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REVIEWS

6. Nickel 1994

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CONTENTS

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INTRODUCTION

This review covers the coordination chemistry of nickel for 1994. Relevant references were obtained from the BIDS database using the keyword "nickel*". The years 1994–1995 (April) were checked, but only references dated 1994 are included. Since the BIDS database is now capable of searching titles, abstracts and keywords, I have not independently checked journals this year. As for the 1990 and 1993 reviews, the traditional subdivision by oxidation state and ligand type has been replaced by ligand type alone.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 are specifically excluded, except in cases where there is exceptional interest to coordination chemists. These compounds are dealt with adequately elsewhere. Similarly, 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.

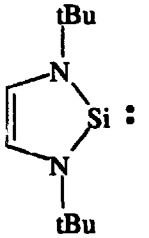
6.1 BORIDES AND BORANE COMPLEXES

The recent discovery of quite high transition temperature (T_c) superconducting rare-earth-Ni–B–C and rare-earth-Ni–B–N phases has re-invigorated research efforts in this area [1–4]. Superconducting $LuNi_2B_2C$ has a structure consisting of alternating square layers of rock salt-like LuC and Ni_2B_2 tetrahedra [1]. The crystal structure of a new phase, $La_3Ni_2B_2N_3$ (T_c = 12–13 K), shows three rock salt-like LaN layers alternating with two Ni_2B_2 layers [2]. Clearly other unusual intermetallic phases with superconducting behaviour may yet be found. Extended Hückel tight-binding calculations on $LnNi_2B_2C$ (Ln = rare-earth element) and non-superconducting LnNiBC phases show that both are highly covalent; to a first approximation they can be regarded as $(Ln^{2+})(Ni^0)_2(B_2C)^{2-}$ and $(Ln^{3+})(Ni^0)(BC)^{3-}$ respectively [4].

The formally Ni(IV) complex $[\textit{commo}\text{-}1,1'\text{-}Ni(B_{11}H_{11})_2]^{4-}$ has been isolated (as the Cs^+ and Ph_3PMe^+ salts) [5], and characterised by ^{11}B and ^1H NMR spectroscopies.

6.2 COMPLEXES WITH GROUP 14 DONOR LIGANDS

Treatment of $[Ni(CO)_4]$ with the stable silylene (**1**) gives the distorted tetrahedral complex $[Ni(CO)_2(1)_2]$ independent of mole ratios employed [6]. The Ni–Si bonds (mean 2.212(2) Å) are shorter than the theoretically predicted 2.29 Å. The ^{29}Si NMR spectroscopic resonance (+97.5 ppm) suggests the silicon nucleus is moderately deshielded upon coordination.



(**1**)

6.3 COMPLEXES WITH HALIDE AND PSEUDOHALIDE LIGANDS

The interaction of axially-bound water with Ni(III) in $[Ni(CN)_4(H_2O)_2]^-$ has been investigated using electron spin echo envelope modulation with different pulse sequences [7,8]. It is hoped to use this technique to characterise the active site of nickel-containing hydrogenases, which have quite similar ESR spectroscopic characteristics. An interesting report claims the *in situ* spectroelectrochemical determination of the Ni(II)/Ni(I) redox potential in molten alkali halide solutions, by measuring relative concentrations of Ni(II) and Ni(I) complex ions as a function of potential [9]. The Ni(I) species (presumably $[NiCl_4]^-$), however, does not have an absorption band (except the low-energy edge of a charge transfer band) in the spectral range studied. The reaction of $NiCl_2$ with pyridinium hydrogen fluoride (PyHF) gives only $(PyH)_2[NiCl_4]$ [10]. Further treatment with KHF_2 gives $KNiF_3$.

The complexation of nickel(II) halides in solution in polar solvents continues to attract attention. With bromide ions in dimethylacetamide (dma), Ni(II) forms six-coordinate $[NiBr(dma)_5]^+$, $[NiBr_2(dma)_4]$ and $[NiBr_3(dma)_3]^-$ [11]. The coordination of Br^- is significantly enhanced compared with dmf, which is unusual as the donor power of these solvents is similar. The involvement of equilibria with species of lower coordination number is suggested by the electronic spectra of the solutions. This area has been reviewed [12]. The crystal structure of a charge transfer salt containing $[NiCl_4]^{2-}$ as anion, $[bis(ethylenedithio)\text{-}tetrathiafulvalene]_3[NiCl_4].H_2O$, has been published in full this year [13]. 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 angle 93.9(1)°].

The crystal structure of $Me_4N[Ni(NO_2)_3]$ reveals infinite chains of Ni^{2+} ions bridged by three *cis*-μ-nitro ligands such that alternate Ni^{2+} ions are chemically distinct, one site octahedrally coordinated by six nitrogens, the other by six nitrite oxygens [14]. The complex is a 1-D Heisenberg antiferromagnet. The structures of $K_4[Ni(NO_2)_6].H_2O$ and $K_3[Ni(NO_2)_5]$ have also been published [15]. In the latter, Ni(II) is coordinated to four nitrite nitrogens, and chelated to the oxygen atoms of the fifth. On heating $K_4[Ni(NO_2)_6].H_2O$ it dehydrates and forms a compound which powder diffraction data shows is a mixture of crystallites of $K_3[Ni(NO_2)_4(O_2N)]$ and KNO_2.

6.4 COMPLEXES WITH OXYGEN DONOR LIGANDS

6.4.1 Neutral ligands

The thermal dehydration of solid $[Ni(H_2O)_6]SO_4$ has been the subject of a detailed kinetic and morphological study [16]. The surface nucleation and growth of the dihydrate from the hexahydrate occurs with small samples in flowing N_2, followed by inward diffusion of the new phase. With larger samples, where the product water is not so readily lost, a non-isothermal mechanism applies, with intermediate tetrahydrate and monohydrate products. The crystal structure of $(NH_4)_2[Ni(H_2O)_6](SO_4)_2$ has been re-determined [17]. An ESR study of $[Ni(H_2O)_6](BF_4)_2$ doped into $[Zn(H_2O)_6](BF_4)_2$ has been reported; differences in spin Hamiltonian parameters between the dilute phases and bulk $[Ni(H_2O)_6](BF_4)_2$ are due to ferromagnetic interactions not present in the magnetically dilute system [18].

The coordination sphere about Ni^{2+} (perchlorate salt) in hexamethylphosphoramide (HMPA) and water has been investigated using EXAFS [19]. In HMPA, the data are consistent with four-coordination. Solutions of nickel acetate in methanol (MeOH) or dmf, in the presence of cellulose-based resin, have been used to spin-coat thin films for subsequent conversion to NiO or Ni films [20]. Finally, the crystal structure of Δ,L-$[Ni(L–L)_3](ClO_4)_2$.MeOH (L–L = $Ph_2P(O)CH_2P(O)Ph_2$) has been determined [21]. The geometry is tetragonally-distorted octahedral (mean $Ni–O_{equatorial}$ = 2.075 Å, mean $Ni–O_{axial}$ = 2.185 Å).

6.4.2 Anionic ligands

6.4.2.1 Oxides and related systems

The ESR spectra of $Li_xNi_{2-x}O_2$ ($0.6 \leq x < 1$), where a phase transition occurs from cubic to layered structure, have been used to characterise the interactions of Ni(II) and Ni(III) [22]. New designs of electrochromic windows employing non-stoichiometric nickel oxide as counter-electrode have been described [23]. Nickel hydrous oxides are also employed in NiCd batteries, and EXAFS has been used *in situ* to characterise some of the effects of introducing Fe and Co on the structural and redox chemistry of this material [24]. The data indicate that single-phase mixed metal materials, with Fe(III) or Co(III) replacing Ni, are produced.

Interest in the effect of Ni-substitution for Cu in ceramic superconductors continues. New phases $LaBa_2Cu_{3-x}Ni_xO_{7+\delta}$ ($0.0 < x < 0.3$) and $LnBa_2Cu_{3-x}NiO_{7-\delta}$ (Ln = Pr, Nd, Sm, Gd, Er; x = 0.1, 0.2; Ni-doped Ln 123) have been characterised; substitution of Ni in $LaBa_2Cu_3O_{7\pm\delta}$ induces an orthorhombic to tetragonal structural change and reduces the barrier to oxygen desorption [25]. The superconducting transition temperature (T_c) of Ni-doped Ln 123 decreases with increasing rare earth radius. In contrast, for $YBa_2(Cu_{1-x}Ni_x)_3O_y$ (x = 0.05) prepared under various conditions, an unusual extension of the orthorhombic regime compared to unsubstituted materials was found by other workers [26]. After annealing at 673 K in oxygen over several days, a superconducting material (T_c *ca.* 74 K) results. Nickel substitution in the 2223 (Bi–Pb) cuprate system has been examined [27]. A new Ni(III) oxide, $YbSr_3NiO_6$, has been characterised [28]. It has a rhombohedral K_4PtCl_6 structure, but has 11% Yb vacancies (or cation substitutions).

The reactivity of the perovskite $LaNiO_3$ as a methanol oxidation catalyst has been examined [29]. In a reducing atmosphere, heating $LaNiO_3$ affords La_2NiO_4, *via* an intermediate $La_2Ni_2O_5$ phase, and above 450 °C decomposition occurs. Also studied was $La_2NiO_{4+\delta}$. X-Ray diffraction patterns of powders show surface enrichment of La and O in these compounds. Between 200 and 400 °C, all three compounds are active methanol oxidation catalysts. The structure of $La_2Ni_2O_5$ has been studied using the Rietveld technique [30]. This revealed one-dimensionally-linked NiO_6 octahedra connected by NiO_4 planar units with, apparently, a cooperative Jahn-Teller distortion in both polyhedra. The latter suggests, most unusually, a mixed valence Ni(III)/Ni(I) compound. Reduction of $LnNiO_3$ (Ln = Pr, Nd) affords phases $Ln_3Ni_3O_7$. The unit cell of $Nd_3Ni_3O_7$ has three NiO_6 and six NiO_4 squares, where an octahedral layer alternates with two NiO_4 layers [31]. The magnetic properties of the ordered perovskite Ba_2NiUO_6 have been examined [32]. Below 25 K, it is ferromagnetic, with a room temperature μ_{eff} of 3.02 BM. The Ni is therefore divalent, and U hexavalent.

XANES spectra of several nickel oxides have been reported [33]. The shift in energy of the K-edge, and the inflexion point energy of the pre-edge structure, correlate well with oxidation state. In β-NiOOH, the valency is Ni(III); $Ni_3O_2(OH)_4$ and commercial 'nickel peroxide' likewise contain trivalent nickel. The edge shift for $KNi^{IV}IO_6$ is also reported. Periodates $MNiIO_6$ (M = Na, K, Rb, Cs or NH_4) have also been the subject of a structural and spectroscopic study [34]. X-Ray powder diffraction shows hexagonal close packed layers of oxide ions, with one third of the octahedral holes in every second layer containing M ions, and in the other layers one third contain Ni and another third I. Ni–O (1.86 – 1.88 Å), Ni...I and Ni...Ni distances were measured using EXAFS. Magnetic moment data suggested the presence of small amounts of Ni(III) or Ni(II) impurities.

