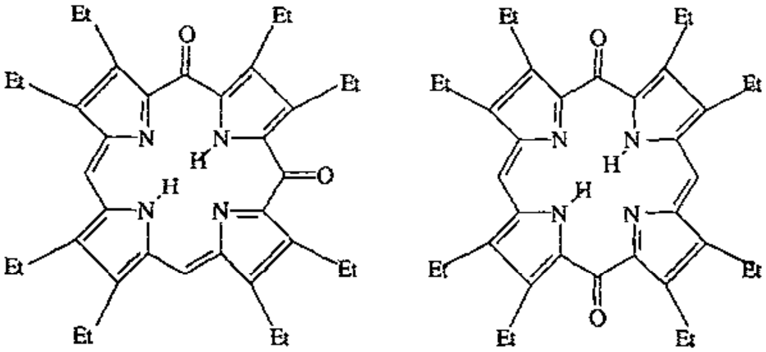


(137)

The oxidative electrochemistry of two Ni(II)–porphyrin complexes [Ni(L)] (H_2L = (**132**: X = Me, R = Ph) and (**133**: n = 2, R = Ph) and a Ni(II) porphycene complex [Ni(L')] (H_2L' = octaethylporphycene) has been studied in benzonitrile at Pt and glassy carbon electrodes [274]. Each complex showed three reversible one–electron oxidations. The most positive process was attributed to formation of a Ni(III) complex of a dication radical ligand. Interestingly, both the ruffled octamethyltetraphenylporphyrin complex and the planar porphycene complex had near–identical redox potentials. While structural studies have indicated that the product of the one–electron oxidation of [Ni(OEP)] is a cofacial dimer $[Ni_2(OEP)_2]^{2+}$ (OEP = octaethylporphyrin dianion), with no σ–bond between the units, on recrystallisation of $[Ni(L)(py)_2]^{\cdot+}$ from CH_2Cl_2/95% EtOH, a dimeric complex forms with a σ–bond between methine carbons *trans* to the oxygenated ring carbon (H_2L = (**136**) [275]. The axial pyridine ligands are lost. In the dimer, the porphyrin rings are ruffled, and lie over each other in an offset manner. Oxidation of [Ni(OEP)] in CH_2Cl_2 with 0.5 equivalents of $(p\text{–}BrC_6H_4)_3NSbCl_6$ yields a complex of stoichiometry $[Ni(OEP)]_2SbCl_6$. This behaves as a simple *S* = 0.5 paramagnet, and has a near–IR band at 1536 nm absent from both [Ni(OEP)] and $[Ni(OEP)]^+$. The crystal structure of this dimer shows two equivalent cofacial rings related by a crystallographic 2–fold axis, with the metal atoms displaced towards each other out of the donor atom plane by *ca.* 0.04 Å [276].

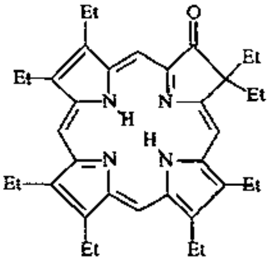
Mixtures of solutions of [Ni(L)] (H_2L = (**132**: X = H, R = *N*–methylpyridinium–4–yl) and 4,4',4'',4'''–tetrasulfonated phthalocyanine complexes have been shown to form well–defined supramolecular assemblies, consisting of hetero–dimers or –trimers, in polar solvents [277]. Affinity of the metal ions for axial ligands both controls, and is enhanced by, the degree of aggregation. Thus, nickel phthalocyanine, which normally has almost no affinity for axial ligands, binds pyridine or DMSO when involved in heterodimers. Another method of assembling multimetallic supramolecular complexes with porphyrins is to use molecules with exocyclic groups containing additional donors. Thus, [Ni(L)] (H_2L = (**137**)) reacts with $[M(DMSO)_4](ClO_4)_2$ (M = Pd, Pt) to afford trinuclear complexes in which a Pd(II) or Pt(II) ion is coordinated by four pyridine nitrogens from two [Ni(L)] units [278]. The crystal structure of the Ni_2Pd complex, $[\{Ni(L)\}_2Pd](ClO_4)_2.8CHCl_3$, shows both the Ni(II) and Pd(II) environments to be square planar, with the dihedral angle between NiN_4 planes and the PdN_4 plane of 67°.

Oxidation of [Zn(OEP)] with $Tl(CF_3CO_2)_3$ gives a mixture of products. Formation of the Ni(II) complexes of these allows them to be separated by chromatography. Further study of the Ni(II) complexes of one of these products (**138**) has now established that it is a mixture of 80% of the *trans* isomer and 20% of the *cis* isomer [279]. For both isomers, the square planar [Ni(L)] react with pyridine to form paramagnetic $[Ni(L)(py)_2]$. The affinity of Ni(II) complexes of β–oxoporphyrins (**139**)–(**141**) for binding additional ligands, and the Ni(II)/Ni(III) redox process for the complexes, have been studied [280]. The crystal structures of all three complexes [Ni(L)] have been obtained. These indicate an increasing degree of ruffling with increasing number of oxo–groups. The affinity of the complexes for imidazole binding also increases with the number of oxo–groups, and this is interpreted in terms of the increasing flexibility and decreasing aromaticity of the ligands. Imidazole binding moves the Ni(II)/Ni(III) potentials to more negative values.

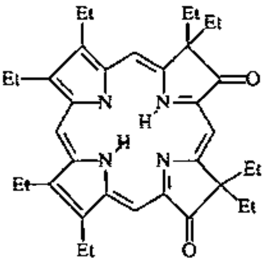


(**138**) (*Cis* and *trans* isomers)

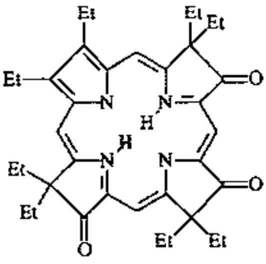
Finally, the syntheses and characterisation of some butoxy–substituted nickel–hemiporphyrazine complexes have been described [281]. These are soluble in common organic solvents.



(139)



(140)



(141)

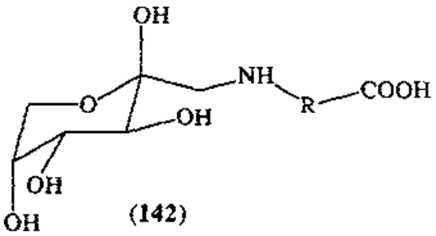
Turning now to phthalocyanine complexes, density functional calculations have been used to assess the relative suitability of nickel–porphyrin and nickel–phthalocyanine complexes for forming one–dimensional 'molecular metals' on partial oxidation [282]. With the smaller ring porphyrin systems, there is little dependence of the degree of inter–ring interaction on torsion angle, so that the latter is probably determined by crystal packing forces. This is not the case with the larger ring phthalocyanines. The effect of the aza–bridges and benzene rings in phthalocyanine complexes is to increase the energy of the a_{1u}, making it the HOMO in [Ni(phthalocyanine)], whereas in [Ni(porphyrin)] the HOMO has metal character. The synthesis of very pure [Ni(phthalocyanine)] requires the metallation of very pure phthalocyanine [283]. The one–dimensional conductor [Ni(phthalocyanine)]I made from this material remain metallic down to 3 K, a much lower temperature than observed previously, and the conductivity at 3 K ($\{1–2\} \times 10^4\ \Omega^{-1}\ cm^{-1}$) is 30 times higher. The electronic properties of [Ni(phthalocyanine)]I as a function of applied pressure have been determined [284]. Oxidative electropolymerisation of [Ni(L)] (H_2L = 4,4',4",4'"-tetraaminophthalocyanine) affords an electronically–conducting layer of poly–[Ni(L)] on the electrode surface. This has been characterised electrochemically [285]. Two of the four structural isomers of a substituted phthalocyanine complex, tetra(tertiary butyl)phthalocyanatonickel(II), have been separated for the first time, using HPLC and MPLC methods [286]. These are the isomers with C_{2v} and C_s symmetry.

6.9 COMPLEXES WITH MIXED NITROGEN–OXYGEN DONOR SETS

6.9.1 Amino acid, peptide, nucleotide and related ligands

Nickel(II) complexes of a range of short oligopeptides have been studied [287]. Complexes of oligopeptides containing histidine in the third position can quench O_2^- more easily than other oligopeptide complexes. Such complexes can also catalyse the disproportionation of H_2O_2 to yield O_2^-. Electronic spectra suggest that whereas the latter complexes are square planar in solution, complexes with oligopeptides without histidine in the third position are six–coordinate. The kinetics of reversible complexation of $[Ni(H_2O)_6]^{2+}$ with the complexes $[N_4Co^{III}(glyH)gly]^{2+}$ (N_4 = $(en)_2$ or trien; glyH = glycine, O–bound) have been investigated by stopped flow methods [288]. The data suggest that reaction occurs by coordination of one of the free $-NH_2$ groups to Ni(II) by an I_d mechanism. The dinuclear species exists in equilibrium between a $[(\{Co(III)\}-H_2N)Ni(H_2O)_5]^{4+}$ species and a chelated form where the carboxyl group also bridges between Ni(II) and Co(III), $[(\{N_4(glyH)Co^{III}(\mu-gly)Ni(H_2O)_4]^{4+}$.

Several papers this year deal with complexes of amino acid hydroxamic acid derivatives. The thermodynamics of Ni(II) complexation by 2,6–diamino–*N*–hydroxyhexanamide (*L*–lysine hydroxamic acid, HL) have been investigated [289]. The formation constants of ternary complexes of Ni(II) with β–alaninehydroxamic acid as primary ligand and en as secondary ligand have been studied [290]. The ternary complexes are more stable, and more resistant to hydrolysis at high pH, than either binary complexes. The complexation of Ni(II) by L–glutamic acid–δ–hydroxamic acid and, for comparison, acetohydroxamic acid–α–alanine ternary systems, have been investigated [291]. The former binds as a tridentate, with no evidence for polynuclear complexes. An equilibrium probably exists between (*O,N,N*)– and (*O,O,N*)–bonded forms.



(142)

R = CH_2, $(CH_2)_2$, $CH(CHMe_2)$, $CH(CH_2CHMe_2)$, $CH(CHEtCH_3)$, $CH(CH_2Ph)$

The complexation of the fructose–amino acid compounds HL (**142**) by Ni(II) has been studied [292]. They bind in amino acid (didentate amine–carboxyl) fashion to give 1:1 complexes Ni(L) at low pH. At higher pH, complexes $[Ni(L)_2]$ and some $[Ni(L_{H-1})]$, with a deprotonated sugar hydroxyl group chelating, also form.

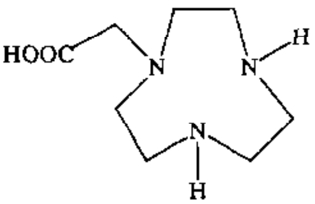
Detection of the binding of Ni^{2+} to specific complexation sites in human blood plasma albumin by single pulse 500 MHz ^1H NMR spectroscopy has been demonstrated [293]. The addition of $NiCl_2/D_2O$ to the plasma results in changes in peaks assigned to His εCH and δCH, and to other resonances due to lysine, consistent with the formation of a square planar (diamagnetic) complex involving these moieties. The binding of adenine nucleosides by sodium dodecylsulfate micelles, of interest in modelling lipid bilayer systems, can be detected by ^1H NMR; the ease of detection can be greatly enhanced by the presence of paramagnetic Ni(II) in the Stern layer around the micelles, which alters the rate of relaxation of the nucleoside protons [294]. Both Ni^{2+} and the nucleoside bind to the micelles.

Complexes of amine–sugars are described in section 6.9.4.

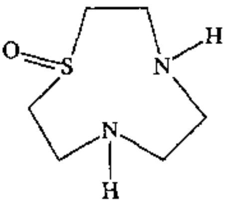
6.9.2 *Amine– and imine–carboxylates and related ligands*

The complex $[Ni(HL)_2(H_2O)_2]$ (H_2L = quinolinic acid [pyridine–2,3–dicarboxylic acid]) has been characterised crystallographically [295]. It is octahedral and centrosymmetric, with Ni(II) coordinated to the two pyridine nitrogens (Ni–N = 2.030(2) Å), two 2–carboxyl oxygens (Ni–O = 2.027(2) Å) and two *trans* water molecules (Ni–O = 2.117(2) Å). There are strong intramolecular H–bonds between the two carboxyl groups in each ligand. An unusual one–dimensional complex with a tripodal ligand acting as both a terminal and bridging ligand has been described [296]. This is $[Ni(L)(Him)]_n(ClO_4)_n$ (HL = $N(CH_2CH_2NH_2)_2(CH_2COOH)$), which X–ray crystallography reveals has a chain structure, with the carboxyl groups bridging along the *c* axis. The amine nitrogens have a *mer* arrangement and the two carboxyl oxygens coordinated to each Ni(II) are mutually *trans* and have the *syn, anti* bridging mode. The magnetic behaviour with temperature could best be described in terms of single–ion anisotropy; any ferromagnetism is very weak. On treatment of this complex in aqueous solution with more Him, a mononuclear complex, $[Ni(L)(Him)_2]ClO_4.H_2O$ was obtained. The crystal structure of this complex showed Ni(II) coordinated to two *cis* imidazoles, with the L^- amines coordinated *fac*, and the sixth site occupied by a unidentate carboxylate oxygen.

The crystal structure of the complex $[Ni(L)_2(H_2O)_2].H_2O$ (HL = 1–aminocyclohexanecarboxylic acid) has been determined [297]. The complex is octahedral, with *trans*–amine (Ni–N 2.054(7), 2.082(7) Å) and *cis*–carboxylate (Ni–O 2.059(4) Å) groups. The amines are in axial positions on the cyclohexyl rings. Another structure determined is that of $[Ni(L)(H_2O)_2](ClO_4)_2$ (L = 4,7–diazadecane–1,10–diamide) [298]. The Ni(II) here is coordinated to both amines (Ni–N 2.052(4), 2.072(4) Å) (*cis*), both amide oxygens (Ni–O 2.067(3), 2.038(4) Å) (*cis*) and two *trans* water molecules.



(143)



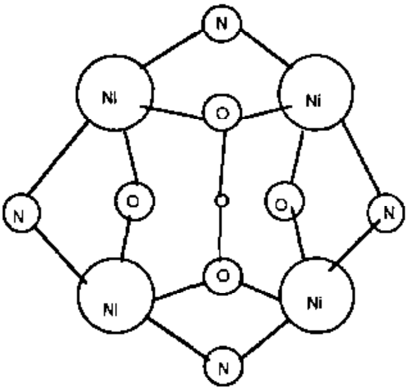
(144)

The stability constants of Ni(II) complexes with **(143)** (HL) have been determined potentiometrically [299]. Whereas for other metal ions, species $[M(L)]^{2+}$ and $[M(L)(OH)]^+$ were detected, for Ni(II) only $[Ni(L)]^{2+}$ (log *K* 17.85(3)) could be detected. The stability constant was 3 orders of magnitude bigger than those for related open–chain ligands. The coordination chemistry of the macrocycle **(144)** (L) and the related open–chain 3–thia–1,5–diaminopentane-*S*–oxide (L'), have been examined [300]. Complexes $[Ni(L')](PF_6)_2$ and $[Ni(L)](ClO_4)_2$ have been obtained, and their crystal structures determined. The former is octahedral, with *cis* O–bound S–O groups, the latter is also octahedral, but has *trans* O–bound S–O groups, and generally shorter metal–ligand bonds.

Finally, in this section mention should be made of some interesting complexes of ligands $[R_2P(O)NR']^-$ published this year. The complex $[Ni\{(^tBu)_2P(O)N^iPr\}_2]$ is very unusual in that it is paramagnetic, has an absorption band at 7300 cm^{-1} and yet is square planar. Now, two isomers of the complex $[Ni\{(^tBu)_2P(O)N(cyclo\text{–}C_6H_{11})\}]$ have been described [301]. One is an olive green solid, the diffuse reflectance spectrum of which is similar to that of planar $[Ni\{(^tBu)_2P(O)N^iPr\}_2]$, and crystallographic data confirm that this isomer is planar (Ni–N 1.900(1) Å, Ni–O 2.120(1) Å). The other is an ink–blue solid, and has diffuse reflectance bands at virtually the same energies as the planar isomer but with significantly greater intensities. The crystal structure of this isomer shows a distorted tetrahedral arrangement (Ni–N 1.945(2) Å, Ni–O 2.059(2) Å; the angle between the Ni–N–O planes for each ligand is 86.2°).

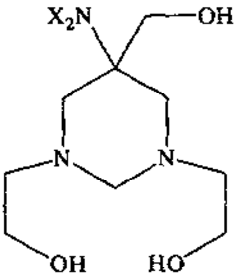
6.9.3 *Amine– and imine–alcohol and –ether ligands*

The first example of a tetranuclear Ni(II) complex with an end–on μ–azide bridge, $[Ni_4(\mu\text{–}N_3)_4(H_2NCH_2CH(O^-)CH_2NH_2)_2(H_2NCH_2CH(OH)CH_2NH_2)_2](ClO_4)_2$, has been characterised [302]. The four Ni(II) ions are related by an S_4 symmetry axis forming a quasi–perfect square. Both the azide ions (end–on) and the oxygen atoms of the amine ligands (hydroxy and hydroxyl) bridge the Ni(II) ions in the arrangement shown in (**145**). The remaining coordination sites at each Ni(II) are occupied by amine donors, one from each of two ligands. The complex is ferromagnetic, $J = +21.3$ cm^{-1}.



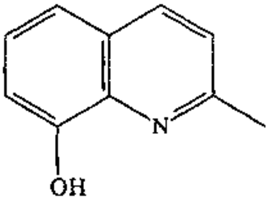
(**145**)

The reaction of Ni(II) ions, 2–aminoethanol, HCHO and CH_3NO_2 yields Ni(II) complexes of H_2L (**146**: X = O) [303], which can be isolated as blue $[Ni(HL)]^+$ or insoluble green [Ni(L)]. These, on the basis of electronic spectral data, are tentatively assigned tetrahedral stereochemistry, and since steric factors probably prohibit chelation of both amine donors, they may have $N(O)(OH)_2$ and $N(O)_2(OH)$ donor sets respectively, although polynuclear formulations are possible. Catalytic hydrogenation of the blue complex afforded Ni(II) complexes of H_2L' (**146**: X = H), one of which, $[Ni(H_2L')_2]ClO_4(CH_3CO_2)$, has been characterised crystallographically. The Ni(II) is coordinated by one of the tertiary amines, the pendant primary amine and one hydroxyethyl oxygen from each ligand. The tertiary amine donors are mutually *trans*.

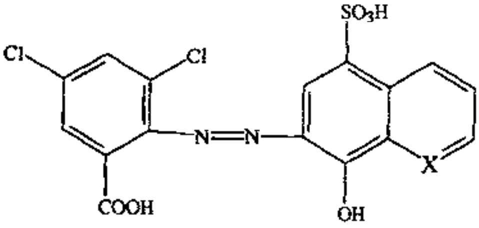


(146) X = O
X = H

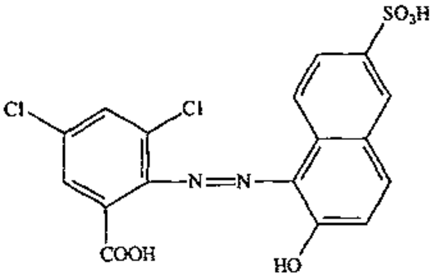
The chemistry of Ni(II) solvent extraction using 2-methyl-8-quinolinol [HL = (**147**)] has been studied [304]. From aqueous solutions of $NiSO_4$, chloroform solutions of the ligand extract Ni(II) predominantly as $[Ni_2(L)_2]$ and $[Ni_3(L)_3]$, but from $Ni(ClO_4)_2$ solutions ion-pair complexes $[Ni_3(L)_5(HL)]ClO_4$ and $[Ni_2(HL)_3(L)_3]ClO_4$ are extracted. The $[Ni_2(L)_2]$ is cleaved symmetrically by phen to give $[Ni(L)_2(phen)]$. X-Ray crystallography reveals that both $[Ni_3(L)_3].2C_2H_5OH$ and $[Ni_3(L)_5(HL)]ClO_4.C_2H_5OH$ have discrete bent trimeric structures, with all the Ni(II) ions octahedrally coordinated by two nitrogens, and phenolate oxygens (a total of two triply-bridging, two bridging and two terminal). The principal structural difference is the presence of a strong intramolecular hydrogen bond between the two phenolate oxygens not involved in bridging in $[Ni_3(L)_5(HL)]ClO_4.C_2H_5OH$. The presence of the 2-methyl group makes coordination of a third ligand to discrete Ni(II) ions less favourable, hence the formation of oligomeric oxygen-bridged species.



(147)

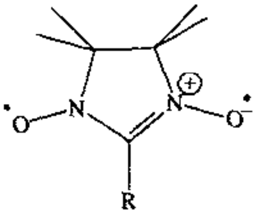


(148)



(149)

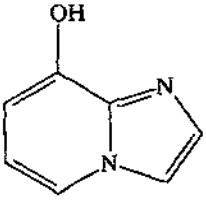
The ligands (**148**) have been synthesised and their complexation by Ni(II) examined [305]. Polarographic and electronic spectral data suggest that whereas Ni(II) complexes (**148**: X = N) only *via* the 8-quinolinolate moiety, the other ligands coordinate as tridentates *via* the quinolinolate and carboxyl oxygens and a nitrogen of the azo group.



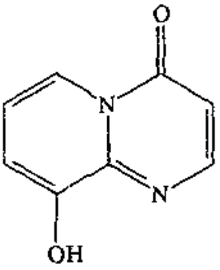
R = 2-pyridyl

(150)

Interest in ligands bearing nitroxide groups, for constructing molecular ferromagnets, continues. The crystal structure of a Ni(II) complex of 3-imidazoline nitroxide (HL), $[Ni_2(HL)_4]$, has been determined [306]. The ligand L (**150**) reacts with $NiCl_2$ in $EtOH/CH_2Cl_2$ to afford $[Ni(L)_2Cl_2]$, the crystal structure of which reveals that the molecule is centrosymmetric with *trans* chloride ligands (Ni–Cl = 3.397(10) Å), and L chelating *via* the pyridyl nitrogens (Ni–N 2.089(1) Å) and nitroxide oxygens (2.064(1) Å) [307]. The complex is less strongly antiferromagnetic than usual for Ni–nitroxide systems ($J = -110\ cm^{-1}$); the chelate ring reduces the degree of orbital overlap. With [Ni(hexafluoroacac)$_2$], the ligand reacts to form [Ni(hexafluoroacac)$_2$(L)], with L again chelating *via* the pyridyl nitrogen (Ni–N 2.073(4) Å) and nitroxide oxygen (2.029(3) Å). This complex is also antiferromagnetic ($J = -167\ cm^{-1}$).

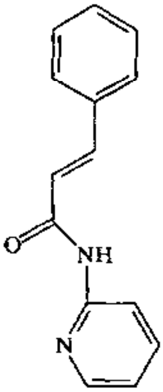


(151)

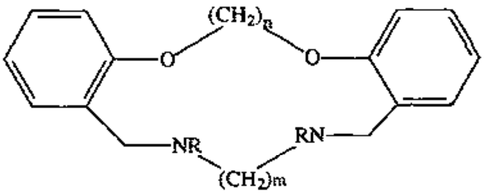


(152)

The coordination of ligands (**151**) and (**152**) (HL) to Ni(II) has been examined [308]. Both ligands bind *via* an oxine-type (N,O^-) donor set to give Ni(L) and $Ni(L)_2$ species. Ligand (**152**) forms considerably more stable complexes, probably because of a better-oriented lone pair on nitrogen. Use of the ligand 2-(2-pyridylmethyleneamino)phenol in analytical determination of Ni(II) by first derivative spectrophotometry has been proposed [309]. Octahedral Ni(II) complexes of 3-(2-hydroxynaphthyl)-5-(4-substituted phenyl)-2-pyrazoline have been isolated for a range of substituents and different anions [310]. With the ligand L (**153**), $Ni(NO_3)_2.6H_2O$ affords light blue $[Ni(L)_2(H_2O)_2](NO_3)_2.H_2O$, for which *cis* stereochemistry is suggested [311].



(153)



R = H, CH_2(2–pyridyl), CH_2CH_2OH,
$CH_2CH_2NEt_2$, CH_2CH_2Cl

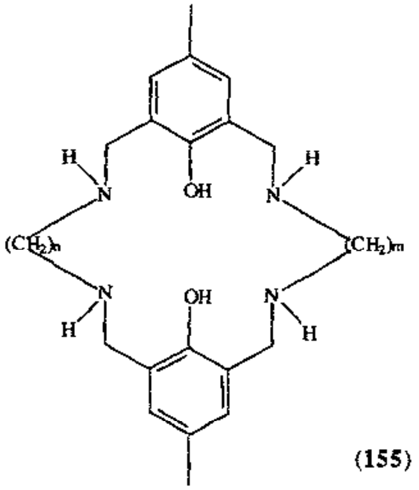
n = 2 or 3

m = 2,3 or 4

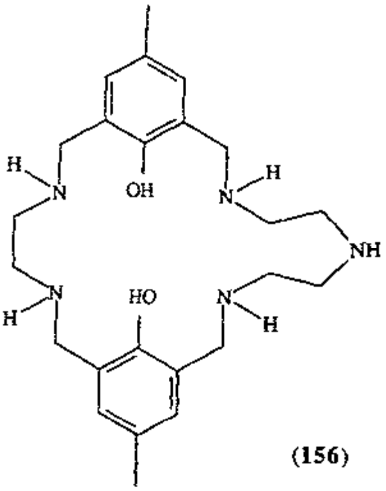
(154)

Turning now to macrocyclic ligands, the synthesis of a series of ligands (**154**) has been reported; many of the ligands were purified by isolation of purple complexes formulated $[Ni(L)(NO_3)]NO_3$, recrystallisation, and subsequent decomplexation with edta [312]. The complexation of the pendant arm ligand *N,N',N'',N'''*–tetrakis(2–hydroxyethyl)cyclam with Ni(II) has been examined [313]. The principal effect of the pendant arms is to labilise the complex to decomposition, when compared with cyclam. Some Ni(II) complexes of the dinucleating macrocycles (**155**) have been described [314]. When the previously–reported complex $[Ni_2(L)(MeOH)_2(ClO_4)_2].2Et_3NHClO_4$ (H_2L = (**155**); m = n = 3) is recrystallised from MeOH in the presence of urea, blue crystals form which X–ray crystallography showed are an inclusion compound $[Ni_2(L)(H_2O)_4](ClO_4)_2.4H_2NC(O)NH_2$. This is centrosymmetric; each Ni(II) is octahedrally coordinated by two amines, two bridging phenolates and two axial water molecules, and there is extensive H–bonding involving the ureas, perchlorate ions, waters and secondary amine protons. On treatment with pyridine, this complex forms square pyramidal $[Ni_2(L)(py)_2](ClO_4)_2$. For (L = (**155**); m = 2, n = 3), the complex $[Ni_2(L)(H_2O)_2]I_2$ was isolated. This has one octahedral Ni(II), in the cavity with the six–membered diamine fragment, and one square planar Ni(II) occupying the smaller cavity. The latter remains square planar on treatment with py, which affords the square pyramidal–square planar complex $[Ni_2(L')(py)]I_2$. Complexes of $Ni(OAc)_2$ with these ligands have also been described [315]. These are of general formula $[Ni_2(L)(OAc)_2]$ (n = m = 2, 3; n = 2, m = 4,5) and $[Ni_2(L)(OAc)(NCS)(CH_3OH)]$ (n = 2, m = 3). The complex $[Ni_2(L)(OAc)_2].10H_2O$ (n = m = 2) has both Ni(II) ions in an octahedral environment; the macrocycle adopts a *cis*, folded structure, and each Ni(II) is additionally coordinated to a didentate acetate ligand. Interestingly, the complexes are all ferromagnetic ($J = +2.1$ to $+10.1$ cm^{-1}).

A Cu(II)–Ni(II) complex of (**156**) (H_2L), $[CuNi(L)](ClO_4)_2$, has been made by transmetallation of the corresponding Cu(II)–Pb(II) complex, in which the Cu(II) occupies the 4–coordinate site and the Pb(II) templates the formation of the 5–coordinate site [316]. Therefore it is assumed that Ni(II) also occupies the 5–coordinate site. The complex is antiferromagnetic and, based on the Heisenberg model, J is calculated as -110 cm^{-1}. A preliminary report describes the

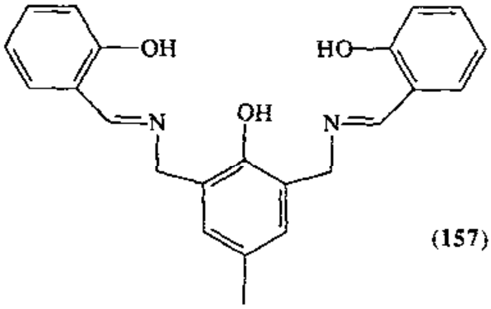


(155)

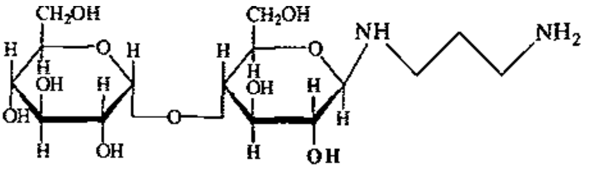


(156)

isolation of a tetranuclear complex, $[Ni_4(L)_2(pz)_2(CH_3OH)]$ (H_3L = (**157**), pz = pyrazolate ion) [317]. This has a zig–zag structure, with the outer two Ni(II) ions in square planar environments coordinated by a bridging pyrazolate, non–bridging and bridging phenoxide oxygens and an imine nitrogen. The inner two Ni(II) ions are in octahedral environments, connected *via* bridging pyrazolate and phenoxide ions to the outer Ni(II) ions, and to each other *via* the remaining two phenoxide ions and the MeOH; their coordination shell is completed by the remaining imine donors. The mixed spin state complex shows weak antiferromagnetism between the high–spin Ni(II) sites (J = −4.7 cm^{-1}). The tetra–imine analogue of (**155**) (n = m = 3) (H_2L) reacts with $Ni(OAc)_2$ in CH_3CN in the presence of PF_6^- to afford a green product, initially formulated $[Ni_2(L)(OAc)]PF_6$ [116]. The crystal structure revealed that this has, in fact, a tetranuclear structure, with each distorted octahedral Ni(II) coordinated to one compartmental N_2O_2 donor set from L^{2-}, a bridging acetate ion, and a phenoxy O–donor from the other half of the dimer. The four Ni(II) ions are disposed in a distorted tetrahedron.