The stabilisation of the low oxidation state Ni(I) within oxide and related environments is a subject of some interest at present. Hydrogen reduction of the Ni(III) material $YSr_5Ni_3O_{11}$ results in a change from tetragonal K_2NiF_4 structure to an orthorhombic Sr_2CuO_3 arrangement $YSr_5Ni_3O_8$, with 1/3 of the bridging oxygens missing from chains of apex-linked nickel oxide square planes [35]. However, the material was contaminated with Ni metal, SrO and Y_2SrO_4. Other compounds $LnSr_5Ni_3O_8$ (Ln = Dy, Ho, Er, Tm) have also been described [36]. Nickel-substituted silicoaluminophosphate 11 made hydrothermally (Ni–APSO 11) or by ion exchange of Ni(II) into H–SAPO 11 (NiH–SAPO 11), on reduction with hydrogen, undergoes reduction to two distinct Ni(I) sites, one isolated Ni(I), the other associated with adsorbed H_2 (Ni–$(H_2)_n$) [37]. With CO, the Ni(I) sites afford Ni(I)–$(CO)_n$ (n = 1–3 for Ni–APSO 11, n = 2,3 only for NiH–SAPO 11). The rate of ethene adsorption onto Ni–APSO 11, where ESR characteristics suggest a framework site for Ni(I), is 1000 times more rapid than onto NiH–SAPO 11. Smectite clays have recently been shown to provide an environment for stabilisation of Ni(I)–oxide complexes; magnesium hydroxyhectorites containing Ni(II) in lattice sites (Mg–NiHect) or in ion-exchange sites (NiMg–Hect) were made, and g-irradiated at 77 K to give Ni(I) sites [38]. The Ni(I) site in NiMg–Hect is not stable, at room temperature, to D_2O or CD_3OH adsorption, but one of the two

Ni(I) species found by ESR spectroscopy in Mg–NiHect is stable to such treatment. The unstable site in the latter is assigned to Ni(I) in an edge framework position, and the stable site to Ni(I) in an interior octahedral framework position.

If a preparation of $VO(HPO_4)\cdot 0.5H_2O$ is attempted in the presence of Ni^{2+} ions, a compound containing 0.15 % by weight Ni is obtained which, in spite of the low Ni content, has a completely different structure, which appears to be similar to that of $VO(PO_4)\cdot 2H_2O$, but with an average V valency of 4.66 [39]. Nickel has been inserted between the intercalated amine layers in an α-zirconium phosphate [40]. X-Ray powder data showed that the structure consists of a three-tiered layer of Ni atoms bridged by hydroxo and acetate groups. On heating to 420 °C, these are converted into oxide layers with ordered magnetic domains. Hydrotalcite-like Fe–Ni–hydroxides $[Ni^{II}{}_{0.66}Fe^{III}{}_{0.33}(OH)_2](CO_3)_{0.166}(H_2O)_y$, $[Ni^{II}{}_{0.75}Fe^{III}{}_{0.25}(OH)_2](CO_3)_{0.125}(H_2O)_y$ and $[Ni^{II/III}{}_{0.75}Fe^{III}{}_{0.25}(OH)_2](CO_3)_{0.14}(H_2O)_y$ have been studied using Mössbauer spectroscopy [41].

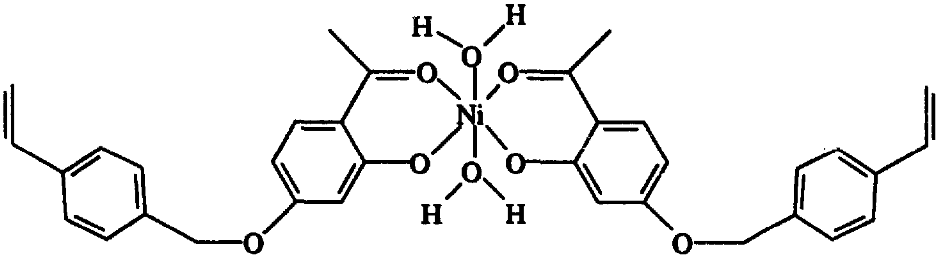
The heteropolytungstate $[Ni_4(H_2O)_2(P_2W_{15}O_{56})_2]^{16-}$ has a rhomb-like Ni_4O_{16} group isolated between two fragments of the polyanion $[P_2W_{15}O_{56}]^{12-}$. It shows ferromagnetic exchange interactions ($J = 8.3$ cm^{-1}, $J' = 3.5$ cm^{-1}) and an $S = 4$ ground state [42].

6.4.2.2 Complexes of carbonate and sulfonate ligands

The crystal structure of $K_2[Ni(CO_3)_2(H_2O)_4]$ shows a *trans* arrangement of monodentate carbonate groups (mean $Ni\text{–}OH_2$ 2.084(3) Å; $Ni\text{–}OCO_2$ 2.046(2) Å) [43]. When sulfonated polystyrene is neutralised by metal ions, ionic-rich domains form, and the material segregates into hydrophobic and hydrophilic microdomains. When 6.1 mol % sulfonated polystyrene was neutralised by Ni^{2+}, and the material analysed using EXAFS, the data was consistent with most Ni^{2+} ions being coordinated by six oxygens, all of which are sulfonate, and two oxygens from three sulfonate groups share two nickel ions [44]. Only on the periphery of microdomains is water coordination required. The effect of stretch alignment upon these systems has been further investigated using EXAFS, thus employing linearly polarised X-rays [45].

6.4.2.3 Complexes of $[RO]^-$ and related ligands

Secondary cellulose acetate (partially hydrolysed cellulose acetate) complexes, including the Ni(II) complex, have been made. Infra red and electronic spectra suggest that the Ni(II) is octahedrally coordinated by two residual waters, and an ester oxygen and RO^- group from two glycoside rings, each unit forming a five-membered chelate ring [46]. Copolymers of 2-acetyl-5-(4-vinylbenzyloxy)phenol, acrylamide and 2,2'-methylenediacrylamide form chelate complexes with divalent metal ions, including Ni(II) [47]. EXAFS and XANES spectra suggest the arrangement shown in (**2**).



(2)

The electrochemistry of two oligosiloxane complexes, $\{[(PhSiO_{1.5})_6]_2(NiO)_6(NaCl)\}$ and $\{[(PhSiO_{1.5})_6]_2(NiO)_4(NaO_{0.5})_4(NaOH)_2\}$, has been examined in dmf. Both undergo a quasi-reversible reduction at *ca.* −2.0 V [48]. However, $\{[(PhSiO_{1.5})_6]_2(NiO)_4(CuO)_2(NaCl)\}$ undergoes at least two irreversible reductions at the same potential. Similar complexes $\{[(PhSiO_{1.5})_{12}]_2(NiO)_6L\}$ (L = ROH, H_2O) have been dispersed on supports (soot, alumina) and tested as catalysts for water oxidation by $[Ru(bpy)_3]^{3+}$ [49]. Although nickel hydroxide does catalyse the reaction, the siloxane complexes do not.

The synthesis and partial hydrolysis reactions of $[Ni_2Sb_4(OEt)_{16}]$ have been examined [50]. The colour of this material changes from green to purple reversibly upon warming; it is suggested that this is due to an octahedral to tetrahedral isomerisation. Five intermediate complexes from the hydrolysis have been isolated. Among these are $[Ni_5Sb_3O_2(OEt)_{15}(ethanol)_4]$ and $[Ni_6Sb_4O_4(OEt)_{16}(ethanol)_4]$.

6.4.2.4 Carboxylic acid, amide and related ligands

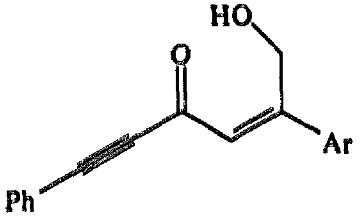
Some examples of the interesting carboxylate-bridged Ni(II) complexes $[Ni_2(\mu\text{-}RCOO)_4L_2]$ (R = Me_2PhC, L = PPh_3, quinoline; R = Me_3C; L = 2-picoline) have been described, and the crystal structure of $[Ni(Me_2PhCCOO)_4(PPh_3)_2]$ has been determined [51]. There are two independent, centrosymmetric molecules in the unit cell; the Ni–Ni distances, 2.752(1) and 2.765(2) Å, exclude significant Ni–Ni interaction. With Ni(II), the anti-inflammatory drug piroxicam forms a 2:1 complex, acting as a chelate with coordination *via* enolate and amide carbonyl oxygens [52]. When hydrated nickel acetate and excess 6-chloro-2-pyridone (Hchp) were fused, and the product extracted into thf, green crystals of a cyclic dodecanuclear complex, $[Ni_{12}(O_2CMe)_{12}(chp)_{12}(H_2O)_6(thf)_6]$ can be obtained in 60% yield [53]. The asymmetric unit contains two nickel ions, each with distorted octahedral O_6 coordination. One Ni is coordinated to three acetate oxygens, two chp oxygens and a water, the other to two acetate oxygens, two chp oxygens, a water and a thf. All ligands except thf are bridging. The variation of magnetic properties with temperature shows that there is a small ferromagnetic coupling, with an $S = 12$ ground state.

Electrochemical oxidation of Ni metal in an acetone solution of lactic (2-hydroxypropanoic) acid (H_2L) afforded a pale blue solid, assigned the formula $[Ni(HL)_2(Me_2CO)(H_2O)].3H_2O$ with lactate chelating *via* carboxylate and hydroxyl oxygens, on the basis of analytical and spectroscopic data [54]. The splitting of the ground state triplet due to spin-orbit coupling in $[Ni(mal)_2(H_2O)_2]$

(mal = malonate) have been calculated using a non-empirical method [55]. The interaction of Ni(II) with various sugar acids has been studied potentiometrically and using ^{13}C relaxation rate measurements [56]. Interaction is weak; octahedral $[Ni(L)_2]^{2-}$ chelates (H_2L = D-glucoheptonic or D-gluconic acid) form in alkaline media with the latter examples. Treatment of nickel carbonate with 2-furancarboxylic acid (HL) affords green needles, the crystal structure of which shows them to be $[Ni(L)(H_2O)_5]L$ ($Ni–O_{carboxylate}$ 2.019(3) Å, $Ni–O_{water}$ 2.033(3)–2.090(3) Å) [57]. With salicylglycine (H_2L) a metabolite of aspirin, Ni(I) forms no complexes at pH<6, and above this pH it interacts weakly to form NiL, for which bonding *via* phenolate, carboxylate and amide oxygens is suggested [58].

6.4.2.5 *β-Diketonato and related ligands*

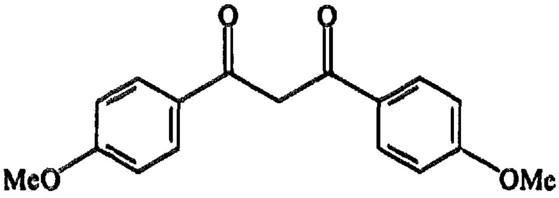
The ligands (3) (HL) have been synthesised [59]. With nickel(II) acetate in ethanol, (3a) forms [Ni(L)(OH)], formulated as a hydroxy-bridged square planar dimer, while (3b) forms octahedral $[Ni(L)_2(H_2O)_2]$. The ligand (4) has been employed in Ni-catalysed oxygenation of α-alkoxy cyclic ketones to give ring-opened acetal lactones (in the presence of a sacrificial aldehyde) [60]. A mechanism has been suggested for the olefin epoxidation reaction, also catalysed by nickel-β-diketonate complexes [61]. This involves the *cis*-coordination of dioxygen and the sacrificial aldehyde to Ni, without change of the nickel oxidation state, and a net favourable interaction of the aldehyde and O_2–Ni unit.



(3)

(Ar = 2-furyl: **a**,

Ar = 2-pyridyl: **b**)



(4)

The quenching of the triplet states of polycyclic aromatics of varying energies by $[Ni(acac)_2]$ and $[Ni(hexafluoroacetylacetonate)_2]$ in acetonitrile or benzene has been examined [62]. Energy transfer to metal-centred excited states or ligand-localised triplet states is adequate to describe the processes. The crystal structure of $[Ni(1,3\text{-bis}\{4\text{-octylphenyl}\}propane\text{-}1,3\text{-dionate})_2]$ has been determined [63]. The complex is non-mesogenic, but there are layer-like and columnar arrangements of molecules in the crystal. Some complexes of substituted 2,4-pentanediones, and their reactions with bpy and phen, have been described [64].

6.5 COMPLEXES OF SULFUR, SELENIUM AND TELLURIUM DONOR LIGANDS

6.5.1 Alkanethiol and related ligands

The crystal structure of the first neutral toroidal nickel-dithiolate complex, $[Ni_6(SCH_2CH_2CH_2S)_6]$ ($[Ni_6L_6]$, has been determined [65]. The complex crystallised as a side-product from the reaction of $\{O(CH_2CH_2SCH_2CH_2CH_2SH\}_2$ with $[NiCl_2(PPh_3)_2]$. The structure consists of a distorted planar hexagonal of nickel atoms, bridged by sulfur atoms arranged in two S_6 planes (to within 0.04 Å) above and below the nickel plane. The ligands bridge in two distinct modes, one with both of its S atoms in the same S_6 plane, and the other with its S atoms in opposite S_6 planes. The Ni–S bond lengths (2.167(9)–2.241(9) Å) cover a large range. The crystal structure of $(Ph_4P)_2[Ni(2\text{-}ClC_6H_4S)_4]$ has also been briefly reported [66], as has that of $[Ni_2(\mu\text{-}SPh)_2(dppe)_2](ClO_4)_2\cdot 2CH_3CN$ (Ni–S 2.251(2), 2.254(2) Å; Ni–P 2.179(2), 2.183(2) Å; S–Ni–S' 87.50(6)°, Ni–S–Ni 92.50(6)°) [67].

The Ni $L_{2,3}$ edge XAFS spectra of Ni–substituted *Pyrococcus furiosus* rubredoxin have been reported for both the Ni(II) and the partially ferricyanide-oxidised forms [68]. The Ni(II) form has a spectrum consistent with strongly distorted T_d symmetry. New features occur on oxidation.

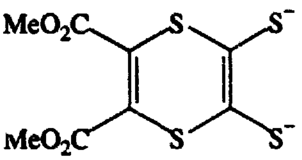
The reaction of NaTeAr (Ar = Ph, 4-MeC_6H_4, 4-ROC_6H_4) with $[NiCl_2(dppe)]$ in ethanol-C_6H_6 gave [NiCl(TeR)(dppe)] and $[Ni(TeR)_2(dppe)]$ [69]. Cyclic voltammetry revealed irreversible Ni(II)/Ni(0) couples at *ca.* –0.8 V in CH_3CN, associated with loss of the telluride ligand(s).

6.5.2 Xanthate, dithiocarbamate and related ligands

The crystal structure of $[Ni(^iPrOCS_2)_2]$ has been determined [70], and some complexes $Ni[M(L\text{-}L)_2]$ [$L\text{-}L^{2-}$ = $(NC)(EtO_2C)C{=}CS_2$; M = Zn(II), Cd(II), Hg(II). $L\text{-}L^{2-}$ = $(EtO_2C)_2C{=}CS_2$; M = Zn, Hg] have been described [71]. The geometry about Ni(II), as determined by magnetic and spectroscopic measurements, was square planar. Complexes of dialkyl dithiophosphates are used as anti-wear and anti-oxidant additives; the hydrolysis of $[Ni\{(EtO)_2PS_2\}_2]$ in water-1,2-dimethoxyethane has been studied by ^{31}P NMR spectroscopy [72]. Hydrolysis was 100 times slower than for the corresponding Zn complex, due to the greater strength of the Ni–S bond, and was proposed to proceed *via* coordination of water at Ni as the first step.

6.5.3 Dithiolenes and related ligands

The green salt $(Et_4N)_2[Ni(L\text{-}L)_2]$ [$L\text{-}L^{2-}$ = (5)] has been described [73]. This undergoes an unusual oxidation on exposure of a CH_3CN solution to air, to the brown dimetallic (6), isolated as its Bu_4N^+ and $AsPh_4^+$ salts; the X-ray crystal structure of the latter shows the remarkable extended planar Ni_2 unit, some 14.9 Å long. The magnetic behaviour of (6) was indicative of antiferromagnetic coupling. Further oxidation of (6) with ferrocenium ion afforded the neutral species.



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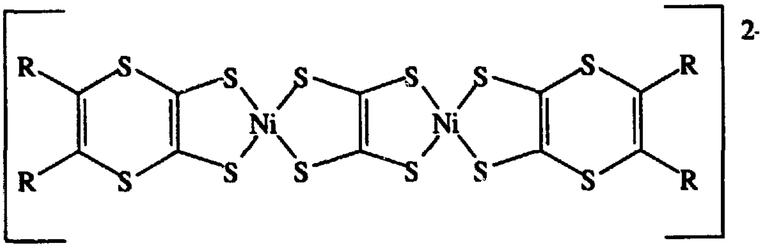
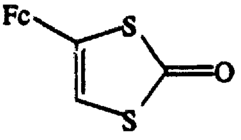


(R = $-CO_2Me$) (6)



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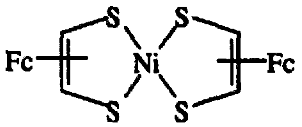
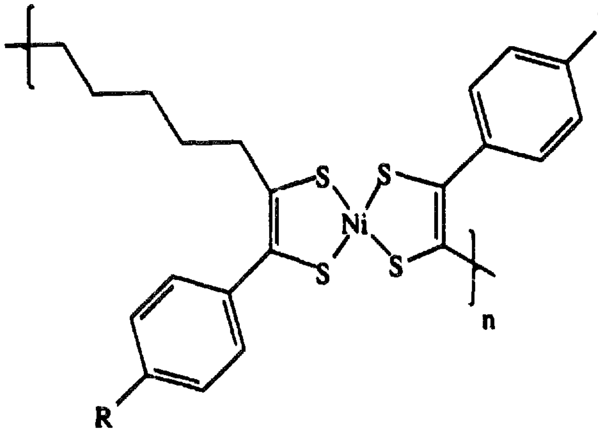


(8)

$[Fc = (C_5H_5)Fe(C_5H_4-)]$

Attempts to build further functionality into nickel-dithiolene complexes are under way. For instance, treatment of (7) with base and nickel dichloride gave (8), as a Bu_4N^+ salt [74]. This showed three quasi-reversible waves in a cyclic voltammetry experiment, assigned to successive ligand-based oxidations at −0.205 and +0.516 V and ferrocene–ferrocenium at +0.758 V. A series of nickel-dithiolene complexes bearing long-chain alkyl or alkylaryl substituents has been synthesised, in an effort further to delineate the factors responsible for promoting liquid crystalline behaviour [75], but none of the complexes made showed any such behaviour.

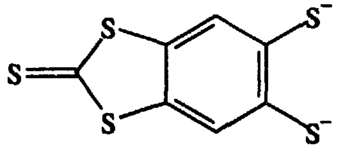
Soluble nickel-dithiolene oligomers of the type (9) have been co-dispersed with polymethylmethacrylate, and spin-coated films of the polymer mixture examined for third-order nonlinear optical properties [76]. Polymeric species proved superior to analogous monomeric complexes in this respect.



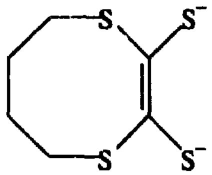
R = H, Bu

(9)

The complexes $(Bu_4N)_n[Ni(L–L)_2]$ [L–L^{2-} = (**10**); n = 1,2] have been described, in attempts to extend the π-conjugation of the superconducting Ni-dmit (dmit = 4,5-dimercapto-1,3-dithiole-2-thione) system [77]. Chemical oxidation of the salt (n = 1) with Br_2 gave a partially-oxidised complex (n = 0.29), and electrocrystallisation gave crystals of the same composition. The salt (n = 0.29) is metallic at room temperature, but the behaviour of its conductivity as a function of temperature between 220 and 40 K is that of a semiconductor. It is metallic again below 40 K.



(**10**)



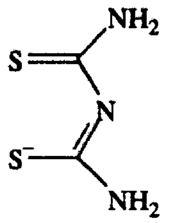
(**11**)

The complex $[Ni(L–L)_2]^-$ [L–L^{2-} = (**11**)] has been described [78]; it is little different from the analogous complex with L–L^{2-} = 1,3-propanediyldithioethylene-1,2-dithiolate. The behaviour of the ion pair charge transfer band as a function of ΔG for electron transfer from the dithiolene complex donor to the dipyridinium acceptor in a series of ion pair charge transfer salts $A[Ni(L–L)_2]$ (A = dipyridinium dication; L–L^{2-} = 1,2-dithiolene ligand) has been studied [79]. The energy of this band increases linearly with ΔG as predicted by the Hush relation. The conductivities of pressed pellets also increases with ΔG in cases where both cation and anion are planar; where this condition is not fulfilled, deviations are found.

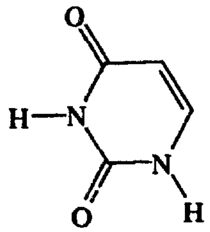
Turning now to dithiooxalate (dto^{2-}) and similar ligands, the thermochemistry of various salts of $[Ni(dto)_2]^{2-}$ (for example, pyridinium [80], 3-methylpyridinium [81], 4-methylpyridinium [82], 4-aminopyridinium [83]) have been examined, along with crystal structures of some examples, in efforts to correlate structure, decomposition pathway and final products. The pyrolysis atmosphere was also varied. In inert atmospheres, NiS was the final product, but in oxygen-containing atmospheres, mixtures of NiS and NiO, and sometimes $NiSO_4$, were found.

Nickel-ketoenolate and related complexes are active olefin oligomerisation catalysts. The reactions are frequently promoted by phosphine co-ligands. Complexes $[NiX(sacsac)(PR_3)]$ (R = Ph, Me, Et, cyclohexyl; X = Cl, Br), $[NiCl(sacac)(PR_3)]$ (R = Et, ^{n}Bu) and $[Ni(sacac)(Ph_2P(CH_2)_nPPh_2]BPh_4$ (n = 1,2) have been reported; conproportionation reactions between $[NiX_2(PR_3)_2]$ and $[Ni(sacsac)_2]$ or $[Ni(sacac)_2]$ were employed to synthesise the monodentate phosphine complexes, which disproportionate to some extent in solution [84]. The crystal structure of $[NiCl(sacac)(PEt_3)]$ shows square planar geometry about Ni, with P *trans* to O and S *trans* to Cl. Changing the phosphine ligand affected the activity and selectivity of the oligomerisation reaction, while exchanging sacac for sacsac increases catalyst activity.

On treatment of $[Ni(L–L)_2]$ [L–L$^-$ = (**12**)] in dmso with uracil (**13**), crystals of a novel 'base pair' adduct form. The central Ni moiety is strongly hydrogen-bonded, *via* two N–H bonds and the central nitrogen in the ligand, to the carbonyl oxygens and the central N–H of uracil respectively [85].



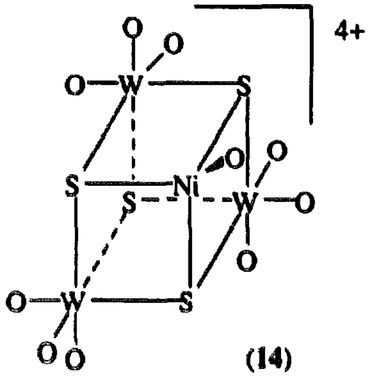
(12)



(13)

6.5.4 Chalcogenide clusters

Reaction of $NiCl_2$ in CH_3CN with, sequentially, dppe, NaTeH and $NaBPh_4$ gave the complex $[\{(dppe)Ni\}_3(\mu_3\text{-}Te)_2](BPh_4)_2$ [86]. Whereas cyclic voltammetric studies of the Pd and Pt analogues gave single, two-electron quasi-reversible reductions in dmf, the Ni complex gave two one-electron couples at −1.51 and −1.69 V.

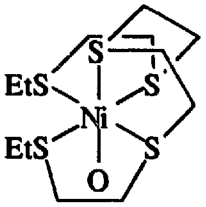


(14)

The cluster $[W_3NiS_4(H_2O)_{10}]^{4+}$ [(14); hydrogens omitted for clarity] is the product of the reaction of $[W_3S_4(H_2O)_9]^{4+}$ and Ni foil [87]. Crystals of the tosylate salt, isolated on ion exchange chromatography, have a dimeric $Ni_2(\mu\text{-}S)_2$ arrangement, with a close Ni–Ni distance (2.561(5) Å) and the Ni-coordinated waters lost.