(157)

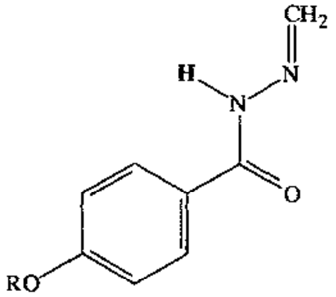


(158)

The reactions of glucose–containing disaccharides (maltose, lactose, cellobiose, melibiose) with $[Ni(tn)_3]X_2.2H_2O$ (X = Cl, Br) in MeOH have been studied [318]. The products are hygroscopic complexes of *N*–D–aldosylpropane–1,3–diamines (L = {for Glcα4Glc, maltose} (**158**)), pseudo-octahedral $[Ni(L)_2]X_2$. The crystal structure of $[Ni(Glc\alpha4Glc\text{–}tn)_2]Br_2.2H_2O$ confirms that the ligands bind *via* both amine nitrogens and the hydroxyl group shown in bold, in a *mer* geometry. The glycosylamine link is β. X–Ray absorption near–edge spectra, and other spectroscopic data, suggest that the other complexes are probably isostructural. A related paper describes the reactions of aldohexoses with $[Ni(tn)_3]X_2.2H_2O$ (X = Cl, Br) [319]. The products are again pseudo-octahedral $[Ni(L)_2]X_2$ with the ligands binding *via* both amine nitrogens and a sugar hydroxyl group. The crystal structure of $[Ni(L\text{–}Rha\text{–}tn)_2]Br_2.2H_2O.MeOH$ shows a very similar arrangement to that of $[Ni(Glc\alpha4Glc\text{–}tn)_2]Br_2.2H_2O$. Some complexes of the aminoglucoside antibiotic kanamycin have been described, including a $NiSO_4$ derivative assigned the formula $[Ni_2(kanomycin)(SO_4)_2(H_2O)_2].H_2O$ [312].

6.9.4 *Schiff's base and related ligands*

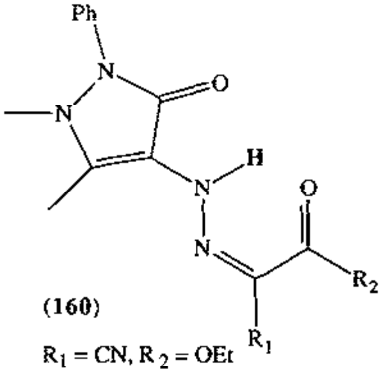
Four–coordinate Schiff base complexes (including those of nickel) have been reviewed [321]. Complexes of a range of dialkyl α–hydroxyiminophosphonates have been prepared; the crystal structure of one example, $[Ni(L)_2Cl_2]$ (L = diethyl *E*–(α)–hydroxyiminopropanephosphonate) shows distorted octahedral coordination at Ni(II), with two symmetry–related didentate L [322]. The complex $[Ni(L)_2]$ (where HL is the unsymmetrical tridentate Schiff's base derived by successive condensation of *o*–phenylenediamine with



(159)

R = C_6H_{13},

$C_{10}H_{21}$ or $C_{12}H_{25}$



(160)

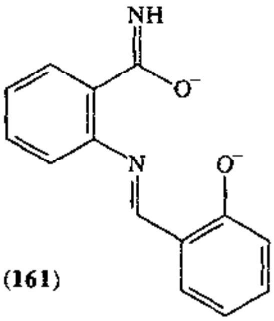
R_1 = CN, R_2 = OEt

or R_1 = C(O)Me, R_2 = Me

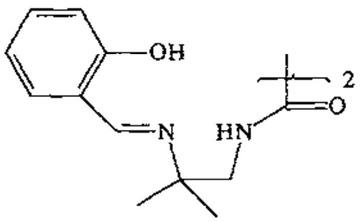
furfuraldehyde and salicylaldehyde) has been described [323]. The complex [Ni(L)] (where H_2L is the tetradentate Schiff's base derived from condensation of *o*–phenylenediamine with 2 equivalents of salicylaldehyde) has been investigated as a catalyst for olefin epoxidation under phase transfer conditions [324].

Aroylhydrazones HL (**159**) (the protons in bold are lost on complex formation) form square planar complexes $[Ni(L)_2]$, with the ligand coordinated as the enolate tautomer. These form smectic C and nematic liquid crystalline phases at elevated temperatures [325]. The ligands acetylacetone–*bis*–benzoylhydrazone $(PhC(O)NHN{=}CMe)_2CH_2$ and –*bis*–isonicotinoylhydrazone $(NC_5H_4C(O)NHN{=}CMe)_2CH_2$ react with $Ni(OAc)_2$ in EtOH to afford square planar [Ni(L)], with the Ni(II) coordinated to the imine nitrogens and enolate oxygens [326]. Two complexes of stoichiometry $Ni(L)_2.H_2O$ have been described, where HL is FcC(Me)=NNHC(O)R (R = 3–pyridyl or 4–pyridyl). While IR spectroscopic data suggest these are coordinated in the enolate form, the coordination geometry is uncertain; although orange, the colour is probably due to the ligand, and the complexes are paramagnetic in dmso solution [327]. The ligands HL (**160**) react with $Ni(OAc)_2.4H_2O$ in $EtOH/H_2O$ to form octahedral $[Ni(L)_2]$, for which *fac* geometries are proposed [328].

On the basis of ^1H NMR and IR spectroscopic data, the ligand L^{2-} (**161**) is thought to bridge *via* the enolate oxygen in the square planar, diamagnetic complex $[Ni_2(L)_2]$ [329]. A series of octahedral complexes $[Ni(HL)_2(L')]$ (H_2L = 2–pyrrole–[*N*–(*o*–hydroxy–aryl)methylimines], aryl = C_6H_5, 5–ClC_6H_4, 5–MeC_6H_4, 4–MeC_6H_4, 3,5–$Me_2C_6H_3$; L' = phen or (aryl = 5–MeC_6H_4) bpy) has been made by oxidation of a sacrificial Ni anode in the presence of H_2L and L' [330]. These were soluble in polar solvents, and the crystal structure of $[Ni(HL)_2(L')].2/3H_2O.2/3CH_3CN$ (L' = bpy, aryl = 5–MeC_6H_4) was obtained. The asymmetric unit contains one and a half independent molecules, each with similar coordination. The Ni(II) is coordinated to the phenolic oxygen and imine nitrogen of two didentate Schiff base monoanions, and to a didentate bpy. The pyrrole nitrogen is therefore not involved in coordination. The oxamide ligand H_4L (**162**) has been synthesised, together with the complex $[Ni_2(L)]$, which is diamagnetic and planar [331]. Unlike earlier complexes of dinucleating oxamide ligands, this example is soluble. Some new polystyrene–supported complexes have been described, made by treatment of the pre–formed polystyrene–anchored ligand (**163**) [332]. The Ni(II) complex isolated had stoichiometry NiL.3dmf, and magnetic measurements and electronic spectroscopy confirm that the complex is octahedral.



(161)

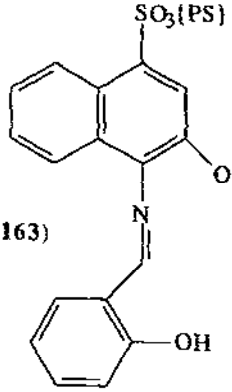


(162)

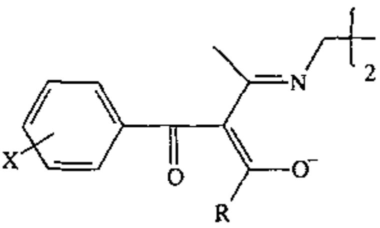
The complexes [Ni(L)] (H_2L = (**164**)) have been prepared, and their structure and dynamics in $CDCl_3$ solution explored using ^1H and ^{13}C NMR spectroscopy [333]. The benzoyl groups are forced perpendicular to the coordination plane by interaction with the R and Me groups.

Complexes of the ligands *N,N'*–(–R–)bis(1,1,1–trifluoro–6–methyl–2–oxoheptan–4–imine) (–R– = ethylene, propylene), including the square planar neutral Ni(II) complex, can be separated by reversed–phase HPLC [334].

Structural studies of macrocyclic and other Schiff base complexes of Ni(II) continue. A crystal structure of a five–coordinate complex [Ni(L)(H_2O)] (H_2L = bis(salicylidene)–1,3–diaminopropane) has appeared [335]. The two halves of the ligand are folded with respect to each other, giving an 'umbrella' shape. The structures of three complexes of Schiff base–ether ligands have been published [336].



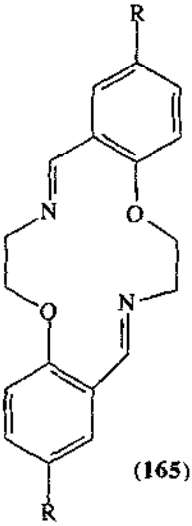
(163)



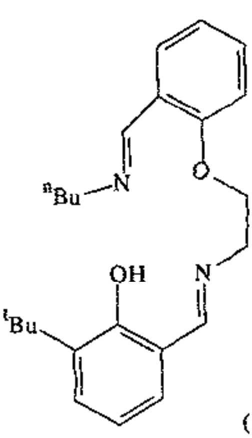
X = H, 3,5–$(NO_2)_2$, R = $CH_2CH_2CHMe_2$

X = H, 3–NO_2, 3,5–$(NO_2)_2$, R = $(CH_2)_3CHMe_2$

(164)



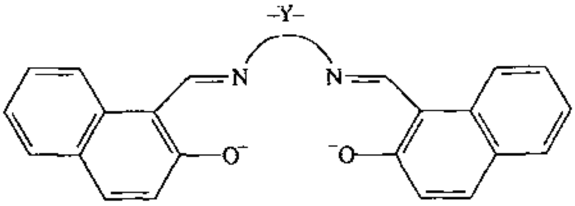
(165)



(166)

In the pseudo-octahedral complex [Ni(L)(NCS)$_2$] (L = (**165**); R = H), the ligand is folded, the isothiocyanate ligands and the imine nitrogen ligands are *cis* and the ether oxygens are mutually *trans*. In contrast, in [Ni(L)Br$_2$] (R = Me), the geometry is all-*trans*. The complex with a similar but partially-cyclised ligand, [Ni(L')I], [HL = (**166**)] has a distorted trigonal bipyramidal geometry with the iodine (Ni–I 2.646(2) Å) and nitrogen (Ni–N 2.02(1) Å) donors equatorial and the oxygen donors (Ni–O[phenoxide] 1.937(9) Å, Ni–O [ether] 2.163(9) Å) axial.

Turning now to redox properties of complexes of this type, the electrochemistry of square planar complexes [Ni(L)] [H$_2$L = (**167**)] in dmso solution have been studied [337]. The complexes undergo quasi-reversible one-electron oxidations at +0.6 – +0.9 V. ESR spectra of the electrochemically-generated oxidised species are consistent with a Ni(III) $(dz^2)^1$, *trans*-[Ni(L)(dmso)$_2$]$^+$ formulation. The crystal structure of [Ni(L)] (H$_2$L = (**167**); R = Me) shows a novel packing arrangement, with significant interaction of neighbouring naphthyl moieties.

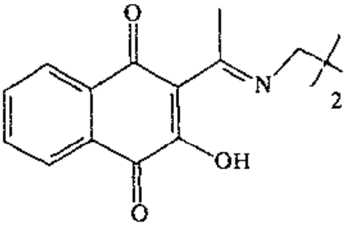


–Y– = –CR$_2$CR$_2$; R = H or R = Me

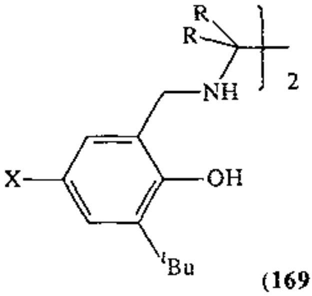
–Y– = –CH$_2$CH$_2$CH$_2$–

(**167**)

The novel redox-active Schiff base ligand H$_2$L (**168**) has been synthesised, the fully-reduced form of which could in principle provide four electrons and four protons in electrocatalytic reactions (for example, O$_2$ reduction to H$_2$O) [338]. The free ligand undergoes two one electron reductions at –0.903 and –1.065 V, as the bis(semiquinone) form is generated, and further reduction at ≤ –1.565 V to the naphthalenediolate. In CH$_2$Cl$_2$, the complex [Ni(L)] (quinone form) underwent reduction to the bis(semiquinone) form at about the same potentials as the free ligand.

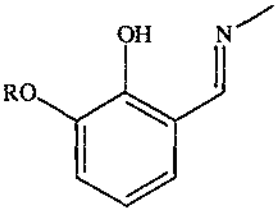


(**168**)



(**169**)

When the complexes [Ni(L)] (H_2L = (**169**); R = H, X = H, Cl, Me) are exposed to oxygen, only one of the two benzyl C–N bonds undergoes oxidative dehydrogenation to form an imine, probably *via* Ni–O_2 species. A study of 3d metal complexes including [Ni(L)] (H_2L = (**169**); R = H, Me; X = H, Cl, Me; also corresponding di–imine ligands) has been reported, in an attempt to shed more light on this system [339]. The complexes are weakly paramagnetic at room temperature. With the saturated ligands, the Ni(II) complexes undergo reversible one–electron oxidation and reduction, but with the imine ligands only the reduction process is reversible. While the Cu(II) complexes of the amines did not react with oxygen, in solution the Ni(II) complexes were oxidised to give the half–Salen complexes as noted before, while the Co(II) complexes were fully oxidised to Co(II)–Salen derivatives. With H_2O_2, the Ni(II) complexes reacted faster, and were eventually fully oxidised to Ni(II)–Salen derivatives. The complex [Ni(Salen)] has been studied as an electrocatalyst for the reduction of $PhCHCl_2$ at Pt electrodes in dmf; products include toluene, dibenzyl and *trans*–stilbene [340].



R = Me, CH_2CH_2OMe

(**170**)

When the methoxy– or methoxyethoxy–substituted salicylaldimine (**170**) reacts with $Ni(OAc)_2$ or $NiSO_4$ in MeOH (2:1 mole ratio), conventional Ni(II) square planar complexes $[Ni(L)_2]$ form [341]. However, the methoxyethoxy–substituted complex can react further with $Ni(OAc)_2$ in MeOH to give a trinuclear aggregate, $Ni_3(L)_4(OAc)_2(H_2O)_5$. The Ni(II) ions are octahedrally–coordinated, and two of the methoxyethoxy side–arms are involved in coordination. When the Ni(II) complex of the methoxy–substituted ligand is allowed to react with sodium picrate in chloroform/acetone, another cluster species, of stoichiometry $Ni_2(L)_4(NaPic)_2.H_2O$ can be isolated. Again, the Ni(II) is octahedral. The alkoxy arms do not exclusively bind sodium ions; one is coordinated to Ni(II), and one is uncoordinated. The sodium ions are coordinated by phenolate oxygens from picrate, nitro group oxygens from picrate, water and bridging phenolate oxygens from the salicylaldimine moieties in addition to the alkoxy oxygens.