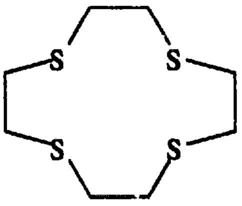
6.5.5 Complexes with thioether and related ligands

The ligand 3,6,9,12,15-pentathiaheptadecane reacts with $[Ni(H_2O)_6]X_2$ ($X^- = ClO_4^-, BF_4^-$) in acetonitrile to afford blue $[Ni(L)(H_2O)]X_2$ [88], the X-ray crystal structure of which shows the ligand arranged about the Ni ion as in (15). The complex remains intact in solution in nitromethane. It is found, on comparing structural and spectroscopic parameters for Ni(II)-multidentate thioether complexes, that Δ_0 is mainly sensitive to donor type, but that the nephelauxetic ratio β is a sensitive function of bond length.



(15)

Treatment of $NiCl_2$ with one equivalent of the macrocycles L [L = **(16–18)**] in nitromethane in the presence of $NaBF_4$ gave $[Ni_2Cl_2(L)_2][BF_4]_2$ [89]. The crystal structures of all three complexes show dichloro-bridged dimeric cations exhibiting edge-sharing octahedral structures with the macrocycles coordinated *cis* about Ni. The shortest Ni–S bonds were found with **(17)** [mean bond lengths 2.3998(28) Å **(16)**, 2.3753(22) Å **(17)**, 2.4277(22) Å **(18)**]; **(17)** has a hole size closest to optimum for this arrangement with high spin Ni(II). The triply chloro-bridged complex $[Ni_2(L)_2Cl_3]BF_4$ (L = 1,4,7-trithianonane) was also reported. In cyclic voltammetry experiments, only irreversible redox processes were observed.



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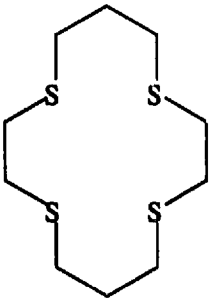

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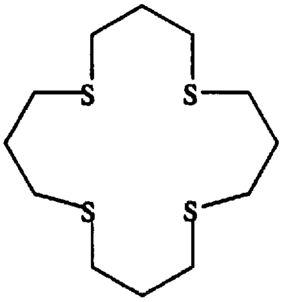


(18)

6.6 COMPLEXES WITH MIXED N,S-DONOR SETS

6.6.1 Metalloenzymes

A theoretical study of Ni(II) carbonyl complexes, for example $[NiCl_2(PMe_3)_2(CO)]$ and $[Ni(SiCl_3)_2(CO)_3]$, has been undertaken, to find out why five-coordinate geometries seem to be favoured for CO binding to Ni(II), a question which may be significant if some current ideas on the nature of the active site in Ni dehydrogenases are correct [90]. For complexes involving strong donor ligands like PMe_3, on reducing the Cl–Ni–Cl angle below 180°, the b_2 orbital loses its degeneracy with the a_2 orbital and moves to higher energy, thus becoming a powerful π-donor orbital towards a CO binding to the vacant site in the trigonal bipyramidal metal complex fragment thus generated.

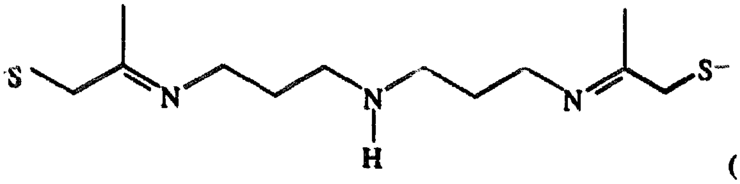
Biochemists are currently devoting much effort to understanding Ni-containing enzymes. Reviews appearing this year include coverage of the active site of nickel hydrogenases [91], nickel-iron [92] and nickel-iron-selenium hydrogenases [93] and specific coverage of the dehydrogenases of *E. coli* [94]. The proceedings of a conference covering the biochemistry, toxicology and ecology of nickel have appeared [95], including a review of nickel enzymes [96]. Other biochemical work of significance includes the isolation of a nickel-binding protein required for hydrogenase synthesis, from *Rhizobium Leguminosarum* [97] and the characterisation of two genes encoding a possible nickel-binding complex involved in hydrogenase expression from *Bradyrhizobium Japonicum* [98].

A study of the puzzling light-induced nickel ESR signals in *Desulfovibrio gigas* hydrogenase at low temperatures has appeared [99]. Illumination of the Ni–C state at below 60 K caused the disappearance of this signal, and its replacement by two others with g = 2.26, 2.11, 2.044 (termed Ni–C_1*) and 2.29, 2.12, 2.044 (termed Ni–C_2*), assigned as due to the presence of two slightly different Ni coordination environments. At 5 K, the rate of disappearance of the Ni–C signal on irradiation was the same as at 30 K, but a new and complex spectrum appeared, interpreted as due to interaction of the reduced paramagnetic [Fe_4S_4] cluster with the Ni site. Above 60 K, only the signal Ni–C_2* appeared, suggesting that one of these sites is an intermediate in the formation of the other. Whereas previous reports had concluded that the Ni–C state of the enzyme was the active intermediate in the redox interconversion between H_2 and $2H^+$, a recent paper [100] concludes that this is not so; in the strict absence of redox mediators or H_2, Ni–C is indefinitely stable, and the form that spontaneously reduces protons is the so-called Ni–R, approximately one electron more reduced than Ni–C, and ESR-silent.

6.6.2 Nitrogen-thiolate and related donor sets

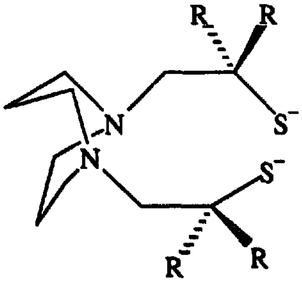
Treatment of $Ni(OAc)_2$ with bis(2-mercaptoethyl)methylamine (H_2L^1) gave dimeric $[Ni(L^1)]_2$, the crystal structure of which revealed square planar Ni(II) with each Ni ligated by a tertiary amine, terminal thiolate and two bridging thiolate donors [101]. The corresponding selenolate complex $[Ni(L^2)]_2$ was isomorphous. One-electron oxidation of either complex gave radicals whose ESR spectra were very similar to those of a reduced, catalytically-viable state of Fe,Ni hydrogenases. Treatment with CN^- gave complexes $[Ni(L^1)(CN)]^-$ and $[Ni(L^2)(CN)]^-$. Interestingly, while treatment of $[Ni(L^1)(CN)]^-$ with O_2 gave a complex of the corresponding monosulfinato-monothiolato ligand, $[Ni(L^2)(CN)]^-$ did not react with oxygen. The significance of this finding to the properties of Fe,Ni,Se hydrogenases is discussed.

A template synthesis employing $Ni(OAc)_2$, 2,5-dihydroxy-2,5-dimethyl-1,4-dithiane and 3,3'-iminobis(propylamine) gave the water-soluble five-coordinate complex [Ni(L)] [L^{2-} = (**19**)], the crystal structure of which shows trigonal bipyramidal coordination of Ni(II) to the central amine and terminal thiolates in the plane; the two imine nitrogens are axial [102]. Solvatochromism of the complex is interpreted in terms of S...H hydrogen bonding, which may be of relevance to the catalytic cycle in hydrogenases.



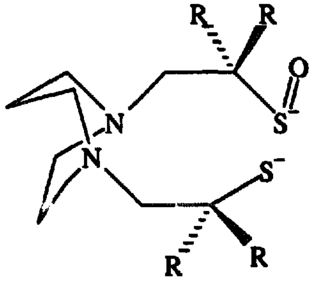
(**19**)

It has been suggested that the deactivation of NiFe hydrogenases by dioxygen may be due to the formation of sulfur-coordinated RSO_2 (sulfinate) or RSO (sulfenate). The complex [Ni(L)] [L^{2-} = (**20**)] reacts with dioxygen in CH_3CN to give a mixture of the corresponding mono- and di-sulfinate complexes; in the presence of water, some [Ni(**20a**)] also forms, which can be separated chromatographically [103]. Cyclic voltammetric or chemical reduction of the latter to $[Ni(L')]^-$ resulted in disproportionation, and formation of [Ni(**20**)] and the corresponding mono-sulfinate complex. The complexes [Ni(L)] [L^{2-} = (**20**), (**21**)] react with SO_2 to afford adducts with SO_2 bound through sulfur to one of the coordinated thiolate groups [104]. The geometry about Ni(II) is rigidly square planar. Green *trans*-$[Ni(Ph_2PCH_2CH_2S)_2]$ also reacts reversibly to give red $[Ni(Ph_2PCH_2CH_2S.SO_2)(Ph_2PCH_2CH_2S)]$. On treatment with O_2, [Ni(L)] [L^{2-} = (**20**)] reacts to give the known thiolate-bridged $[Ni\{Ni(L)\}_2]^{2+}$ ion as the sulfate salt (the sulfate having originated as SO_2), together with oxidised (disulfide) ligand.

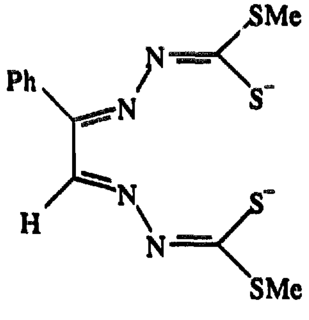


R = –H (**20**)

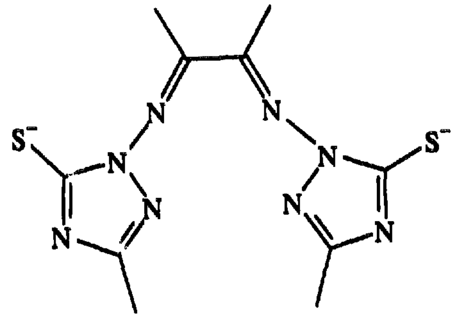
R = $-CH_3$ (**21**)



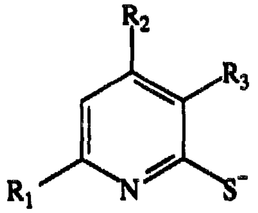
(**20a**)



(**22**)



(**23**)



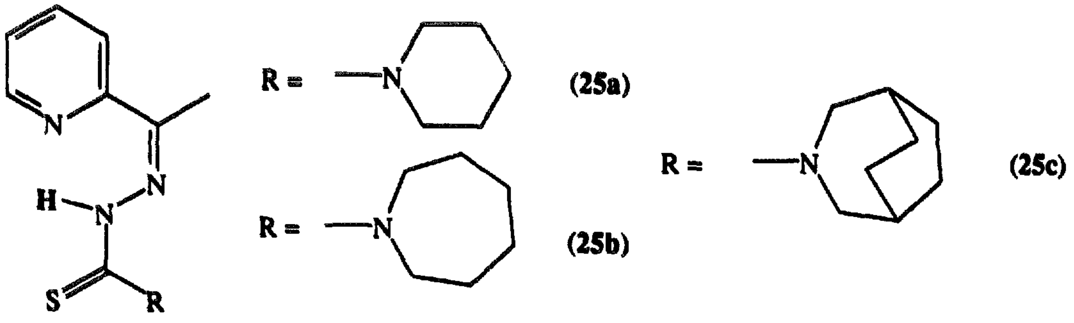
(**24**)

The reaction of $[Ni(aet)_2]$ with Pd^{2+} in water in the presence of Br^- gave the S-bridged hexanuclear $[Pd_2\{Ni(aet)_2\}_4]Br_2$ (aet = $H_2NCH_2CH_2S^-$) [105]. The structure consists of four *cis*-$[Ni(aet)_2]$ units bridging two square planar Pd(II) moieties in a turnstile arrangement. Treatment of $[Pd(aet)_2]$ with Ni(II) gave a mixture of products $[Pd_2\{Ni(aet)_2\}_{4-x}\{Pd(aet)_2\}_x]Br_4$ (x = 0–4), showing that ligand transfer from Pd(II) to Ni(II) occurs under these conditions.