The thermodynamics of additional ligand binding by planar bis(*N*–ethyl–n–nitrosalicylaldiminato)nickel(II) (n = 3, 5), bis(*N*–propyl–5–nitrosalicylaldiminato)nickel(II) and bis(*N*–ethyl–3–nitro–5–tertiarybutylsalicylaldiminato)nickel(II) in acetone have been studied [342]. Also examined were the ligand displacement reactions of these complexes with salenH_2 and the corresponding diamine ($[H_4]$salenH_2). These reactions proceed *via* a six–coordinate Ni(II) complex with the nitrogen donors of the incoming tetradentate coordinated to Ni(II). Finally, the reactions of the deprotonated diamide complex $[Ni(L)]^{2-}$ (L^{4-} = *N,N'*–ethylenedisalicylamidato) with edta and *trans*–cyclohexane–1,2–diamine–*N,N',N'',N'''*–tetraacetic acid have been studied [343]. The pH–dependence of the reactions suggest that the diprotonated complex [Ni(L)] is an intermediate.

6.10 COMPLEXES WITH PHOSPHINES AND RELATED LIGANDS

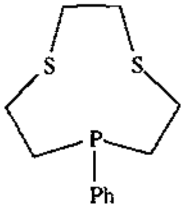
6.10.1 Ligands with a single phosphine donor

Upon recrystallisation of tetrahedral $[NiCl_2(PPh_3)_2]$ from CH_2Cl_2, red crystals of the square planar solvate $[NiCl_2(PPh_3)_2].2CH_2Cl_2$ can be obtained; the crystal structure of this isomer has been determined [344]. The bond lengths (Ni–Cl 2.163(5) Å, Ni–P 2.241(6) Å [centrosymmetric]), particularly Ni–P, are shorter than those in the tetrahedral isomer. The treatment of surface OH groups on the layer silicate hectorite with Ph_2PCl gives anchored $Ph_2PO–Si$ moieties, to which $NiCl_2$ can be coordinated [345].

The reactions of Ni powder with R_3PX_2 in dry ether give a variety of complexes depending on R and X [346]. When R = alkyl (not Me) and X = I, Ni(II) complexes of stoichiometry $[R_3PI][NiI_3(PR_3)]$ are isolated, which, on the basis of electronic spectroscopic measurements, the fact that ^{31}P NMR signals could be resolved, and the fact that powder patterns were not isomorphous with the tetrahedral $[R_3PI][CoI_3(PR_3)]$, were assigned square planar geometry. This is unusual in view of the apparently rather weak donor set, and the fact that crystal structures of $[Ph_4As][NiI_3(PPh_3)]$ and of $[Bu_4N][NiBr_3(P^tBu_3)]$ show these examples to be tetrahedral. When R = Me and X = I, the trigonal bipyramidal Ni(III) complex $[NiI_3(PR_3)_2]$ is obtained. When Me_2PhPI_2 is employed, a mixture of the corresponding Ni(III) complex and Ni(II) anion are obtained. For compounds R_3PBr_2, no reaction occurred for trialkyl derivatives. However, with $PhMe_2PBr_2$, a mixture of the known square planar $[NiBr_2(PPhMe_2)_2]$ and a blue complex of stoichiometry $NiBr_4(PPhMe_2)_2$ form. The latter is assigned as $[Me_2PhPBr]_n[Ni(PPhMe_2)Br_3]_n$ with polymeric (bromide–bridged) octahedral anions, on the basis of the low observed molar extinction coefficients.

Treatment of $[NiX_2(PR_3)_2]$ (X = Cl, Br; $R_3 = Ph_3, Et_3, PhMe_2$) with LiPhNNNPh affords only decomposition products when $R_3 = Ph_3$, but $[NiX(PhNNNPh)(PR_3)_2]$, with a monodentate azenido ligand, in the other cases [347]. Didentate, azenido–bridged complexes $[\{Ni(\mu–PhNNNPh)(PR_3)_2\}_2]$ form when these complexes are treated with $AgClO_4$. Chelate complexes $[Ni(mesityl)(PhNNNPh)(PR_3)]$ could be isolated on treatment of $[NiX(mesityl)(PR_3)_2]$ with LiPhNNNPh ($R_3 = Ph_3, (PhCH_2)_3$). Reactions of $[NiX_2(PR_3)_2]$ with LiPhNC(Ph)NPh did not yield any isolable product. The reaction of $[NiCl_2(Me_2PhP)_2]$ with *nido*–7,8–$As_2B_9H_9{}^{2-}$ ion gives a mixture of the icosahedral 1,1–$(Me_2PhP)_2$–*closo*–1,2,3–$NiAs_2B_9H_9$ and 1–Cl–1,5–$(Me_2PhP)_2$–*closo*–1,2,3–$NiAs_2B_9H_8$ [348]. The complexes $[Ni\{S_2C_2(CN)_2\}(PR_3)_2]$ ($PR_3 = PMePh_2$, P^nBuPh_2) have been synthesised by ligand exchange with $Ni\{S_2C_2(CN)_2\}(PPh_3)_2]$, and their one–electron reduction products characterised by ESR spectroscopy as Ni(I) species [349].

Turning now to Ni(II) complexes of hybrid ligands containing one phosphine donor, the reaction of *trans*–$[Ni(SCH_2CH_2PPh_2)_2]$ with $[Mo(norbornadiene)(CO)_4]$ gives the thiolate–bridged complex $[Ni(\mu–SCH_2CH_2PPh_2)_2Mo(CO)_4]$, the crystal structure of which shows that rearrangement to the *cis* form at Ni(II) has occurred [350]. The dihedral angle defined by the NiS_2 and MoS_2 planes is the smallest yet found (103.4°) and this places one of the carbonyl ligands in quite close proximity to an axial site at Ni(II). The nickel coordination sphere of the highly active alkene isomerisation catalyst formed when $Ph_2PCH_2C(CF_3)_2OH$ is added to [Ni(1,5-cyclooctadiene)$_2$] has been characterised, using ^1H and ^{31}P NMR spectroscopy and *in situ* Ni K-edge extended X-Ray absorption fine structure (EXAFS) measurements, as [NiH($Ph_2PCH_2C(CF_3)_2O$–*O,P*)($Ph_2PCH_2C(CF_3)_2OH$–*P*)] [351]. An interesting phosphine-containing macrocycle, L (**171**), has been synthesised and the complex $[Ni(L)_2]^{2+}$ isolated [352]. By comparison with the Ni(II) complex of 1,4,7–trithiacyclononane, substitution of the third thioether by phenylphosphine results in a less positive potential for the Ni(II)/Ni(III) couple (by 0.70 V), but interestingly a marginally less negative potential for the Ni(I)/Ni(II) couple (by *ca.* 0.1 V) as well.



(171)

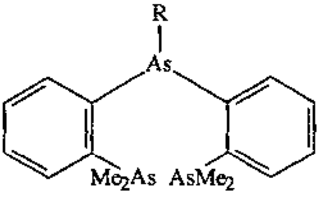
Several papers describe Ni(0) complexes of phosphine ligands this year. The structure of the first nickel–halogeniminophosphine complex, $[Ni(PEt_3)_2(Cl–P=NAr)_2]$ (Ar = 2,4,6–tri*tert*–butylphenyl), has been obtained; the complex is almost perfectly tetrahedral with the chloroiminophosphine η^1–bonded as a consequence of its carbene–like frontier orbitals [353]. Some reactions of this and related complexes are described. In contrast, the reaction of (diisopropylamino)phosphaethyne with $[Ni(CO)_3(P\{C_6H_{11}\}_3)]$ affords the 16e Ni(0) complex $[Ni\{\eta^2–PCN(^iPr)_2\}(CO)(P\{C_6H_{11}\}_3)]$ [354]. The complexes $[Ni(PPh_3)_3(\eta^1–NCR)]$ (R = $PhCH_2$, 2–MeC_6H_4, Me_3Si) have been synthesised, and the crystal structure of one example (R = Me_3Si) obtained [355]. The structure of $[Ni(PEt_3)_4]$ has been determined, surprisingly the first of a homoleptic Ni(0)–trialkylphosphine complex. Crystals of the latter were obtained serendipitously, on recrystallising the product of reaction between $[NiCl_2(PEt_3)_2]$ and lithium 2–bis(trimethylsilyl)methylpyridine. There are distortions from overall tetrahedral geometry (Ni–P 2.210(1), 2.151(1) Å; C_{2v} symmetry) caused by the steric requirements of the ligand (cone angle 132°) [356]. The use of $[Ni\{P(CH_2OH)_3\}_4]$ as a catalyst for the hydrophosphination of formaldehyde to afford $P(CH_2OH)_3$ has been examined [357].

The FTIR and Raman spectra of $[Ni(CO_2)(P\{C_6H_{11}\}_3)_2]$ have been assigned with the aid of $^{13}CO_2$ and $C^{18}O_2$ labelling, normal coordinate analysis and NMR data. It is suggested that the fluxional behaviour, and the fact that two 'C–O' stretches (1150, 1093 cm^{-1}) are seen, can best be explained by the existence of an unstable end–on $Ni(\eta^1–CO_2)$ isomer in both the solid state and solution [358].

The bonding in the unique $[Ni(P^tBu)_6]$, in which Ni lies at the centre of a near–planar hexagon of P^tBu moieties, has been investigated theoretically, using extended Hückel and *ab initio* calculations [359]. This complex could be regarded as essentially a 16e Ni(0) species, with three of the six P–P σ–bonds interacting with the central Ni atom. The calculations also suggest that isolobal analogues $[Ni(R_2Si)_6]$ might be worthwhile targets for synthesis.

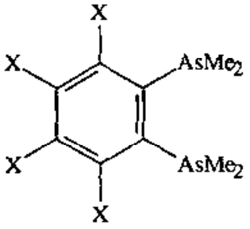
6.10.2 Di– and multidentate phosphine donors

A range of five–coordinate mixed Ni(II)–arsine complexes of the ligands (**172**)–(**174**) of formula $[Ni(L_3)(L_2)]^{2+}$ (L_3 = tridentate, L_2 = didentate; perchlorate or tetrafluoroborate salts), together with the homoleptic $[Ni(L_3)_2]^{2+}$ which are five coordinate with a single 'dangling' $-AsMe_2$ group, have been the subject of an electrochemical study [360]. All complexes showed two oxidations and two reductions in CV experiments in CH_3CN. The second oxidation process was only reversible (at 100 mV s^{-1}) for $[Ni(L_3)_2]^{2+}$, and scan rates in excess of 500 mV s^{-1} or temperatures $\leq 0°$ C were necessary to obtain reversible behaviour for this process with $[Ni(L_3)(L_2)]^{2+}$. The rates of the first oxidation process, and the second reduction process, were slower than the other processes. The second process is irreversible in CH_2Cl_2 for $[Ni(L_3)(L_2)]^{2+}$, presumably because of the need to coordinate a sixth donor atom to stabilise the formally low–spin d^6 Ni(IV). The reductions are assigned to Ni(I)/Ni(II) and Ni(0)/Ni(I) couples; the relative stability of the five–coordinate Ni(I) complex with these ligands makes an interesting contrast with $[Ni(diars)]^{2+}$ which is reduced to Ni(0) in a single two–electron process. Thus, these arsine donor sets stabilise (on the voltammetric timescale) all Ni oxidation states from (0) to (IV). Protonation of $[Ni(dmpe)_2]$ with NH_4PF_6 in thf affords $[Ni(H)(dmpe)_2]PF_6$, which can also be made electrochemically by two–electron reduction in the presence of NH_4^+ [361]. The hydride reacts with metal-carbonyl complexes to generate metal–formyl species.



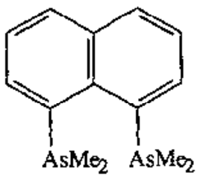
(R = Ph, Me)

(**172**)



(X = H or F)

(**173**)

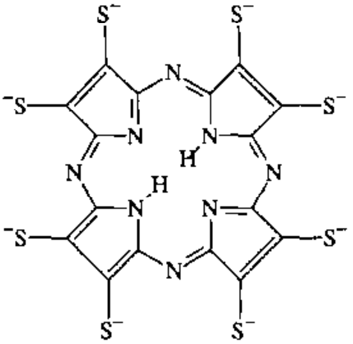


(**174**)

The complex $[NiCl_2(dppm)_2]$, first made in 1966 and presumed to be square planar with monodentate dppm ligands, has been characterised crystallographically, and shown to be $[NiCl_2(\eta^2$–dppm)(η^1–dppm)] in the solid state [362]. The geometry is intermediate between square pyramidal and trigonal bipyramidal. However, in solution the NMR and electronic spectral data are not consistent with this structure and it is clear that different species are present at different concentrations; the solution chemistry of the $NiCl_2$–dppm system is complex. The complexes $[Ni(CO)_2(\eta^1$–dppm$)_2]$, $[Ni_2(\mu$–dppm$)_2(\mu$–CO)(CO$)_2]$ and $[Ni_2(\mu$–dppm$)_2(CO)_4]$ have all been isolated by minor modifications of the same synthetic procedure, BH_4^- reduction of a solution of $NiCl_2.6H_2O$ and dppm in MeOH under CO [363], and are interconvertible in solution. Reaction of CO with $[Ni(CO)_2(\eta^1$–dppm$)_2]$ gives $[Ni(CO)_3(\eta^1$–dppm)]. The cluster $[Ni(\mu_3$–I$)_2(\mu$–dppm$)_3]$, synthesised by comproportionation of $[Ni(1,5\text{-cyclooctadiene})_2]$, NiI_2 and dppm, is oxidised reversibly to $[Ni(\mu_3\text{-}I)_2(\mu\text{-dppm})_3]^+$ at –0.69 V [364]. Both complexes have been characterised crystallographically; they are structurally similar, with triangles of Ni atoms bridged by dppm ligands and capped by the two I^- ions. The Ni–Ni bonds are somewhat longer in the cation. Interestingly, the neutral complex reduces CO_2 in the presence of light to give $CO_2^{\cdot -}$, which has been trapped by its reaction with cyclohexene.

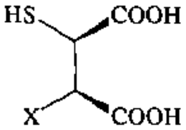
The reaction of $LiPh_2PYPPh_2$ (Y = CH, N) with $[NiX_2L_2]$ (X = Cl, Br; L = PPh_3, PMe_2Ph, PEt_3) has been examined [365]. Only with Y = N and L = PEt_3 could a stable mononuclear product be obtained, $[NiX(Ph_2PNPPh_2)(PEt_3)]$. With the PPh_3 and PMe_2Ph complexes, only $[\{Ni(\mu\text{-}Cl)(Ph_2PNPPh_2)\}_2]$ formed. The reaction of $LiPh_2PNPPh_2$ with $NiCl_2$ in toluene under prolonged reflux gives a complex $[Ni(Ph_2PNP(Ph)_2NPPh_2)_2]$, together with $N(PPh_2)_3$, Ni metal and LiCl [366]. The complex is intermediate between square planar and tetrahedral geometry (Ni–P 2.219(3), 2.270(3), 2.236(3), 2.272(3) Å; P–Ni–P angles 87.2(1)°, 96.2(1)°, 146.2(1)°, 148.2(1)°), but is essentially diamagnetic.

The structures of $[Ni(NCS)_2(Et_2PCH_2CH_2PPh_2)]$ and $[Ni(NCS)_2\{Ph_2PCH_2CH_2)_2P(Et)\}]$ have been determined [367]. The former is square planar with N–bonded thiocyanate (Ni–N 1.876(3), 1.885(2) Å, Ni–P 2.1413(8), 2.145(1) Å), the latter square pyramidal, with N–bonded thiocyanate (Ni–N_{axial} 2.088(7) Å, Ni–N_{basal} 1.896(6) Å; Ni–P 2.223(2), 2.150(2) (PEt), 2.189(2) Å). The photolysis of $[Ni(N_3)_2(P\text{–}P)]$ (P–P = dppe, dppp) has been studied. In contrast with the analogous Pd and Pt complexes, no luminescense from the photoproduct $[Ni^0(P\text{–}P)]$ was observed [368].


(175)

Some mixed phosphine–dithiolate complexes have been described. The porphyrazine complex $[Ni(\mathbf{175})]^{8-}$ reacts with $[NiCl_2(dppe)]$ to afford $[Ni(dppe)]_4[Ni(\mathbf{175})]$, with the Ni(dppe) moieties additionally coordinated by chelating $^-SC{=}CS^-$; the porphyrazine *m*–nitrogen atoms are not involved in coordination [369]. A better route to this complex is transmetallation of $[{}^tBu_2Sn]_4[Ni(\mathbf{175})]$ with $[NiCl_2(dppe)]$ in dmso/thf. The latter route has also been employed for the analogous complexes $[NiCl_2(P\text{–}P)]$ (P–P = *cis*–$Ph_2PCH{=}CHPPh_2$, 1,2–$(Ph_2P)_2C_6H_4$, $(C_6H_{11})_2PCH_2CH_2P(C_6H_{11})_2$). The syntheses and electrochemistry of $[Ni(S_2C_2R_2)(P\text{–}P)]$ (R = CN, Ph; P–P = *cis*–$Ph_2PCH{=}CHPPh_2$, 1,2–$(Ph_2P)(PRPh)C_6H_4$ (R = Me, ^{n}Bu), 1,2–$(PhMeP)_2C_6H_4$) and of diphosphine–bridged $\{[Ni(S_2C_2R_2)(P\text{–}P)]\}_2$ (P–P = *trans*–

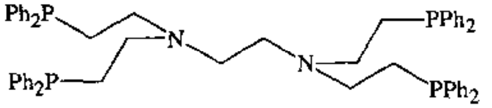
$Ph_2PCH{=}CHPPh_2$, *trans*–PhMePCH=CHPMePh) have been described [349]. Redox products were characterised using ESR spectroscopy. The results show that the first reduction product is a Ni(I) species, but the first oxidation process is primarily ligand–based, affording a Ni(II)–stabilised phosphine radical cation.



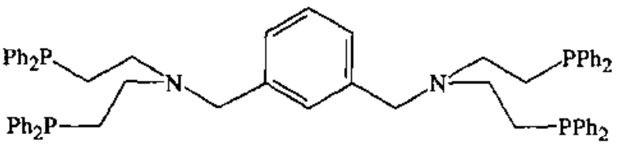
X = HS: **(176)**
X = H: **(177)**

The complexes [Ni(dppe)(H_2L–*S,S'*)] (H_4L = **(176)**) and [Ni(dppe)(HL–*S,O*)] (H_3L = **(177)**) have been synthesised and the reactions of sodium 2,3–dimercaptopropanesulfonate, sodium 1–thio–b–D–glucopyranosate and dithiothreitol with [NiX_2(dppe)] (X = Cl, Br) have been investigated using ^{31}P NMR spectroscopy [370]. The conformations of the chelate rings have been explored using ^1H–^1H coupling constants. The amphiphilic thiolates allowed many of the Ni(II)–dppe complexes to dissolve in water. The asymmetric cross coupling of aryl magnesium bromides with crotyl alcohol derivatives, catalysed by [Ni(P–P)Br_2] (P–P = *trans*–bis–1*R*,2*R*–(diphenylphosphino)cyclopentane, or the 1*S*,2*S*–isomer), has been studied by ^{31}P NMR spectroscopy and circular dichroism [371]. Complexes observed by ^{31}P NMR include [Ni(P–P)Br(Ar)], [Ni(P–P)$(Ar)_2$] and [Ni(P–P)].

Sodium dithiocarbamate reacts with the mixed–valent adamantoid cage complex $Mo(CO)_4[^iPr_2NPO]_4Mo(CO)_2I_2$ and selectively removes the Mo(II) centre, affording the complex $Mo(CO)_4[^iPr_2NPO]_4$, with two uncoordinated –O–P($^iPr_2N$)–O– moieties in the $[^iPr_2NPO]_4$ ring. On reaction with $NiBr_2$.dimethoxyethane in refluxing hexane, the heterodimetallic complex $Mo(CO)_4[^iPr_2NPO]_4NiBr_2$ is formed [372]. The crystal structure of this complex shows the Ni(II) in a tetrahedral environment, consistent with the magnetic data. Coordination of other metal centres to the cage modulates the CO stretching frequencies of the *cis*–$Mo(CO)_4$ fragment, showing that there is some transmission of electronic effects via the cage atoms.



(178)



(179)

Finally, some Ni(II) complexes of the ligands L (**178**) and L′ (**179**) have been described [373]. With $NiCl_2$, both L and L′ afford the complex $[Ni_2(L^{(\prime)})Cl_2]^{2+}$, isolated as the BPh_4^- salts. With $Ni(ClO_4)_2$, L affords $[Ni(L)](ClO_4)_2$, while L′ affords $[Ni_2(L')(H_2O)_2](ClO_4)_4$, which on recrystallisation gives $[Ni(L')](ClO_4)_2$. The crystal structure of $[Ni(L)](ClO_4)_2.CH_2Cl_2$ shows the Ni(II) ion in a slightly distorted square planar environment, coordinated by two phosphine and two tertiary amine donors. There is one free phosphine–bearing substituent attached to each amine. The dinuclear complexes are diamagnetic, and square planar structures are proposed in which each Ni(II) is coordinated by one half of the hexadentate ligand (two phosphines and the tertiary amine), with the water or halide ligand completing the coordination sphere.

REFERENCES

1. J.P. Zebrowski, R.K. Hayashi and L.F. Dahl, *J. Am. Chem. Soc.*, 115 (1993) 1142.
2. P. Gans, J.B. Gill and L.H. Johnson, *J. Chem. Soc., Dalton Trans.*, 1993 345.
3. A.J. Kim and L.G. Butler, *Inorg. Chem.*, 32 (1993) 178.
4. K.–M. Park and T. Iwamoto, *J. Chem. Soc., Dalton Trans.*, (1993) 1875.
5. S.H. Ashworth, F.J. Grieman, J.M. Brown, P.J. Jones and I.R. Beattie, *J. Am. Chem. Soc.*, 115 (1993) 2978.
6. J.C. Fitzmaurice, A.M.Z. Slawin, D.J. Williams and J.D. Woollins, *J. Chem. Soc., Chem. Commun.*, (1993) 1479.
7. P.B. Hitchcock, K.R. Seddon and T. Welton, *J. Chem. Soc., Dalton Trans.*, (1993) 2639.
8. D. Ferry, G. Picard and Y. Castrillejo, *J. Appl. Electrochem.*, 23 (1993) 735.
9. E. Lopez–Salinas, N. Tomita, T. Matsui, E. Suzuki and Y. Ono, *J. Mol. Catal.*, 81 (1993) 397.
10. M.R. Bond and R.D. Willett, *Acta Crystallogr., Sect. C*, 49 (1993) 668.
11. G.W. Neilson, R.D. Broadbent, I. Howell and R.H. Tromp, *J. Chem. Soc., Faraday Trans.*, (1993) 2927.
12. H. Suzuki and S. Ishiguro, *Bull. Chem. Soc. Jpn.*, 66 (1993) 83.
13. D.H. Kerridge and S.A. Tariq, *Aust. J. Chem.*, 46 (1993) 917.
14. R. Vicente, A. Escuer, J. Ribas, X. Solans and M. Font–Bardía, *Inorg. Chem.*, 32 (1993) 6117.
15. H. Ptasiewicz, I. Olovsson and G.J. McIntyre, *Acta Crystallogr., Sect. B*, 49 (1993) 192.
16. G.J. McIntyre, H. Ptasiewicz–Bak and I. Olovsson, *Acta Crystallogr., Sect. B*, 46 (1990) 27.
17. J.R. Hester, E.N. Maslen, A.M. Glazer and K. Stadnicka, *Acta Crystallogr., Sect. B*, 49 (1993) 641.
18. F.A. Cotton, L.M. Daniels, C.A. Murillo and J.F. Quesada, *Inorg. Chem.*, 32 (1993) 4861.
19. A.V. Dudin, *Russ. Chem. Bull.*, 42 (1993) 417.
20. S.M. Godfrey, C.A. McAuliffe, G.C. Ranger and D.G. Kelly, *J. Chem. Soc., Dalton Trans.*, (1993) 2809.
21. M. James and J.P. Attfield, *J. Solid State Chem.*, 105 (1993) 287.
22. M. Strunk and Hk. Müller–Buschbaum, *Z. Anorg. Allg. Chem.*, 619 (1993) 343.
23. I.J. Pickering, G.N. George, J.T. Lewandowski and A.J. Jacobsen, *J. Am. Chem. Soc.*, 115 (1993) 4137.
24. R. Borromei, E. Cavalli and L. Oleari, *Inorg. Chim. Acta*, 204 (1993) 159.
25. A. Feltz, J. Töpfer and B, Neidnicht, *Z. Anorg. Allg. Chem.*, 619 (1993) 39.
26. U. Bemm, R. Norrestam, M. Nygren and G. Westin, *Inorg. Chem.*, 32 (1993) 1597.
27. W. Burow, J. Birx, F. Bernhardt and R. Hoppe, *Z. Anorg. Allg. Chem.*, 619 (1993) 923.
28. C.W. Bauschlicher, S.R. Langhoff, H. Partridge and M. Sodupe, *J. Phys. Chem.*, 97 (1993) 856.
29. M.F. Richardson, G. Wulfsberg, R. Marlow, S. Zaghonni, D. McCorkle, K. Shadid, J. Gagliardi and B. Farris, *Inorg. Chem.*, 32 (1993) 1913.
30. A.C. Dash, R.K. Nanda and A.N. Acharya, *J. Chem. Soc., Dalton Trans.*, (1993) 1023.
31. J.J. Vittal and C.J. Willis, *Can. J. Chem.*, 71 (1993) 1051.
32. K.M. Corbin, J. Glerup, D.J. Hodgson, M.H. Lynn, K. Michelson and K.M. Nielsen, *Inorg. Chem.*, 32 (1993) 18.
33. Y.J. Li and A.E. Martell, *Inorg. Chim. Acta*, 214 (1993) 103.

34. R.D. Cannon, U.A. Jayasooriya, L. Montri, A.K. Saad, E. Karu, S.K. Bollen, W.R. Sanderson, A.K. Powell and A.J. Blake, *J. Chem. Soc., Dalton Trans.*, (1993) 2005.
35. R.P. White, J.A. Stride, S.K. Bollen, N. C. Sa–ard, G.J. Kearley, U.A. Jayasooriya and R.D. Cannon, *J. Am. Chem. Soc.*, 115 (1993) 7778.
36. G. Smith, D.E. Lynch, T.C.W. Mak, W.–H. Yip and C.H.L. Kennard, *Polyhedron*, 12 (1993) 203.
37. M. Ruiz, R. Ortiz, L. Perello, A. Castiñeiras and M. Quirós, *Inorg. Chim. Acta*, 211 (1993) 133.
38. F.–C. Xue, Z.–H. Jiang, D.–Z. Liao, S.–L. Ma, S.–P. Yan, G.–L. Wang, X.–K. Yao and R.–J. Wang, *Polyhedron*, 12 (1993) 2787.
39. M.C. Guillem, J. Latorre, R. Martínez–Máñez, J. Payá, S. García–Granda, E. Pérez–Carreño and F. Gómez–Beltrán, *Polyhedron*, 12 (1993) 1681.
40. R. Kaplonek, G. Fechtel, U. Baumeister and H. Hartung, *Z. Anorg. Allg. Chem.*, 619 (1993) 1616.
41. K. Yamada, Y. Fukuda, T. Kawamoto, Y. Kushi, W. Mori and K. Unoura, *Bull. Chem. Soc. Jpn.*, 66 (1993) 2758.
42. P. Román, C. Guzmán–Miralles and A. Luque, *Acta Crystallogr., Sect. C*, 49 (1993) 1336.
43. M. Ohba, H. Tamaki, N. Matsumoto and H. Okawa, *Inorg. Chem.*, 32 (1993) 5385.
44. M. Mitsumi, H. Okawa, H. Sakiyama, M. Ohba, N. Matsumoto, T. Kurisaki and H. Wakita, *J. Chem. Soc., Dalton Trans.*, (1993) 2991.
45. A. Gulbrandsen, J. Sletten, K. Nakatani, Y. Pei and O. Kahn, *Inorg. Chim. Acta*, 212 (1993) 271.
46. G.M. Escandar, L.F. Sala and M.G. Sierra, *Polyhedron*, 12 (1993) 143.
47. K. Sugawara, S. Tanaka, K. Hasebe and M. Taga, *J. Electroanal. Chem.*, 347 (1993) 393.
48. S.–L. Ma, D.–Z. Liao, Z.–H. Jiang, S.–P. Yan and G.–L. Wang, *Polyhedron*, 12 (1993) 1523.
49. B.S. Garg, V. Kumar and M.J. Reddy, *Transition Met. Chem.*, 18 (1993) 364.
50. K. Ozutsumi, M. Koide, H. Suzuki and S. Ishiguro, *J. Phys. Chem.*, 97 (1993) 500.
51. A.M.A. Hassan and M.G. Marei, *J. Indian Chem. Soc.*, 70 (1993) 64.
52. T. Maruyama and T. Tago, *J. Mat. Sci.*, 28 (1993) 5345.
53. M.L.J. Reimer, J.B. Westmore and M. Das, *Can. J. Chem.*, 71 (1993) 1450.
54. F.D. Lewis, G.D. Salvi, D.R. Kanis and M.A. Ratner, *Inorg. Chem.*, 32 (1993) 1251.
55. M. Helliwell, B. Gallois, B.M. Kariuki, V. Kaucic and J.R. Helliwell, *Acta Crystallogr., Sect. B*, 49 (1993) 420.
56. K.–H. Lii, L.–S. Wu and H.–M. Gau, *Inorg. Chem.*, 32 (1993) 4153.
57. R.C. Haushalter, V. Soghomonian, Q. Chen and J. Zubieta, *J. Solid State Chem.*, 105 (1993) 512.
58. K.–H. Lii, P.–F. Shih and T.–M. Chen, *Inorg. Chem.*, 32 (1993) 4373.
59. M.D. Marcos, P. Amorós, F. Sapiña, A. Beltrán–Porter, R. Martínez–Máñez and J.P. Attfield, *Inorg. Chem.*, 32 (1993) 5044.
60. B. Elbali, A. Boukhari, E.M. Holt and J. Aride, *Acta Crystallogr., Sect. C*, 49 (1993) 1131.
61. I. Abrahams and K.S. Easson, *Acta Crystallogr., Sect. C*, 49 (1993) 925.
62. G. Kura and T. Tsukuda, *Polyhedron*, 12 (1993) 865.
63. H. Keppler and D.C. Ruble, *Nature (London)*, 364 (1993) 54.
64. P. Alemany and R. Hoffmann, *J. Am. Chem. Soc.*, 115 (1993) 8290.
65. A.L. Rheingold, K.S. Beall, P.J. Riggs and S.E. Groh, *Acta Crystallogr., Sect. C*, 49 (1993) 542.
66. A. Silver, S.A. Koch and M. Millar, *Inorg. Chim. Acta*, 205 (1993) 9.
67. A. Wilk, M.A. Hitchman, W. Massa and D. Reinen, *Inorg. Chem.*, 32 (1993) 2483.
68. G.R. Frauenhoff and D.H. Busch, *J. Coord. Chem.*, 29 (1993) 175.
69. S. Mukhopadhyay and D. Ray, *J. Chem. Soc., Dalton Trans.*, (1993) 1159.
70. T. Konno, K. Okamoto and J. Kidaka, *Acta Crystallogr., Sect. C*, 49 (1993) 222.
71. Y.–H Huang, J.–B. Park, M.W.W. Adams and M.K. Johnson, *Inorg. Chem.*, 32 (1993) 375.
72. Y.–H Huang, I. Moura, J.J.G. Moura, J. LeGall, J.–B. Park, M.W.W. Adams and M.K. Johnson, *Inorg. Chem.*, 32 (1993) 406.
73. C. Bagyinka, J.P. Whitehead and M.J. Maroney, *J. Am. Chem. Soc.*, 115 (1993) 3576.
74. J.P. Whitehead, R.J. Gurbiel, C. Bagyinka, B.M. Hoffman and M.J. Maroney, *J. Am. Chem. Soc.*, 115 (1993) 5629.
75. W. Liu and H.H. Thorp, *Inorg. Chem.*, 32 (1993) 4102.
76. O. Sorgenfrei, A. Klein and S.P.J. Albracht, *FEBS Letters*, 332 (1993) 291.
77. K.A. Bagley, C. Van Garderen, S.P.J. Albracht and W.H. Woodruff, *Biophys. J.*, 64 (1993) A276.
78. L.F. Wu and M.A. Mandrand, *FEMS Microbiol. Revs.*, 104 (1993) 243.
79. M. Kumar, W.–P. Lu, L. liu and S.W. Ragsdale, *J. Am. Chem. Soc.*, 115 (1993) 11646.