Turning now to imine-thiolate ligands, the reactions of the complex [Ni(L)] [L^{2-} = (**22**)] with various amines and with hydrazine have been studied [106]. Aromatic or aliphatic primary and secondary amines displace one –SMe group; mass spectral evidence suggests preferential displacement of the –SMe conjugated to the phenyl ring. Complexes of the ligand (**23**) have been reported; $[Ni(L)(H_2O)_2]$ is apparently octahedral, and spectroscopic data suggests coordination to the exocyclic imine nitrogens and thiolate donors [107].

The polymeric complex $[Ni(L)_2]\cdot2.75H_2O$, and monomeric $[Ni(L)_2(L\text{–}L)]\cdot1.5H_2O$ [L^- = (**24**); R_1, R_2 = Me, R_3 = H; L–L = bpy, phen] have been prepared from the corresponding pyridimidine-2-thione using the sacrificial anode technique [108]. All have octahedral geometry according to spectroscopic data, although some of the magnetic moments are rather high. Similar 2:1 complexes with 1,3-thiazolidine-2-thionato, 1,3-thiazoline-2-thionato and 2-mercaptobenzothiazolato ligands (N,S) have also been prepared using this electrochemical method [109], and these also form octahedral monomeric $[Ni(N,S)_2(L)_2]$ or $[Ni(N,S)_2(L\text{–}L)]$ (L = primary amine or pyridine donor; L–L = bpy, phen, 2,9-Me_2phen). The crystal structure of $[Ni(N,S)_2(2,9\text{-}Me_2phen)]$ (N,S = 2-mercaptobenzothiazolato) was determined. Complexes $[Ni(N,S)_2L_2]$ [N,S = (**24**); R_1 = Ph, R_2 = p-XC_6H_4, R_3 = CN; X = Cl, Me, MeO, Me_2N; L = pyridine, methylimidazole) have been prepared using conventional syntheses [110]. An all-*trans* octahedral geometry is suggested for these complexes.

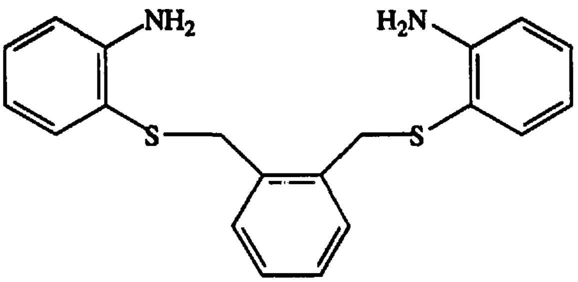
Complexes of Ni(II) with 2-thiouracil and various 5-arylazo-2-thiouracils have been reported [111]. With thiouracil itself, a green complex analysing as $Ni(L)(OH)\cdot2H_2O$ was obtained, assigned a dinuclear OH-bridged octahedral geometry. With the arylazo-substituted compounds, brown $Ni(L)(OH)\cdot nH_2O$ (n = 1,2) were obtained, assigned tetrahedral geometry on account of their high magnetic moments. The green [Ni(*o,o'*-dibutyldithiophosphate)$_2$(L)$_2$] (L = 4-aminopyridine) has been characterised crystallographically [112]. It is octahedral; the 4-aminopyridines are mutually *trans*, bound through the pyridine nitrogens (Ni–N = 2.091(2) Å, Ni–S 2.509(1) Å).



Nickel complexes of the thiosemicarbazones (**25**) have been reported [113]. Whereas five-coordinate paramagnetic $[Ni(HL)Cl_2]$ is obtained, nickel(II) bromide affords [Ni(L)Br] which is square planar [HL = (**25a**); proton in bold lost on anion formation]. Whereas (**25b**) gave only paramagnetic $[Ni(HL)X_2]$ (X = Cl, Br), (**25c**) gave only complexes analysing as [Ni(L)X]. Although the chloride is presumably planar (magnetic moment 0.5 BM), the bromide had a significant magnetic moment (1.5 BM); its formulation is therefore unresolved.

6.6.3 Nitrogen-thioether donor sets

Reaction of 2-aminobenzenethiol, NaOEt, 1,2-$(BrCH_2)_2C_6H_4$ and $[Ni(H_2O)_6](ClO_4)_2$ in ethanol afforded a green solid [114]. Spectroscopic data and, in particular, its magnetic moment (3.65 BM) suggest that this is octahedral $[Ni(L)Br_2]$ [L = (26)]. Interestingly, this complex could not be made from pre-formed (26) and Ni(II) salts. There are four reports of macrocyclic nitrogen-thioether donor macrocycles this year. The complexes $[Ni(L)]ClO_4$ [L^- = (27)] have been synthesised in low yield, and the complex (R = H) characterised crystallographically [115]. Cyclic voltammetric experiments revealed a single reversible reduction (R = H) at −0.82 V, which shifted anodically and became less reversible when CO was present.



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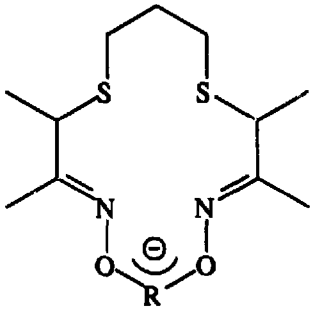
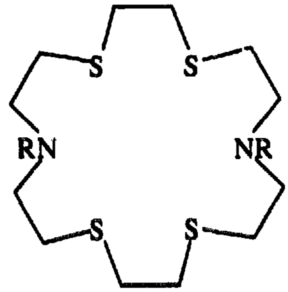


R = H, BF_2

(27)



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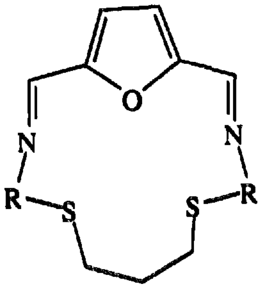
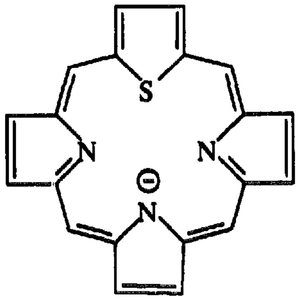


R = $-CH_2CH_2-$

$-C_6H_4-$

(29)



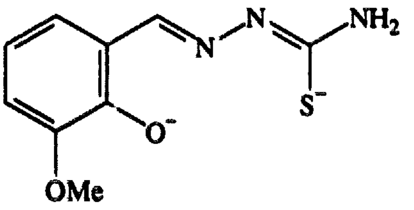
(30)

The complexes $[Ni(L)][PF_6]_2$ [L = (28)] have been characterised [116]. The crystal structure (R = H) shows Ni(II) nearly encapsulated in an octahedral geometry, the ligand adopting *rac* geometry (mean Ni–N 2.096(13) Å, mean Ni–S 2.414(6) Å). Both diastereoisomers possible with this geometry are found in approximately a 1:1 ratio in the crystal. Cyclic voltammetry revealed that the complex (R = H) has two quasi-reversible redox processes at +1.56 V and −0.93 V, assigned to Ni(III)/Ni(II) and Ni(II)/Ni(I) processes respectively. In contrast, the Ni(II)/Ni(I) wave for the complex (R = Me) was at −0.58 V, and the Ni(III)/Ni(II) process was irreversible, and at +2.09 V. This effect, on substituting tertiary for secondary amine donors, is typical of Ni(II)–macrocycle complexes. The complexes $[Ni(L)]X_2$ [L = (29); X = Cl, Br, NO_3], made by template synthesis employing the appropriate amine–thiol, 2,5-diformylfuran and 1,3-dibromopropane, are square planar; the furan oxygen is not coordinated [117].

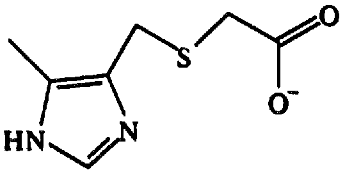
Detection of ESR signals attributable to Ni(I) in the enzymatic cycle of methanogenic bacteria has stimulated considerable effort in the study of reduced nickel-porphyrin and related complexes. An ESR and ^{2}H NMR spectroscopic study of selectively deuterated reduced complexes [Ni(L)] [L^- = (**30**)], including examples enriched in ^{61}Ni (I= 3/2), showed that the SOMO involves comparable contributions from ligand radical anion and Ni(I) [118]. The coordination of additional ligands (pyridine, imidazole, SO_2, $MePh_2P$) to the reduced complex was also investigated.

6.7 COMPLEXES WITH O,S- AND N,O,S-DONOR LIGANDS

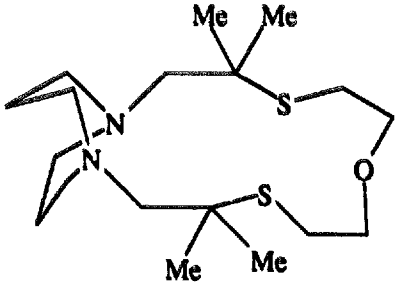
The complex [Ni(L)(H_2O)] is reported to be the product on complexation of Ni(II) by the ligand (**31**) [119]; the magnetic moment (2.30 BM) is reported to be due to equilibrium between square planar and tetrahedral forms. However, normal ^{1}H NMR spectroscopic data are reported for the complex. The ligand HL (**32**) forms octahedral, insoluble [Ni(L)$_2$] which, on the basis that its IR spectrum is very similar to that of other crystallographically-characterised metal complexes, is assigned all-*trans* geometry [120].



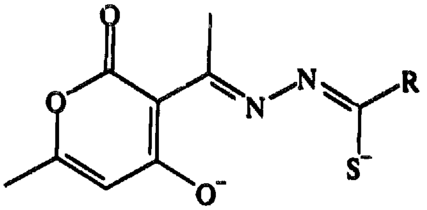
(**31**)



(**32**)



(**33**)



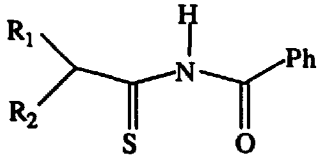
R = SMe, NH_2

(**34**)

An attempt has been made to prepare a pentacoordinate Ni(II) complex with a N_2S_2O donor set, using the ligand (**33**) derived from *N,N'*-bis(2-mercapto-2-methylpropane)-1,5-diazacyclooctane [121]. However, the ligand afforded a complex [Ni(L)]I_2 which X-ray crystallography showed had square planar N_2S_2 coordination. The crystal structure of the precursor complex was also reported.

The ligands L^{2-} (**34**) form dimeric, square planar complexes [Ni(L)]$_2$, with phenoxy O^-, nitrogen and two bridging sulfur atoms coordinated to each Ni, which, on treatment with pyridine or

PPh_3 (L') give monomeric planar [Ni(L)L'] [122]. Complexes $[Ni(L)_2]$ [HL = (35)] are square planar and diamagnetic; whether the geometry is *cis* or *trans* could not be established by spectroscopy [123].



$R_1 = R_2$ = Me, Et, Pr, Bu, Ph

R_1 = Me, R_2 = benzyl

R_1, R_2 = morpholine or piperidine

(35)

Electrochemical oxidation of Ni metal in CH_3CN solutions of 2-pyridinone (HOpy) and 2-pyridine methanethiol-1-oxide (HPMTO), or 2,2'-dithiodimethyldipyridine-1,1'-dioxide (DPMTO) gave, respectively, $[Ni(Opy)_2]\cdot 2H_2O$ and $[Ni(PMTO)_2]\cdot 2H_2O$ [124]. The electronic spectra and magnetic moments of these complexes suggest tetrahedral geometries. With bpy or phen, octahedral $[Ni(Opy)_2(L\text{–}L)]$ or $[Ni(PMTO)_2(L\text{–}L)]$ (L–L = bpy, phen) could also be isolated.