80. W. Shin, M.E. Anderson and P.A. Lindahl, *J. Am. Chem. Soc.*, 115 (1993) 5522.
81. M. Zdravkova, N.D. Yordanov and G. Gochev, *Polyhedron*, 12 (1993) 2645.
82. H. Isci, Ö. Dag and W.R. Mason, *Inorg. Chem.*, 32 (1993) 3909.
83. K. Ramalingam, G. Aravamudan and V. Venkatachalam, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1554.
84. A.M. Bond, R. Colton, A. D'Agostino, J. Harvey and J.C. Traeger, *Inorg. Chem.*, 32 (1993) 3952.
85. I.H. Anderson, A.J. Blake and G.A. Heath, *Acta Crystallogr., Sect. C*, 49 (1993) 87.
86. M.G. Papadopoulos, J. Waite, C.S. Winter and S.N. Oliver, *Inorg. Chem.*, 32 (1993) 277.
87. C.S. Winter, S.N. Oliver, J.D. Rush, C.A.S. Hill and A.E. Underhill, *Mol. Cryst. Liq. Cryst.*, 235 (1993) 181.
88. N.D. Lowe and C.D. Garner, *J. Chem. Soc., Dalton Trans.*, (1993) 2197.
89. S.P. Best, S.A. Ciniawsky, R.J.H. Clark and R.S. McQueen, *J. Chem. Soc., Dalton Trans.*, (1993) 2267.
90. S. Schenk, I. Hawkins, S.B. Wilkes, A.E. Underhill, A. Kobayashi and H. Kobayashi, *J. Chem. Soc., Chem. Commun.*, (1993) 1648.
91. O.A. Dyachenko, S.V. Konovalikhin, A.I. Kotov, G.V. Shilov, E.B. Yagubskii, C. Faulmann and P. Cassoux, *J. Chem. Soc., Chem. Commun.*, (1993) 508.
92. F. Qi, Y. Xiao–Zeng, C. Jin–Hua and H. Mei–Yun, *Acta Crystallogr., Sect. C*, 49 (1993) 1347.
93. J.P. Cornelissen, B. Pomarède, A.L. Spek, D. Reefman, J.G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 32 (1993) 9.
94. C. Faulmann, A. Errami, J.P. Legros, P. Cassoux, E.B. Yagubskii and A.I. Kotov, *Synth. Met.*, 56 (1993) 2057; C. Faulmann, P. Cassoux, E.B. Yagubskii and L.V. Vetoshkina, *New. J. Chem.*, 17 (1993) 385.
95. R.D. Bereman and H. Lu, *Inorg. Chim. Acta*, 204 (1993) 53.
96. P. Román, J.I. Beitia, A. Luque and A. Aranzabe, *Polyhedron*, 12 (1993) 1345.
97. P. Román, J.I. Beitia and A. Luque, *Polyhedron*, 12 (1993) 2831.
98. S.A. Mirza, M.A. Pressler, M. Kumar, R.O. Day and M.J. Maroney, *Inorg. Chem.*, 32 (1993) 977.
99. T. Yamamura, S. Sakurai, H. Arai and H. Miyamae, *J. Chem. Soc., Chem. Commun.*, (1993) 1656.
100. M. Cha, S.C. Shoner and J.A. Kovacs, *Inorg. Chem.*, 32 (1993) 1860.
101. L. Escriche, M.–P. Almajano, J. Casabó, F. Teixidor, J. Rius, C. Miravitlles, R. Kivekäs and R. Sillampää, *J. Chem. Soc., Dalton Trans.*, (1993) 2969.
102. A.J. Blake, R.O. Gould, M.A. Halcrow and M. Schröder, *J. Chem. Soc., Dalton Trans.*, (1993) 2909; A.J. Blake, M.A. Halcrow and M. Schröder, *Z. Kristallogr.*, 205 (1993) 295.
103. K.K.P. Srivastava, K.K. Surerus, R.C. Conover, M.K. Johnson, J.–B. Park, M.W.W. Adams and E. Münck, *Inorg. Chem.*, 32 (1993) 927.
104. J.M. McConnachie, J.C. Bollinger and J.A. Ibers, *Inorg. Chem.*, 32 (1993) 3923.
105. J.M. Moratal, J. Salgado, A. Donaire, H.R. Jimenez, J. Castells and M.J. Martinez–Ferrer, *Mag. Res. Chem.*, 31 (1993) 41.
106. J.M. Moratal, J. Salgado, A. Donaire, H.R. Jimenez and J. Castells, *J. Chem. Soc., Chem. Commun.*, (1993) 110.
107. A. Müller, K.U. Johannes, M. Straube, E. Krickemeyer and H. Bögge, *Z. Anorg. Allg. Chem.*, 619 (1993) 1037.
108. W.J. Barreto and P.S. Santos, *J. Coord. Chem.*, 30 (1993) 337.
109. F. Chen, S. Muralidharan and H. Freiser, *Langmuir*, 9 (1993) 3656.
110. R. Castro, J.A. Garcia–Váquez, J. Romero, A. Sousa, A. Castiñeiras, W. Hiller and J. Strähle, *Inorg. Chim. Acta*, 211 (1993) 47.
111. R. Castro, J.A. Garcia–Váquez, J. Romero, A. Sousa, C.A. McAuliffe and R. Pritchard, *Polyhedron*, 12 (1993) 2241.
112. T. Yamamura, M. Tadokoro, K. Tanaka and R. Kuroda, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1984.
113. P.J. Farmer, T. Solouki, T. Soma, D.H. Russell and M.Y. Darensbourg, *Inorg. Chem.*, 32 (1993) 4171.
114. I. Font, R. Buonomo, J.H. Reibenspies and M.Y. Darensbourg, *Inorg. Chem.*, 32 (1993) 5897.
115. P.J. Farmer, J.H. Reibenspies, P. Lindahl and M.Y. Darensbourg, *Inorg. Chem.*, 32 (1993) 4665.
116. A.J. Atkins, A.J. Blake and M. Schröder, *J. Chem. Soc., Chem. Commun.*, (1993) 1662.
117. R. Shukla, S. Mandal and P.K. Bharadwaj, *Polyhedron*, 12 (1993) 83.
118. M. Mikuriya, M. Handa, S. Shigematsu, S. Funaki, T. Fujii, H. Okawa, K. Toriumi, T. Koshiba and H. Terauchi, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1105.

119. E. Bermejo, A. Castiñeiras, R. Domínguez, J. Strähle and W. Hiller, *Acta Crystallogr., Sect. C*, 49 (1993) 1919.
120. E. Bermejo, A. Castiñeiras, R. Domínguez, J. Strähle and W. Hiller, *Acta Crystallogr., Sect. C*, 49 (1993) 324.
121. B. Adhikary, S. Liu and C.R. Lucas, *Inorg. Chem.*, 32 (1993) 5957.
122. R. Carballo, A. Castiñeiras, J. Strähle and W. Hiller, *Polyhedron*, 12 (1993) 1083.
123. R. Bastida, A. de Blas, D.E. Fenton and T. Rodríguez, *Inorg. Chim. Acta*, 206 (1993) 47.
124. Z.H. Choan and S. Kausar, *Chem. Pharm. Bull.*, 41 (1993) 951.
125. D.X. West, M.A. Lockwood, A. Castiñeiras and A.E. Liberta, *Polyhedron*, 12 (1993) 1887.
126. D.X. West, H. Gebremedhin, R.J. Butcher, J.P. Jasinski and A.E. Liberta, *Polyhedron*, 12 (1993) 2489.
127. D.X. West, M.A. Lockwood, A.E. Liberta, X. Chen and R.D. Willett, *Transition Met. Chem.*, 18 (1993) 221.
128. M.E. Hossain, J. Begum, M. Nurul Alam, M. Nazimuddin and M. Akbar Ali, *Transition Met. Chem.*, 18 (1993) 497.
129. G. Kanagaraj and G.N. Rao, *Polyhedron*, 12 (1993) 383.
130. D.X. West, A.C. Whyte, F.D. Sharif, H. Gebremedhin and A.E. Liberta,*Transition Met. Chem.*, 18 (1993) 238.
131. M.M. Rahman and M. Akbar Ali, *Transition Met. Chem.*, 18 (1993) 396.
132. K. Wasielewski and R. Mattes, *Z. Anorg. Allg. Chem.*, 619 (1993) 158.
133. D. Funkemeier and R. Mattes, *J. Chem. Soc., Dalton Trans.*, (1993) 1313.
134. T.M. Donlevy, L.R. Gahan, R. Stranger, S.E. Kennedy, K.A. Byriel and C.H.L. Kennard, *Inorg. Chem.*, 32 (1993) 6023.
135. M. Shakhir, S.P. Varkey and P.S. Hameed, *J. Chem. Res. (S)*, (1993) 442.
136. D. Sellman, W. Prechtel, F. Knoch and M. Moll, *Inorg. Chem.*, 32 (1993) 538.
137. B. Lorenz, T. Zimmermann, R. Hübener and U. Abram, *Z. Anorg. Allg. Chem.*, 619 (1993) 1905.
138. Z. Lu, C. White, A.L. Rheingold and R.H. Crabtree, *Inorg. Chem.*, 32 (1993) 3991.
139. J. Sanmartin, M.R. Bermejo, J.A. García–Váquez, J. Romero and A. Sousa, *Transition Met. Chem.*, 18 (1993) 187.
140. R. Bastida, A. de Blas, D.E. Fenton, C. Rial, T. Rodriguez and A. Sousa, *J. Chem. Soc., Dalton Trans.*, (1993) 265.
141. D.M. Wambeke, W. Lippens, G.G. Herman and A.M. Goeminne, *J. Chem. Soc., Dalton Trans.*, (1993) 2017.
142. M.S. Nair, P.T. Arasu, M.S. Pillai and C. Natarajan, *J. Chem. Soc., Dalton Trans.*, (1993) 917.
143. E. Bouwman, P. Evans, H. Kooijman, J. Reedijk and A.L. Spek, *J. Chem. Soc., Chem. Commun.*, (1993) 1747.
144. S. Jayasree and K.K. Aravindakshan, *Polyhedron*, 12 (1993) 1187.
145. S. Karmakar, S.B. Choudhury, D. Ray and A. Chakravorty, *Polyhedron*, 12 (1993) 291.
146. S. Karmakar, S.B. Choudhury, D. Ray and A. Chakravorty, *Polyhedron*, 12 (1993) 2325.
147. G. Alzuet, S. Ferrer, J. Borrás, X. Solans and M. Font–Bardía, *Inorg. Chim. Acta*, 203 (1993) 257.
148. A.E. Tapper, E.J. Billo and J.A. Golen, *Inorg. Chim. Acta*, 210 (1993) 71.
149. E. Durcanska, J. Kozisek, J. Durik and V. Kettmann, *Acta Crystallogr., Sect. C*, 49 (1993) 535.
150. M. Yamashita, E. Tsuruta, K. Inoue, M. Oyama and K. Toriumi, *Inorg. Chem.*, 32 (1993) 363.
151. A. McAuley, S. Subramanian and T.W. Whitcombe, *J. Chem. Soc., Dalton Trans.*, (1993) 2209.
152. J. Ribas, M. Monfort, C. Diaz, C. Bastos and X. Solans, *Inorg. Chem.*, 32 (1993) 3557.
153. R. Vicente, A. Escuer, J. Ribas, M.S. el Fallah, X. Solans and M. Font–Bardia, *Inorg. Chem.*, 32 (1993) 1920.
154. A. Escuer, R. Vicente, J. Ribas, M.S. el Fallah, X. Solans and M. Font–Bardia, *Inorg. Chem.*, 32 (1993) 3727.
155. M. Monfort, J. Ribas and X. Solans, *J. Chem. Soc., Chem. Commun.*, (1993) 350.
156. M. Yashiro, K. Matsumoto, N. Seki and S. Yoshikawa, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1559.
157. S. Osanai, R. Yanagihara, A. Okumara and S. Yoshikawa, *J. Chem. Soc., Perkin Trans. 2*, (1993) 1937.
158. R. Kempe, J. Sieler, D. Walther, J. Reinhold and K. Rommel, *Z. Anorg. Allg. Chem.*, 619 (1993) 1105.
159. K. Yamada, K. Hori and Y. Fukuda, *Acta Crystallogr., Sect. C*, 49 (1993) 445.
160. A. Taha, W. Linert, Y. Fukuda, *J. Coord. Chem.*, 30 (1993) 53.
161. N. Shintani, J. Kotaki, K. Sone and Y. Fukuda, *Bull. Chem. Soc. Jpn.*, 66 (1993) 784.

162. P.V. Bernhardt, P. Comba, T.W. Hambley, I. Sóvágó and K. Várnagy, *J. Chem. Soc., Dalton Trans.*, (1993) 2023.
163. A.A. Freer, G.M. McDermott, J.C. Melville and D.J. Robins, *Acta Crystallogr., Sect. C*, 49 (1993) 2115.
164. A. Marzotto, D.A. Clemente and G. Valle, *Acta Crystallogr., Sect. C*, 49 (1993) 1252.
165. A. Bencini, A. Bianchi, V. Fusi, P. Paoletti, B. Valtancoli, A. Andres, J. Aragó and E. Garcia–España, *Inorg. Chim. Acta*, 204 (1993) 221.
166. H. Chakravorty and M.L. Rahman, *Transition Met. Chem.*, 18 (1993) 545.
167. K. Kurotaki and S. Kawamura, *J. Chem. Soc., Faraday Trans.*, 89 (1993) 3039.
168. P.V. Bernhardt and P. Comba, *Inorg. Chem.*, 32 (1993) 2798.
169. O.V. Mikhailov, *J. Photog. Sci.*, 41 (1993) 199.
170. H.–K. Fun, T.–J. Lee, T. Tahirov, T.–H. Lu, H. Luh and C.–S. Chung, *J. Chinese Chem. Soc.*, 40 (1993) 429.
171. T.–H. Lu, F. Tseng, H. Luh and C.–S. Chung, *Acta Crystallogr., Sect. C*, 49 (1993) 666.
172. G.E. Efe and E.O. Schlemper, *Polyhedron*, 12 (1993) 2869.
173. R. Hirota, Y. Yoshida and Y. Iida, *Polyhedron*, 12 (1993) 1817.
174. M. Bonamico, V. Fares, A. Flamini, N. Poli, Y. Yamashita and K. Imaeda, *J. Chem. Soc., Dalton Trans.*, (1993) 3463.
175. R. Lopez–Garzon, M.N. Moreno–Carretero, M.A. Sales–Peregrin and J.M. Sales–Peregrin, *Polyhedron*, 12 (1993) 507.
176. T. Astley, J.M. Gulbis, M.A. Hitchman and E.R.T. Tiekink, *J. Chem. Soc., Dalton Trans.*, (1993) 509.
177. V.H. Arali, V.K. Revankar and V.B. Mahale, *Transition Met. Chem.*, 18 (1993) 158.
178. M.B. Roy, P.C. Mandal and S.N. Bhattacharyya, *J. Chem. Soc., Dalton Trans.*, (1993) 2485.
179. M. Maekawa, M. Munakata, T. Kuroda and Y. Nozaka, *Inorg. Chim. Acta*, 208 (1993) 243.
180. M. Prasad, H.N. Pandey and P. Mathur, *Transition Met. Chem.*, 18 (1993) 356.
181. S. Materazzi, G. D'Ascenzo, R. Curini and L. Fava, *Thermochim. Acta*, 228 (1993) 197.
182. Md. A.A. Miah and D.J. Phillips, *Inorg. Chim. Acta*, 214 (1993) 181.
183. G. Liptay, G. Kennesey and P. Bukovec, *J. Thermal Anal.*, 40 (1993) 543.
184. K.H. Halawani and A.H. Mostafa, *Transition Met. Chem.*, 18 (1993) 564.
185. E. Jona, I. Horvath and M. Kubranova, *Thermochim. Acta*, 221 (1993) 41.
186. L. Lavelle and L.R. Nassimbeni, *J. Inclusion Phenom. and Mol. Recog. in Chem.*, 16 (1993) 25.
187. L.A. Belfiore, M.P. McCurdie and E. Ueda, *Macromolecules*, 26 (1993) 6908.
188. P. Segl'a and M. Jamnicky, *Inorg. Chim. Acta*, 205 (1993) 22.
189. K.J. Izod and P. Thornton, *Polyhedron*, 12 (1993) 1613.
190. K. Bernauer, F. Gretillat, H. Stoeckli–Evans and R. Warmuth, *Helv. Chim. Acta*, 76 (1993) 545.
191. P. Bonhôte, M. Ferigo, H. Stoeckli–Evans and W. Marty, *Acta Crystallogr., Sect. C*, 49 (1993) 2102.
192. K.H. Sugiyarto, D.C. Craig, A.D. Rae and H.A. Goodwin, *Aust. J. Chem.*, 46 (1993) 1269.
193. R.J. Letcher, W. Zhang, C. Bensimon and R.J. Crutchley, *Inorg. Chim. Acta*, 210 (1993) 183.
194. M. Hvastijová, J. Kohout, M. Okruhlica, J. Mrozinski and L. Jäger, *Transition Met. Chem.*, 18 (1993) 579.
195. S. Kasselouri, A. Garoufis, G. Kalkanis, S.P. Perlepes and N. Hadjiliadis, *Transition Met. Chem.*, 18 (1993) 531.
196. P.N. Bartlett and V. Eastwick–Field, *Electrochim. Acta*, 38 (1993) 2515.
197. K.T. Potts, M. Keshavarz–K, F.S. Tham, H.D. Abruña and C. Arana, *Inorg. Chem.*, 32 (1993) 4436.
198. E.C. Constable, M.A.M. Daniels, M.G.B. Drew, D.A. Tocher, J.V. Walker and P.D. Wood, *J. Chem. Soc., Dalton Trans.*, (1993) 1947.
199. E.C. Constable, M.J. Hannon and D.A. Tocher, *J. Chem. Soc., Dalton Trans.*, (1993) 1883.
200. N. Armaroli, L. De Cola, V. Balzani, J.–P. Sauvage, C.O. Dietrich–Buchecker, J.–M. Kern and A. Bailal, *J. Chem. Soc., Dalton Trans.*, (1993) 3241.
201. A. Escuer, T. Comas, R. Vicente and J. Ribas, *Transition Met. Chem.*, 18 (1993) 43.
202. G. De Munno, M. Julve, F. Lloret and A. Derory, *J. Chem. Soc., Dalton Trans.*, (1993) 1179.
203. E. Jóna, M. Koman and R. Boca, *Polyhedron*, 12 (1993) 7.
204. E.P. Day, J. Peterson, M.S. Sendova, M.J. Todd and R.P. Hausinger, *Inorg. Chem.*, 32 (1993) 634.
205. H.E. Wages, K.L. Taft and S.J. Lippard, *Inorg. Chem.*, 32 (1993) 4985.
206. M. Hirai, R. Kawai–Hirai, T. Hirai and T. Ueki, *Eur. J. Biochem.*, 215 (1993) 55.

207. J. Benko, O. Vollárová, S. Alshehri, J. Burgess and R.I. Haines, *Transition Met. Chem.*, 18 (1993) 551.
208. R.I. Haines, L. Butt, M.K. Park and D. Wheeler, *Can. J. Chem.*, 71 (1993) 976.
209. A. Escuer, R. Vicente and J. Ribas, *Transition Met. Chem.*, 18 (1993) 478.
210. I.A. Fallis, L.J. Farrugia, N.M. MacDonald and R.D. Peacock, *J. Chem. Soc., Dalton Trans.*, (1993) 2759.
211. G. De Santis, L. Fabbrizzi, M. Licchelli, C. Mangano, P. Pallavicini and A. Poggi, *Inorg. Chem.*, 32 (1993) 854.
212. J. Chen, N. Ye, N.W. Alcock and D.H. Busch, *Inorg. Chem.*, 32 (1993) 904.
213. J.H. Cameron and E.L. Scott, *J. Chem. Soc., Dalton Trans.*, (1993) 397.
214. A. Escuer, R. Vicente, J. Ribas, M.S. El Fallah and X. Solans, *Inorg. Chem.*, 32 (1993) 1033.
215. A. Escuer, R. Vicente, J. Ribas, M.S. El Fallah, X. Solans and M. Font–Bardia, *J. Chem. Soc., Dalton Trans.*, (1993) 2975.
216. R. Ruiz, M. Julve, J. Cano, J. Soto, R. Martinez–Máñez, C. Muñoz and J. Payá, *Transition Met. Chem.*, 18 (1993) 523.
217. H. Oshio, *Inorg. Chem.*, 32 (1993) 4123.
218. A. McAuley, T. Palmer and T.W. Whitcombe, *Can. J. Chem.*, 71 (1993) 1792.
219. Q. Yao, A. Bakak and J.H. Espenson, *Inorg. Chem.*, 32 (1993) 1488.
220. D.E. Linn, S.D. Rumage and J.L. Grutsch, *Int. J. Chem. Kinetics*, 25 (1993) 489.
221. J. Nishimoto, E. Iwamoto, T. Fujiwara and T. Kumamaru, *J. Chem. Soc., Faraday Trans.*, 89 (1993) 535.
222. J. Nishimoto, A. Hironaka, E. Iwamoto and T. Kumamaru, *Bull. Chem. Soc. Jpn.*, 66 (1993) 1669.
223. C. Boudon, J.–P. Gisselbrecht, M. Gross, T. Benabdallah and R. Guglielmetti, *J. Electroanal. Chem.*, 345 (1993) 363.
224. G. De Santis, L. Fabbrizzi, M. Licchelli, C. Mangano and P. Pallavicini, *Inorg. Chim. Acta*, 214 (1993) 193.
225. E. Kimura, M. Haruta, T. Koike, M. Shionoya, K. Takenouchi and Y. Iitaka, *Inorg. Chem.*, 32 (1993) 2779.
226. P.V. Bernhardt, P. Comba and T.W. Hambley, *Inorg. Chem.*, 32 (1993) 2804.
227. N.F. Curtis, G.J. Gainsford, A. Siriwardena and D.C. Weatherburn, *Aust. J. Chem.*, 46 (1993) 755.
228. S. Ozaki, H. Matsushita and H. Ohmori, *J. Chem. Soc., Perkin Trans. 1*, (1993) 649.
229. S. Ozaki, H. Matsushita and H. Ohmori, *J. Chem. Soc., Perkin Trans. 1*, (1993) 2339.
230. C.I. Smith, J.A. Crayston and R.W. Hay, *J. Chem. Soc., Dalton Trans.*, (1993) 3267.
231. G.B. Balazs and F.C. Anson, *J. Electroanal. Chem.*, 361 (1993) 149.
232. M.G.B. Drew, N.J. Jutson, P.C.H. Mitchell, R.J. Potter and D. Thompsett, *J. Chem. Soc., Faraday Trans.*, 89 (1993) 3963.
233. D. Coucouvanis, S.G. Jonasdottir, D. Christodoulo, C.G. Kim and J.W. Kampf, *Inorg. Chem.*, 32 (1993) 2987.
234. S.G. Jonasdottir, C.G. Kim and D. Coucouvanis, *Inorg. Chem.*, 32 (1993) 3591.
235. F. Bonosi, F. Lely, G. Ricciardi, M. Romanelli and G. Martini, *Langmuir*, 9 (1993) 268.
236. T. Kajiwara, T. Yamaguchi, H. Kido, S. Kawabata, R. Kuroda and T. Ito, *Inorg. Chem.*, 32 (1993) 4990.
237. J. Costa and R. Delgado, *Inorg. Chem.*, 32 (1993) 5257.
238. J.A. Duro, J.M. Ontoria, A. Sastre, W. Schäfer and T. Torres, *J. Chem. Soc., Dalton Trans.*, (1993) 2595.
239. V.M. Leovac, V.I. Cesljevic, N.V. Gerbeleu, Y.A. Simonov, A.A. Dvorkin and V.B. Arion, *Transition Met. Chem.*, 18 (1993) 309.
240. I. Madden and D.H. Busch, *J. Coord. Chem.*, 29 (1993) 337.
241. I. Zilbermann, A. Meshulam, H. Cohen and D. Meyerstein, *Inorg. Chim. Acta*, 206 (1993) 127.
242. S.–G. Kang, S.–K. Jung, J.K. Kweon and M.–S. Kim, *Polyhedron*, 12 (1993) 353.
243. S.V. Rosokha, Y.D. Lampeka and I.M. Maloshtan, *J. Chem. Soc., Dalton Trans.*, (1993) 631.
244. M.P. Suh and S.K. Kim, *Inorg. Chem.*, 32 (1993) 3562.
245. K. Mochizuki, H.Y. Lu and Y. Suzuki, *Inorg. Chim. Acta*, 204 (1993) 267.
246. A. De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, A.M. Manotti Lanfredi, P. Morosini, P. Pallavicini and F. Ugozzoli, *J. Chem. Soc., Dalton Trans.*, (1993) 1411.
247. A. De Blas, G. De Santis, L. Fabbrizzi, M. Licchelli, A.M. Manotti Lanfredi, P. Pallavicini, A. Poggi and F. Ugozzoli, *Inorg. Chem.*, 32 (1993) 106.
248. A. Bencini, A. Bianchi, P. Dapporto, V. Fusi, E. Garcia–España, M. Micheloni, P. Paoletti, P. Paoli, A. Rodriguez and B. Valtancoli, *Inorg. Chem.*, 32 (1993) 2753.

249. I.J. Clark, I.I. Creaser, L.M. Engelhardt, J.M. Harrowfield, E.R. Krausz, G.M. Moran, A.M. Sargeson and A.H. White, *Aust. J. Chem.*, 46 (1993) 111.
250 L.M. Engelhardt, J.M. Harrowfield, A.M. Sargeson and A.H. White, *Aust. J. Chem.*, 46 (1993) 127.
251. A. Ertan, I. Csöregh, K. Wärnmark, L. Mäler and C. Moberg, *Inorg. Chim. Acta*, 203 (1993) 21.
252. M. Shakir, S.P. Varkey and P.S. Hameed, *Polyhedron*, 12 (1993) 2775.
253. P. Chinn, D.H. Busch and N.W. Alcock, *Acta Crystallogr., Sect. C*, 49 (1993) 1284.
254. R.W. Hay, M. Tofazzal, M.M. Hassan and S.E. Blatchford, *Transition Met. Chem.*, 18 (1993) 55.
255. C.-C. Cheng, S.E. Rokita and C.J. Burrows, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 277.
256. C. Holliger, A.J. Pierik, E.J. Reijerse and W.R. Hagen, *J. Am. Chem. Soc.*, 115 (1993) 5651.
257. G.K. Lahiri and A.M. Stolzenberg, *Inorg. Chem.*, 32 (1993) 4409.
258. A.D. Procyk, A.M. Stolzenberg, and D.F. Bocian, *Inorg. Chem.*, 32 (1993) 627.
259. A.D. Procyk and D.F. Bocian, *Inorg. Chem.*, 32 (1993) 366.
260. G.K. Lahiri and A.M. Stolzenberg, *Angew. Chem., Int. Ed. Engl.*, 32 (1993) 429.
261. A. Stichternath, R. Schweitzer–Stenner, W. Dreybrodt, R.S.W. Mak, X. Li, L.D. Sparks, J.A. Shelnutt, C.J. Medforth and K.M. Smith, *J. Phys. Chem.*, 97 (1993) 3701.
262. C. Piffat, D. Melamed and T.G. Spiro, *J. Phys. Chem.*, 97 (1993) 7441.
263. K.K. Anderson, J.D. Hobbs, L. Luo, K.D. Stanley, J.M.E. Quirke and J.A. Shelnutt, *J. Am. Chem. Soc.*, 115 (1993) 12346.
264. M.O. Senge, *J. Chem. Soc., Dalton Trans.*, (1993) 3539.
265. M.O. Senge, C.J. Medforth, L.D. Sparks, J.A. Shelnutt and K.M. Smith, *Inorg. Chem.*, 32 (1993) 1716.
266. E. Unger, U. Bobinger, W. Dreybrodt and R. Schweitzer–Stenner, *J. Phys. Chem.*, 97 (1993) 9956.
267. K.M. Barkigia, M.W. Renner, L.R. Furenlid, C.J. Medforth, K.M. Smith and J. Fajer, *J. Am. Chem. Soc.*, 115 (1993) 3627.
268. L.M. Henling, W.P. Schaefer, J.A. Hodge, M.E. Hughes and H.B. Gray, *Acta Crystallogr., Sect. C*, 49 (1993) 1743.
269. S. Hu, A. Mukherjee and T.G. Spiro, *J. Am. Chem. Soc.*, 115 (1993) 12366.
270. M.O. Senge, N.W. Smith and K.M. Smith, *Inorg. Chem.*, 32 (1993) 1259.
271. M. D'Ambrosio, A. Guerriero, C. Debitus, O. Ribes and F. Pietra, *Helv. Chim. Acta*, 76 (1993) 1489.
272. R. Kitagawa, Y. Kai, G.V. Ponomarev, K.-I. Sugiura, V.V. Borovkov, T. Kaneda and Y. Sakata, *Chem. Lett.*, (1993) 1071.
273. N.N. Daeid and K.B. Nolan, *Inorg. Chim. Acta*, 211 (1993) 55.
274. K.M. Kadish, E. Van Caemelbecke, P. Boulas, F. D'Souza, E. Vogel, M. Kisters, C.J. Medforth and K.M. Smith, *Inorg. Chem.*, 32 (1993) 4177.
275. A.L. Balch, B.C. Noll, S.M. Reid and E.P. Zovinka, *J. Am. Chem. Soc.*, 115 (1993) 2531.
276. W.R. Scheidt, B. Cheng, K.J. Haller, A. Mislanker, A.D. Rae, K.V. Reddy, H. Song, R.D. Orosz, C.A. Reed, F. Cukiernik and J.-C. Marchon, *J. Am. Chem. Soc.*, 115 (1993) 1181.
277. J.F. Lipskier and T.H. Tran–Thi, *Inorg. Chem.*, 32 (1993) 722.
278. L.K. Woo, M.R. Maurya, R.A. Jacobson and S.L. Ringrose, *Inorg. Chim. Acta*, 212 (1993) 337.
279. A.L. Balch, M.M. Olmstead and S.L. Phillips, *Inorg. Chem.*, 32 (1993) 3931.
280. P.A. Connick, K.J. Haller and K.A. Macor, *Inorg. Chem.*, 32 (1993) 3256.
281. M. Hanack, K. Haberroth and M. Rack, *Chem. Ber.*, 126 (1993) 1201.
282. A. Rosa and E.J. Baerands, *Inorg. Chem.*, 32 (1993) 5637.
283. J.A. Thompson, K. Murata, D.C. Miller, J.L. Stanton, W.E. Broderick, B.M. Hoffman and J.A. Ibers, *Inorg. Chem.*, 32 (1993) 3546.
284. K. Murata, Y. Ohashi, K. Murata, J.A. Thompson, M. Mori and B.M. Hoffman, *Synth. Met*, 56 (1993) 1777.
285. X.H. Mu and F.A. Schultz, *J. Electroanal. Chem.*, 361 (1993) 49.
286. M. Hanack, D. Meng, A. Beck, M. Sommerauer and L.R. Subramanian, *J. Chem. Soc., Chem. Commun.*, (1993) 58.
287. J. Ueda, T. Ozawara, M. Miyazaki and Y. Fujiwara, *Inorg. Chim. Acta*, 214 (1993) 29.
288. N. Das, *Transition Met. Chem.*, 18 (1993) 372.
289. E. Leporati, *J. Coord. Chem.*, 28 (1993) 173.
290. B. Kurzak and D. Kroczewska, *Transition Met. Chem.*, 18 (1993) 295.
291. E. Farkas, D.A. Brown, R. Cittaro and W.K. Glass, *J. Chem. Soc., Dalton Trans.*, (1993) 2803.