6.8 COMPLEXES WITH NON-MACROCYCLIC NITROGEN DONORS

6.8.1 Complexes of mono- and didentate amine and related ligands

Complexes of Ni(II) with *N*-methylmorpholine (L^1) and *N,N'*-dimethylpiperazine (L^2) have been the subject of thermochemical study [125]. Both $[Ni(L^1)Cl_2]$ and $[Ni(L^2)Cl_2]$ are reportedly polymeric and tetrahedral. Calculations of electrostatic interactions between NH_3 groups undergoing correlated rotations in $[Ni(NH_3)_6]^{2+}$ have been reported [126].

The ligand *N,N'*-bis(2-hydroxyethyl)oxamide (H_2L) reacts with Ni(II) in basic conditions to afford square planar $K_2[Ni(L)_2]\cdot 3H_2O$, with the Ni(II) apparently coordinated to four deprotonated amide nitrogens [127]. Several Ni(II) complexes of 2-nitrosoanilines (HL) have been synthesised; the aromatic amine is deprotonated on complexation to give square planar $[Ni(L)_2]$ [128]. The complexes have less tendency to increase their coordination number than corresponding Ni(II)-2-nitrosophenolate complexes.

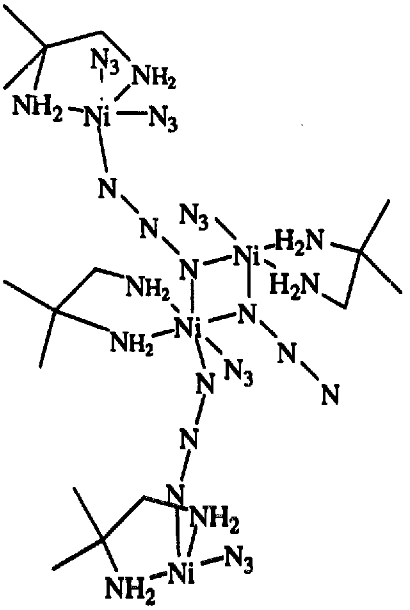
Several papers this year report studies of thermochromism in Ni(II)-diamine complexes. Several NiI_2 complexes of diamines forming six-membered chelate rings have been studied in this way [129]. Octahedral $[Ni(tn)_3]I_2$ and square planar $[Ni(N\text{-methylpropane-1,3-diamine})_2]I_2$ decompose to NiI_2. Pink $[Ni(tn)_2(H_2O)_2]I_2$ loses water at 90 °C; the new green complex is formulated as *trans*-$[Ni(tn)_2I_2]$. Purple $[Ni(2,2'\text{-dimethylpropane-1,3-diamine})_3]I_2\cdot 2H_2O$ loses water, then loses a mole of diamine, becoming light blue, at 182 °C. Pre-formed planar orange $[Ni(2,2'\text{-dimethylpropane-1,3-diamine})_2]I_2$ also isomerises to this light blue metastable form at 210–260 °C. A study of five-membered chelate ring diamine complexes of NiI_2 has also appeared [130]. Here, 3:1 complexes of *N*-monosubstituted diamines were found to undergo loss of one mole of diamine affording *trans*-$[Ni(diamine)_2I_2]$ except for complexes of 2-methylpropane-1,2-

diamine and *N*-isopropylethylenediamine which gave square planar [Ni(diamine)$_2$]I$_2$. Dehydration of [Ni(diamine)$_2$(H$_2$O)$_2$]I$_2$ resulted in anation, the *trans* geometry being preserved except for [Ni(en)$_2$I$_2$] where *cis* geometry was found. The complexes [Ni(bn)$_2$(H$_2$O)$_2$]X$_2$ (bn = *d,l*-2,3-butanediamine, X = Cl, Br) undergo dehydration to form yellow square planar [Ni(bn)$_2$]X$_2$ at 70–90 °C, then anation to form light blue [Ni(bn)$_2$X$_2$] at 180–190 °C; the kinetics and thermodynamics of these processes have been studied using DSC [131].

The thermochemistry of a large number of complexes [Ni(diamine)$_3$]X$_2$ (diamine = various unsubstituted, *C*-substituted and *N*-substituted diamines; X = Cl, Br, NO$_3$] has been examined, with particular emphasis on formation of [Ni(diamine)$_2$X$_2$] [132]. Of the twelve examples of the latter isolated, all but [Ni(en)$_2$X$_2$] (X = Cl, Br) and [Ni(2-methylpropane-1,2-diamine)$_2$Cl$_2$] were found to be *trans* (as determined by near-IR spectra). The solid state thermal reactions of 2:1 complexes of *d,l*-4-methyl-1,2-pentanediamine with Ni(II) have also been studied; [Ni(diamine)$_2$]Cl$_2$ underwent reversible anation [133]. Finally, the square planar [Ni(*N*-isopropyl-2-methylpropane-1,2-diamine)$_2$](NO$_3$)$_2$ underwent anation to *cis*-[Ni(L)$_2$(NO$_3$)]NO$_3$ on heating to 180 °C [134].

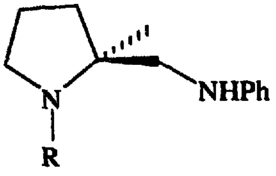
Solvatochromism amongst Ni(II)-tertiary amine complexes with β-diketonate co-ligands continues to attract attention. Equilibria exist between four-, five- and six-coordinate complexes [Ni(β-dik)(diam)L$_n$]$^+$ (diam = tmen, *N,N,N'*-trimethylethylenediamine, *N,N,N',N'*-tetraethylethylenediamine) in mixtures of nitroethane with the different donor solvents (L) [135]. Increasing donor strength of the solvent and increasing electron-withdrawing effect of substituents in the β-diketonate both favour the formation of six-coordinate complexes. A similar study of mixed β-diketonate-diamine complexes, exploring the role of substituents (on both diamine and β-diketonate), and the charge-balancing anion, has also appeared [136]. Coordinating anions (halide, nitrite, nitrate) afford complexes [Ni(β-dik)(diam)(H$_2$O)X] or [Ni(β-dik)(diam)(O$_2$NO$_n$)] (n = 0,1) whereas with non-coordinating anions Y$^-$, square planar complexes [Ni(β-dik)(diam)]Y are favoured. With diam = *N,N'*-diphenyl-1,2-diaminoethane, comproportionation of [Ni(β-dik)$_2$(H$_2$O)$_2$] and [Ni(diam)$_2$]X$_2$ (X = NO$_3$, ClO$_4$) afforded complexes [Ni(diam)$_2$(β-dik)]ClO$_4$, [Ni(diam)(β-dik)(O$_2$NO)] or [Ni(β-dik)$_2$(diam)] [137]. The crystal structure of [Ni(diam)$_2$(tfacac)]ClO$_4$ (diam = *N,N'*-diphenyl-1,2-diaminoethane, tfacac = trifluoroacaetylacetonate) has been determined [138]. The Ni–O bonds (mean Ni–O = 2.006 Å) are nearly identical despite the asymmetric substitution of the β-diketonate, and the diamine chelate rings adopt the gauche conformation, as suggested previously for complexes of this type on the basis of infrared data. Similar dimetallic complexes have been described, employing the tetraketonates 1,1,2,2-tetraacetylethanediide (taet) or 1,2-diacetyl-1,2-dibenzoylethanediide, and the diamine tmed [139]. The crystal structure of one example, [Ni$_2$(taet)(tmed)$_2$](ClO$_4$)$_2$·3H$_2$O has been determined. Unusually, one of the Ni(II) centres is square planar, the other octahedral. However, in the tetraphenylborate salt both Ni(II) centres are planar, while in the nitrate, both Ni(II) centres are octahedral. The dinuclear 5-coordinate complex [Ni$_2$(taet)(pmdt)$_2$]$^{2+}$ (pmdt = *N,N,N',N'',N''*-pentamethyldiethylenetriamine) has also been described; this forms mono- or bis-octahedral species in donor solvents [140].

Magnetic studies on azide-bridged Ni(II)-amine complexes continue. The complexes $[\{Ni(en)_2\}_2(\mu\text{-}N_3)_2](ClO_4)_2$, $[\{Ni(en)(\mu\text{-}N_3)_2\}_n]$, $[\{Ni(tn)(\mu\text{-}N_3)_2\}_n]$ and $[\{Ni(Me_2tn)(\mu\text{-}N_3)_2\}_n]$ (tn = 1,3-propanediamine; Me_2tn = 2,2'-dimethyl-1,3-propanediamine) have been isolated, crystallographically characterised and their magnetic properties studied as a function of temperature [141,142]. The first complex cation is an end-on azide-bridged dimer, ferromagnetically coupled as usually observed with this bridging mode for azide complexes. The second two complexes have very similar structures with neutral Ni(II) centres chelated by one diamine ligand and bridged end-on by four azide ligands to two neighbouring Ni(II) centres in *cis* fashion. These complexes are ferromagnetically coupled with some metamagnetism at low temperatures. The final complex has the arrangement shown in (36), with each Ni(II) coordinated to a chelating diamine, one terminal azide ligand and three other azides each shared by two other nickel ions. Each azide coordinates two Ni(II) ions in end-on mode, but also coordinates the third Ni(II) in end-to-end mode. Overall, the complex shows 2D antiferromagnetism down to 60 K, then undergoes long-range magnetic ordering.



(36)

The complexes $[\{Ni_2(L\text{–}L)_3(NCS)_2\}(\mu\text{-}NCS)_2]_2[Ni(L\text{–}L)_2(NCS)_2]$ and $[Ni_2(L\text{–}L)_4(\mu\text{-}NCS)_2](PF_6)_2$ (L–L = 1,2-diamino-2-methylpropane) have been structurally characterised [143]. The dimeric unit in the first structure has a *cis*-$Ni(diamine)_2$ and a $Ni(diamine)(NCS)_2$(terminal) moiety connected by end-to-end bridging NCS^- ions. The second structure consists of two *cis*-$Ni(diamine)_2$ units end-to-end bridged by NCS^- ions. The complex $\{$*catena*-$(\mu\text{-}NCS)[Ni(en)_2]\}(PF_6)$ has also been described; this has *cis*-$Ni(en)_2$ units linked by two NCS^- ions, one coordinated through N, the other through S, at each Ni(II) [144]. All the NCS^--bridged complexes show weak ferromagnetic coupling. An unusual structure elucidated this year was that of $[Ni(N_3)_2(tmed)]_n$ [145]. This consists of zig-zag chains of $\{Ni(tmed)\}_2(\mu\text{-}N_3)_3$ (end-on azide bridged) dimers, linked by a further end-to-end azide bridge completing octahedral coordination at each Ni. The complex had net antiferromagnetism.



(R = C_5H_{11} for best results)

(37)

In the presence of a large excess of ligands (37), $NiCl_2$-catalysed enantioselective coupling of diethylzinc to chalcones proceeds with high yield and high enantioselectivity [146]. Complexes *trans*-[Ni(L–L)$_2$X$_2$] (L–L = $Et_2NCH_2CH_2NH_2$, $MeHNCH_2CH_2NMeH$; X = NO_2, NO_3, NCS) have been employed in the photochemical production of thin films of nickel metal [147]. A study of clathrates including [Ni(en)$_2$Ni(CN)$_4$]·2PhNH$_2$ has appeared [148].

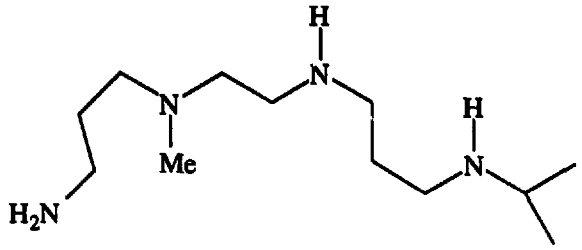
6.8.2 Complexes of multidentate amine and related ligands

An example of geometric isomerism in [Ni(dien)$_2$](NCS)$_2$ has been discovered [149]. The stable form has the symmetrical *fac* arrangement (terminal amines of each ligand *cis*; secondary amines *trans*). On heating, this complex undergoes an endothermal phase transition (162–180 °C) giving the *mer* isomer; both isomers may be prepared from solution using slightly different conditions, and both have been characterised crystallographically. The complex [{Ni(L)(NCS)(μ-SCN)}$_n$] (L = bis(3-aminopropyl)methylamine) has been characterised crystallographically [150]. It has an unusual structure in which *mer*-[Ni(L)(NCS)] units are connected by *trans* SCN bridges. It is very weakly ferromagnetic.