292. B. Gyurcsik, T. Gajda, L. Nagy, K. Burger, A. Rockenbauer and L. Korecz, *Inorg. Chim. Acta*, 214 (1993) 57.
293. S.U. Patel, P.J. Sadler, A. Tucker and J.H. Viles, *J. Am. Chem. Soc.*, 115 (1993) 9285.
294. J.A. Zoltewicz and L.B. Bloom, *J. Phys. Chem.*, 97 (1993) 2755.
295. M.A.S. Goher, A.A. Youssef, Z.–Y. Zhou and T.C.W. Mak, *Polyhedron*, 12 (1993) 1871.
296. Z. Mao, D. Fu, Q. Hang, W. Tang and K. Yu, *J. Chem. Soc., Dalton Trans.*, (1993) 3169.
297. H.H. Haendler, *Acta Crystallogr., Sect. C*, 49 (1993) 239.
298. T.–J. lee, A. Wang, T.–Y. Chi and C.–S. Chung, *Acta Crystallogr., Sect. C*, 49 (1993) 1485.
299. H.–Z. Cai and T.A. Kaden, *Helv. Chim. Acta*, 76 (1993) 557.
300. A. Löwe, R. Mattes and K. Wasielewski, *Z. Anorg. Allg. Chem.*, 619 (1993) 905.
301. T. Frömmel, W. Peters, H. Wunderlich and W. Kuchen, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 907.
302. J. Ribas, M. Monfort, R. Costa and X. Solans, *Inorg. Chem.*, 32 (1993) 695.
303. N.F. Curtis, K.R. Morgan, A. Siriwardena and D.C. Weatherburn, *Aust. J. Chem.*, 46 (1993) 1389.
304. A. Yuchi, H. Murakami, M. Siro, H. Wada and G. Nakagawa, *Bull. Chem. Soc. Jpn.*, 65 (1993) 3362.
305. M. Hirohata, F. Kai, K. Kurosawa, H. Huang, K. Ishii, Y. Matsuoka, K. Komori and M. Nakamura, *J. Coord. Chem.*, 30 (1993) 379.
306. G.V. Romanenko and N.V. Podberezskaya, *J. Struct. Chem.*, 34 (1993) 406.
307. D. Luneau, G. Risoan, P. Rey, A. Grand, A. Caneschi, D. Gatteschi and J. Laugier, *Inorg. Chem.*, 32 (1993) 5616.
308. N. Youyou, P. Decock, D. Blondeau, J. Urbanska and H. Kozlowski, *J. Coord. Chem.*, 30 (1993) 283.
309. Z. Grabaric, Z. Lazarevic and N. Koprivanac, *Anal. Let.*, 26 (1993) 2455.
310. P.R. Athappan, P. Shanthi, R. Murugesan and C. Natarajan, *Synth. React. Inorg. Met. Org. Chem.*, 23 (1993) 1445.
311. A. Bouayad, N. Bitit, E. Deydier, M.–J. Menu, M. Dartiguenave, Y. Dartiguenave, H. Duran, L. Gorrichon, M. Simard and A.L. Beauchamp, *Polyhedron*, 12 (1993) 479.
312. L.F. Linday, B.W. Skelton, S.V. Smith and A.H. White, *Aust. J. Chem.*, 46 (1993) 363.
313. B. Dey, J.H. Coates, P.A. Duckworth, S.F. Lincoln and K.P. Wainwright, *Inorg. Chim. Acta*, 214 (1993) 77.
314. K.K. Nanda, R. Das, K. Venkatsubramanian, P. Paul and K. Nag, *J. Chem. Soc., Dalton Trans.*, (1993) 2515.
315. Y. Aratake, M. Ohba, H. Sakiyama, M. Tadokoro, N. Matsumoto and H. Okawa, *Inorg. Chim. Acta*, 212 (1993) 183.
316. H. Okawa, J. Nishio, M. Ohba, M. Tadokoro, N. Matsumoto, M. Koikawa, S. Kida and D.E. Fenton, *Inorg. Chem.*, 32 (1993) 2949.
317. M. Mikuriya, K. Nakadera and T. Kotera, *Chem. Lett.*, (1993) 637.
318. T. Tanase, R. Nouchi, Y. Oka, M. Kato, N. Nakamura, T. Yamamura, Y. Yamamoto and S. Yano, *J. Chem. Soc., Dalton Trans.*, (1993) 2645.
319. S. Yano, M. Kato, H. Shioi, T. Takahashi, T. Tsubomura, K. Toriumi, T. Ito, M. Hidai and S. Yoshikawa, *J. Chem. Soc., Dalton Trans.*, (1993) 1699.
320. A. Mashaly, *Polyhedron*, 12 (1993) 745.
321. A.D. Garnovskii, A.L. Nivorozhkin and V.I. Minkin, *Coord. Chem. Revs.*, 126 (1993) 1.
322. S.W.A. Bligh, N. Choi, D. St.C. Green, H.R. Hudson, C.M. McGrath, M. PcPartlin and M. Planka, *Polyhedron*, 12 (1993) 2887.
323. F. Dianzhong and W. Bo, *Transition Met. Chem.*, 18 (1993) 101.
324. D. Chatterjee, H.C. Baja, S.B. Halligudi and K.N. Bhatt, *J. Mol. Catal.*, 84 (1993) L1.
325. M.N. Abser, M. Bellwood, M.C. Holmes and R.W. McCabe, *J. Chem. Soc., Chem. Commun.*, (1993) 1062.
326. K.N. Narang and V.P. Singh, *Transition Met. Chem.*, 18 (1993) 287.
327. C. Dongli, J. Handong, Z. Hongyun, C. Deji, Y. Jina and L.B. Jian, *Polyhedron*, 12 (1993) 57.
328. E.A. El–Saied, M.M. Aly and A.M. Anwar, *Transition Met. Chem.*, 18 (1993) 588.
329. V.R. Rao, K.G. Reddy, U.V. Seshaiah and V. Jayathyagaraju, *Transition Met. Chem.*, 18 (1993) 258.
330. J.A. Castro, J. Romero, J.A. Garcia–Vazquez, A. Castiñeiras and A. Sousa, *Z. Anorg. Allg. Chem.*, 619 (1993) 601.
331. J.–P. Laurent, J.–P. Costes and G. Pradie, *Inorg. Chim. Acta*, 213 (1993) 57.
332. A. Syamal and M.M. Singh, *Reactive Polymers*, 21 (1993) 149.
333. M. Fujiwara, Y. Ichiki and H. Wakita, *Polyhedron*, 12 (1993) 2989.

334. M.Y. Khuhawar and A.I. Soomro, *J. Chromatog.*, 639 (1993) 371.
335. Y. Elerman, M. Kabak and O. Atakol, *Acta Crystallogr., Sect. C*, 49 (1993) 1905.
336. D.J. Macchia, W.F. Furey and R.A. Lalancette, *Acta Crystallogr., Sect. C*, 49 (1993) 1706.
337. M.A.A.F. de C.T. Carrondo, B. de Castro, A.M. Coelho, D. Domingues, C. Freire and J. Morais, *Inorg. Chim. Acta*, 205 (1993) 157.
338. W.S. Durfee and C.G. Pierpont, *Inorg. Chem.*, 32 (1993) 493.
339. A. Böttcher, H. Elias, E.–G. Jäger, H. Langfelderova, M. mazur, L. Müller, H. Paulus, M. Rudolph and M. Valko, *Inorg. Chem.*, 32 (1993) 4131.
340. A.J. Fry and P.F. Fry, *J. Org. Chem.*, 58 (1993) 3496.
341. O.F. Schall, K. Robinson, J.L. Atwood and G.W. Gokel, *J. Am. Chem. Soc.*, 115 (1993) 5962.
342. H. Hoss and H. Elias, *Inorg. Chem.*, 32 (1993) 317.
343. S. Tripathy and S.D. Bhattamisra, *J. Chem. Soc., Dalton Trans.*, (1993) 1907.
344. J. Sletten and J.A. Kovacs, *J. Crystallogr. Spectrosc. Res.*, 23 (1993) 239.
345. A. Meister, G. Süss–Fink, B. Kübler, G. Rumley, K.–H. Bergk and M. Porsch, *Z. Anorg. Allg. Chem.*, 619 (1993) 801.
346. S.M. Godfrey, C.A. McAuliffe and R.G. Pritchard, *J. Chem. Soc., Dalton Trans.*, (1993) 2875.
347. M. Gómez, G. Muller and J. Sales, *Polyhedron*, 12 (1993) 1171.
348. S.A. Jasper, S. Roach, J.N. Stipp, J.C. Huffman and L.J. Todd, *Inorg. Chem.*, 32 (1993) 3072.
349. G.A. Bowmaker and J.P. Williams, *J. Chem. Soc., Dalton Trans.*, 1993 3593.
350. S.S. Chojnacki, Y.–M. Hsiao, M.Y. Darensbourg and J.H. Reibenspies, *Inorg. Chem.*, 32 (1993) 3573.
351. P. Andrews and J. Evans, *J. Chem. Soc., Chem. Commun.*, (1993) 1246.
352. R.J. Smith, A.K. Powell, N. Barnard, J.R. Dilworth and P.J. Blower, *J. Chem. Soc., Chem. Commun.*, (1993) 54.
353. E. Niecke, J.F. Nixon, P. Wenderoth, B.F.T. Passos and M. Nieger, *J. Chem. Soc., Chem. Commun.*, (1993) 846.
354. J. Grobe, D. Le Van, M. Hegemann, B. Krebs and M. Läge, *Chem. Ber.*, 126 (1993) 63.
355. D. Wilhelm, T. Hoffman, E. Wenschuh, G. Reck and G. Winter, *Z. Anorg. Allg. Chem.*, 619 (1993) 1801.
356. M.B. Hursthouse, K.J. Izod, M. Motevalli and P. Thornton, *Polyhedron*, 12 (1993) 151.
357. P.A.T. Hoyle, P.G. Pringle, M.B. Smith and K. Warboys, *J. Chem. Soc., Dalton Trans.*, (1993) 269.
358. C. Jegat, M. Fouassier, M. Tranquille, J. Mascetti, I. Tommasi, M. Aresta, F. Ingold and A. Dedieu, *Inorg. Chem.*, 32 (1993) 1279.
359. H. Tang, D.M. Hoffman, T.A. Albright, H. Deng and R. Hoffmann, *Angew. Chem. Int. Ed. Engl.*, 32 (1993) 1616.
360. A.J. Downard, L.R. Hanton, D.A. McMorran and R.L. Paul, *Inorg. Chem.*, 32 (1993) 6028.
361. A. Miedaner, D.L. DuBois, C.J. Curtis and R.C. Haltiwanger, *Organometallics*, 12 (1993) 299.
362. L. Manojlovic–Muir, A.H. Mirza, N. Sadiq and R.J. Puddephatt, *Inorg. Chem.*, 32 (1993) 117.
363. V.A. Trumpy, T.A. Oriskovich and S. Schreiner, *Inorg. Chim. Acta*, 205 (1993) 149.
364. D.A. Morgenstern, R.E. Wittrig, P.E. Fanwick and C.P. Kubiak, *J. Am. Chem. Soc.*, 115 (1993) 6470.
365. M. Gómez, G. Muller, J. Sales and X. Solans, *J. Chem. Soc., Dalton Trans.*, (1993) 221.
366. J. Ellermann, J. Sutter, C. Schelle, F.A. Knoch and M. Moll, *Z. Anorg. Allg. Chem.*, 619 (1993) 2006.
367. B. Juma, F.R. Fronczek and G.G. Stanley, *Acta Crystallogr., Sect. C*, 49 (1993) 1325.
368. H. Hennig, K. Ritter and H. Knoll, *Inorg. Chim. Acta*, 211 (1993) 117.
369. C.S. Velázquez, T.F. Baumann, M.M. Olmstead, H. Hope, A.G.M. Barrett and B.M. Hoffman, *J. Am. Chem. Soc.*, 115 (1993) 9997.
370. P.S. Jarrett, O.M. Ni Dhubhghaill and P.S. Sadler, *J. Chem. Soc., Dalton Trans.*, (1993) 1863.
371. V.A. Pavlov, E.A. Mistryukov, M.G. Vinogradov and G. Snatzke, *J. Mol. Catal.*, 79 (1993) 55.
372. S. Zhang, G. Huang, M. Shao and Y. Tang, *J. Chem. Soc., Chem. Commun.*, (1993) 37.
373. P. Paul, K. Venkatasubramanian and S. Purohit, *J. Coord. Chem.*, 28 (1993) 279.