The complexes *trans*-[Ni(333-tet)(μ-N$_3$)]$_n$(ClO$_4$)$_n$ and *cis*-[Ni(333-tet)(μ-N$_3$)]$_n$(PF$_6$)$_n$ (333-tet = *N,N'*-bis(3-aminopropyl)-1,3-propanediamine) crystallise from aqueous mixtures of the ligand, sodium azide and, respectively, nickel(II) perchlorate or nickel(II) nitrate and KPF$_6$ [151]. In the first complex, two kinds of alternating centrosymmetric azide bridges are present, both coordinated end-to-end (Ni–N = 2.077(3) Å, 2.204(3) Å respectively; Ni–N–N = 142.4(3)° and 123.6(2)° respectively); there is strong antiferromagnetic coupling ($J = -80.7$ cm^{-1}, $\alpha = 0.46$). In the *cis* complex, an unprecedented arrangement for end-to-end azide bridges, the antiferromagnetic coupling is weaker ($J = -18.5$ cm^{-1}). The complex *trans*-[{Ni(323-tet)(μ-NCO)}$_n$](ClO$_4$)$_n$ (323-tet = *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine) has also been isolated; use of the tetradentate ligand promotes formation of the *trans*-bridged arrangement of cyanato ligands [152]. The complex is weakly ferromagnetic ($J = +2.3$ cm^{-1}).

Oxalato-bridged complexes (μ-ox)[Ni(triamine)(H$_2$O)]$_2$(ClO$_4$)$_2$·nH$_2$O (triamine = bis(3-aminopropyl)amine, 3,3'-diamino-*N*-methyl-dipropylamine, *N*-(2-aminoethyl)-1,3-propanediamine; n = 0,2,0 respectively) have been synthesised, and the crystal structures of the first two complexes have been determined [153]. The tridentate amines are *mer* in both complexes, with the water coordinated in the same plane as the oxalate oxygens. As is usual for oxalate-bridged Ni(II) complexes, these are antiferromagnetic, but the *J* values are smaller than analogous complexes with tetradentate nitrogen donors. The complex $[\{Ni_2(bis(3\text{-aminopropyl})amine)_2(\mu\text{-ox})(\mu\text{-}N_3)\}_n](PF_6)_n$ has also been crystallised [154]. This adopts an unusual geometry in which one Ni(II) centre is coordinated by a *mer* triamine ligand, two oxygens from the bridging oxalate (one *trans* to the secondary amine of the triamine), and the bridging azide nitrogen, while the other Ni(II) centre is coordinated by a *fac* triamine with its primary amines *trans* to the two oxalate oxygens, and the other bridging azide nitrogen bonded *cis* to the oxalate unit. The complex is antiferromagnetic, $J = -27.4\ cm^{-1}$, alternating parameter $\alpha = 0{\cdot}1$.

The crystal structure of $[Ni(4RS,7SR,11RS\text{-}L)](ClO_4)_2$ [L = (38)] has been solved [155]. This is square planar (Ni–N = 1.915(7) – 1.951(6) Å).



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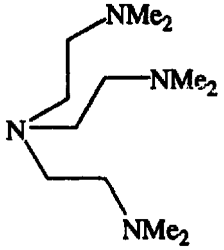


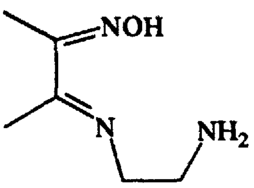
(39)

The difference in stability constants for complex formation between the ligand tren and (39), due to the additional steric effects and weaker donor power of (39), reaches a maximum for Ni(II) [log K = 14.95(4) (tren), 7.14(4) (39)]; this has been interpreted in terms of the difference in CFSE between octahedral coordination and the trigonal bipyramidal coordination favoured by (39) [156].

6.8.3 Imines, oximes and related ligands

The reactions of Ni(IV) complexes $[Ni(L_1)_2]^{2+}$ and $[Ni(L_2)]^{2+}$ [L_1 = (40), L_2 = (41)] with sulfite have been investigated in aqueous solution as a function of pH [157]. Below pH *ca.* 5, the process is a single step two-electron transfer, but above this pH, the initial one-electron transfer is distinctly faster. The stoichiometry varied depending on whether oxidant or reductant was present in excess; both dithionate and sulfate were formed. The mechanism is inner-sphere, although probably with initial formation of a H-bonded adduct. The crystal structure of $[Ni(L)]SO_4{\cdot}3H_2O$ [L = (42)] establishes that this ligand acts as a neutral hexadentate with both amines and all four oxime nitrogens coordinated [158]. In this respect it differs from the structurally similar $edta^{4-}$ which forms $[Ni(edta)(H_2O)]^{2-}$ with one $-COO^-$ uncoordinated.

Several Ni(II) complexes of Schiff base adducts of 2-acetylpyrrole have been characterised crystallographically [159]. With ammonia or methylamine, only bis(Schiff base) complexes were obtained, with coordination of square planar Ni(II) to *trans* pyrrolyl nitrogens and Schiff base nitrogens. With bulkier amines at elevated temperatures, similar products were obtained, but at room temperature, planar complexes [Ni(Schiff base)(2-acetylpyrrolyl)] could also be isolated. With nickel(II) perchlorate, the ligand (43) forms dinuclear $[Ni_2(L)_2](ClO_4)_4$ which was assigned pseudotetrahedral geometry on the basis of magnetic moment and electronic spectral data [160].



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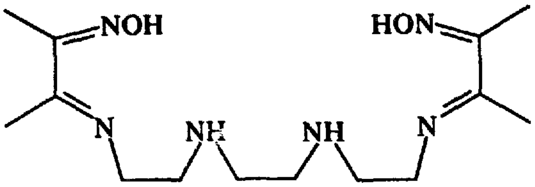
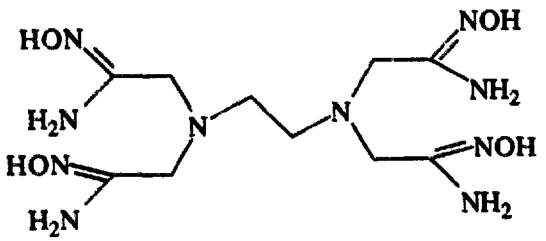


(41)



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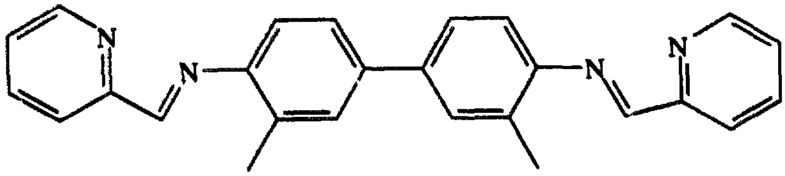

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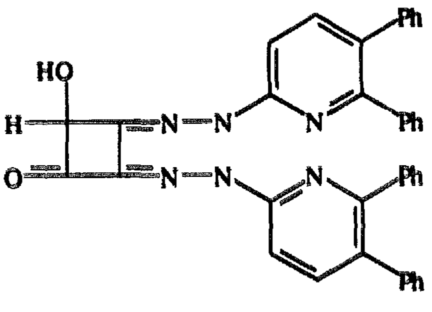

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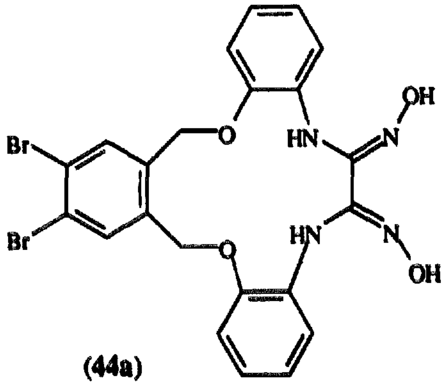
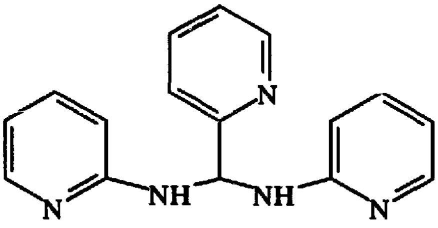


(44a)

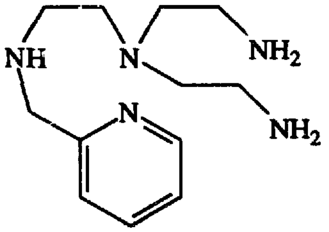
The synthesis of the ligand H_4L (44) and details of the formation of the complex $[Ni_2(L)]$, with Ni(II) coordinated both to the exocyclic oxygens and to the imine nitrogens adjacent to the four-membered ring, have been described [161]. The ligand (44a) reacts with Ni(II) in basic methanol to afford only $[Ni(H_3L)_2]$, with square planar Ni(II) coordinated only to the exocyclic dioxime function [162]. Finally, reaction of $[Ni(Hdmg)_2]$ with $GaEt_3$ gave $[Ni(dmg.GaEt_2)_2]$, with the $GaEt_2$ moieties each coordinated to two glyoxime oxygens [163]. This complex has been tested as a single source precursor for $GaNi_2$ films.

6.8.4 Amine-aromatic imine mixed donor ligands

The reaction of L (45) with nickel(II) perchlorate in CH_3CN gave pseudo-octahedral $[Ni(L)_2](ClO_4)_2{\cdot}2CH_3CN$, without oxidative degradation of the ligand in contrast to similar reactions with Mn(II) and Fe(II) salts [164]. The complex was *fac* pseudo-octahedral, with the ligand coordinated through two of the three pyridyl nitrogens and one of the secondary amines, in such a manner as to give only five- and six-membered chelate rings. With **(46)**, nickel(II) perchlorate afforded $[Ni(L)(OH_2)](ClO_4)_2{\cdot}H_2O$, which on treatment with NaN_3 in aqueous methanol gave end-to-end azide-bridged $[Ni_2(L)_2(\mu\text{-}N_3)]ClO_4$ [165]. The latter is antiferromagnetic ($J = -26.8$ cm^{-1}).

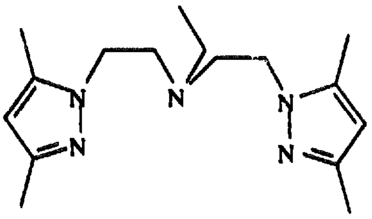


(45)



(46)

The ligand ddae **(47)**, when treated with nickel(II) nitrate in ethanol$(EtO)_3CH$, gave octahedral $[Ni(ddae)(NO_3)_2]$, and with nickel(II) tetrafluoroborate, '$[Ni(ddae)(H_2O)(BF_4)_2]$' [166]. The nitrato complex is assigned an octahedral structure, with ddae as a *fac* tridentate, one mono- and one didentate nitrate ion, on the grounds that it is isomorphous with the corresponding Co(II) complex which has that structure. The tetrafluoroborate is also octahedral, and there is IR spectroscopic evidence for BF_4^- coordination although structural data was not obtained.



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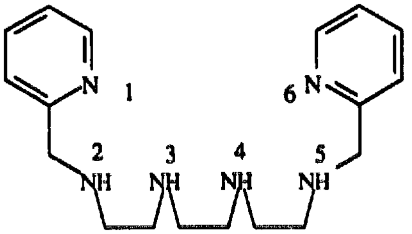

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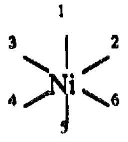
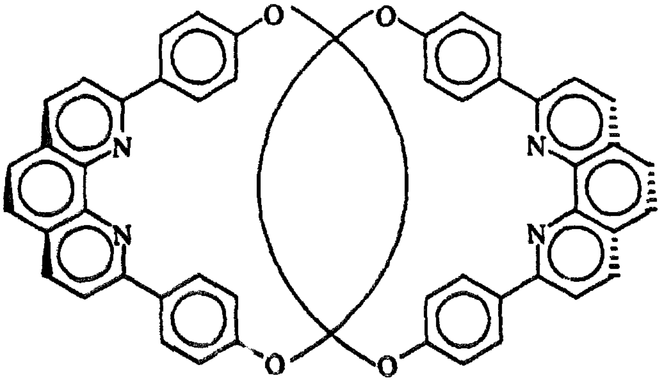


(49)

The hexadentate **(48)**, with nickel(II) perchlorate in ethanol, afforded violet $[Ni(\mathbf{48})](ClO_4)_2$ [167]. A crystal structure determination showed distorted octahedral coordination, with the arrangement of donors as in **(49)** [mean Ni–N(pyridyl) 2.103(5) Å; mean Ni–(amine) 2.105(5) Å]. In CH_3CN, the complex shows a quasi-reversible redox process, assigned to Ni(III)/Ni(II), at + 1.44 V; this is *ca.* 0.7 V more anodic than the process for $[Ni(tacn)_2]^{2+/3+}$.

6.8.5 Aromatic imine and related donor ligands

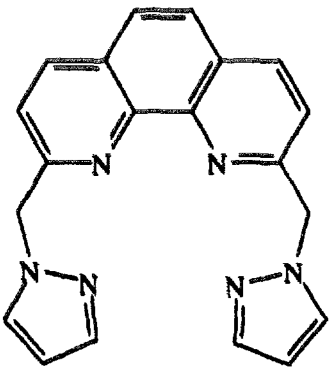
The catenane ligand **(50)** strongly stabilises Ni(I) with respect to Ni(II) because of the overwhelming preference of this ligand for tetrahedral coordination; the Ni(I) complex could be generated by constant potential electrolysis of $[Ni(\mathbf{50})]^{2+}$ at –0.45 V in CH_3CN and, furthermore, a second reversible one-electron transfer (assigned to Ni(I)/Ni(0)) was found at –1.325 V [168]. Crystal structures of Ni(II) and Ni(I) complexes have been obtained. The orange Ni(II) complex is very distorted four-coordinate, with the Ni(II) ion lying almost in a plane surrounded by three of the four nitrogen atoms [mean Ni–N 2.01 ± 0.04) Å]. This geometry may in part be due to the maximising of π–π interactions in the ligands. However, the Ni(I) ion is at the centre of a tetrahedral coordination sphere [mean Ni–N 1.98 ± 0.02 Å] and π–π stacking interactions are no longer as significant. The synthesis and characterisation of a range of Ni(II) complexes of 2- and 2,9-substituted 1,10-phenanthrolines (L–L) have been reported [169], where the substituents are *o*-substituted phenyl groups. These sterically demanding ligands give tetrahedral complexes [$NiCl_2$(L–L)] or (with nickel(II) perchlorate) [Ni(L–L)(H_2O)$_2$](ClO_4)$_2$ or [Ni(L–L)$_2$]$^{2+}$ depending upon the mole ratio. The crystal structure of [$NiCl_2$(L–L)] (L–L = 2,9-bis(2-methoxyphenyl)-1,10-phenanthroline) was determined. Interestingly, like the catenate complexes described earlier, the [Ni(L–L)$_2$]$^{2+}$ complexes undergo two reversible one-electron reductions in CH_3CN, at +0.12 to −1.30 V and −1.25 to −1.46 V depending upon substituents. The great range of Ni(II)/Ni(I) potentials is noteworthy.



(Linking group is

$-O(CH_2CH_2O)_4CH_2CH_2O-$)

(50)



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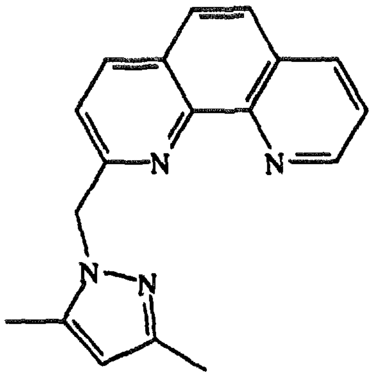


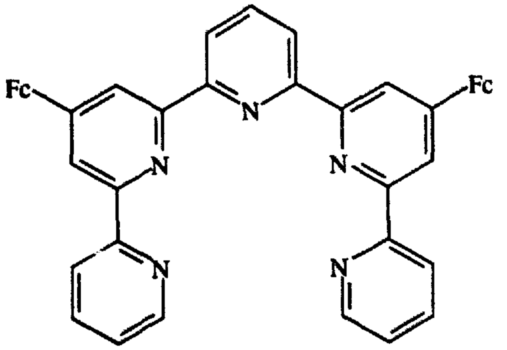
(52)

With the ligand (**51**), which combines soft phenanthroline and harder pyrazolyl nitrogens, octahedral [Ni(**51**)(H_2O)$_2$]$^{2+}$ was isolated [169,170]. The crystal structure of both the latter distorted octahedral complex (as the chloride salt), and the trigonal bipyramidal [$NiCl_2$(L)]·CH_3CN [L = (**52**)], have been solved [137]. The complex of (**51**) shows only an irreversible reduction at −0.50 V, but the complex of (**52**) shows a quasi-reversible wave at −0.66 V attributed to a Ni(II)/Ni(I) process. Turning now to bpy and related ligands, the crystal structure of

$[Ni(bpy)_3]_2[Ag(CN)_2]_3Cl\cdot 9H_2O$ has been reported [171]; the water molecules and anions form an extended 3-dimensional hydrogen-bonded network, with the dications in cavities within this network. The structure of $[Ni(NCO)_2(bpy)_2]$ has also appeared; this has *N*-bonded cyanate ligands, confirming the original assignment of its structure based on IR spectroscopic evidence (ν_{NC} 2200 cm^{-1}) [172]. The complexes *cis*-*catena*-$[(\mu\text{-}N_3)\{Ni(bpy)_2\}](X)$ ($X = ClO_4, PF_6$) have been structurally characterised [173]. Both have end-to-end azido bridges, and are antiferromagnetic ($J = -33.0$ and $-22.4\ cm^{-1}$ for the ClO_4^- and PF_6^- salts respectively). Combination of $CuCl_2$, terpy and $[Ni(terpy)(N_3)_2]\cdot H_2O$ (1:1:1) in methanol/H_2O afforded, first, crystals of a complex $[\{Cu_{0.75}Ni_{0.25}(terpy)(N_3)_2\}_2]\cdot 2H_2O$ and subsequently $[Cu(terpy)(N_3)Cl]$ [174]. The structure of the Cu–Ni mixed complex shows two *mer*-[M(terpy)] units linked by two *cis* end-on azide bridges, with a terminal azide ligand coordinated to each M completing six-coordination. Although X-ray diffraction could not distinguish whether the lattice contains only Cu_2 and Ni_2 units in a 3:1 mole ratio, or whether heterodinuclear molecules exist, single-crystal ESR spectra are only consistent with the former. The magnetic properties of the mixed-metal complex are consistent with global ferromagnetic interactions ($J = +20.1\ cm^{-1}$). Complexes $[Ni(L)_2]_2[Cu(pba)](ClO_4)_2$ (L = phen, bpy, 5-nitrophen, 4,4'-dimethylbpy; pba = propylene-1,3-bis(oxamato) tetraanion) have been synthesised [175]. The central Cu(II) moiety is coordinated to four deprotonated amide nitrogens in a square planar arrangement, while the Ni(II) ions are coordinated by two diimine ligands and two amide oxygen donors. The complexes are antiferromagnetic, $J = -106\ cm^{-1}$ for $[Ni(phen)_2]_2[Cu(pba)](ClO_4)_2\cdot H_2O$.

Nickel complexes of bpy and related ligands are active electrocatalysts for CO_2 reduction. $[Ni(terpy)_2]^{2+}$ undergoes two successive one-electron reductions at −1.20 and −1.38 V in dmf [176]. In the presence of CO_2, the cathodic peak current for the first process is enhanced greatly. Electrodes modified with films of poly-$[Ni(4'\text{-vinylterpy})_2](PF_6)_2$ (grown by repetitive cyclic voltammetry between 0.00 and −1.70 V of a solution of the complex in CH_3CN) were also active for CO_2 electroreduction in dmf, and, unlike the complex in solution, for O_2 reduction in water. Interestingly, both two-electron O_2 reduction (giving H_2O_2) and four-electron reduction to H_2O occurred.

Interest in polypyridyl ligands for supramolecular complex formation continues. The ligand (**53**) has been synthesised, and the double helicate complex $[Ni_2(\mathbf{53})_2(H_2O)_2](PF_6)_4$ prepared [177]. The latter has been characterised using paramagnetic ^1H NMR spectroscopy as having one Ni in an octahedral $[Ni(terpy)_2]^{2+}$ environment, the other an octahedral $[Ni(bpy)_2(H_2O)_2]^{2+}$ environment. In this respect the ligand behaves essentially in the same way as the unsubstituted quinquepyridine. The four ferrocene moieties undergo oxidation at the same potential (+0.21 V *vs* ferrocene/ferrocenium). Reductive dehalogenation (by zerovalent nickel-phosphine complexes) of the corresponding dihalo compounds gave poly(pyridine-2,5-diyl), poly(2,2'-dipyridine-5,5'-diyl), 3-, 4-, and 6-methylated poly(pyridine-2,5-diyl)s, poly(6-hexyl-2,2'-dipyridine-5,5'-diyl) and poly(6,6'-dihexyl-2,2'-dipyridine-5,5'-diyl) [178]. Complexation of some of the poly(dipyridine) polymers to Ni(II) and Ni(0) has been explored. The poly-'$NiCl_2(bpy)$' thus obtained showed activity as an electrocatalyst for the reduction of CO_2 to CO. In the cyclic voltammogram of a polymer complex-modified electrode, peaks due to both the reduction of the Ni(II) centre to Ni(0), and to the n-doping (reduction) of the polymer were observed.



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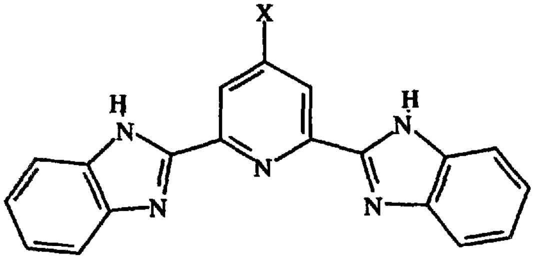
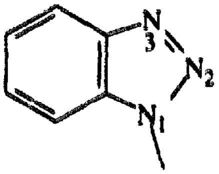


(54)

A series of ligands (**54**) has been synthesised, largely in order to study the effect of the substituent on spin-crossover behaviour in their iron(II) complexes, but several Ni(II) complexes $[Ni(L)_2](ClO_4)_2$ were also made since the 10*Dq* value for these complexes is easy to measure, and correlates well with the spin-crossover behaviour [179]. The values of 10*Dq* were (X = Cl) 11,500 cm^{-1} (X = H) 11,620 cm^{-1} and (X = OH) 11,500 cm^{-1}. The crystal structures of $[NiX_2(pyridazine)]$ (X = Cl, Br) have been solved *ab initio* from X-ray powder diffraction data [180]. Both compounds have infinite polymer chains of nickel ions bridged by both pyridazines and X (Ni–Cl 2.422(1) Å, Ni–Br 2.560(2) Å), with an overall *trans* (D_{4h}) X_4N_2 donor set.



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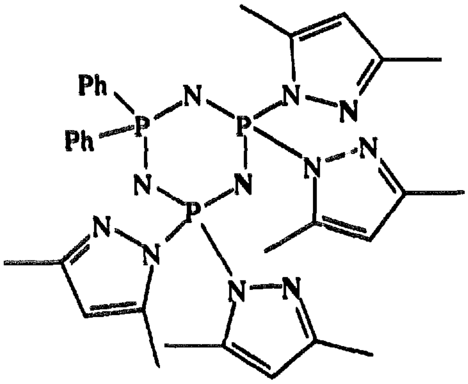

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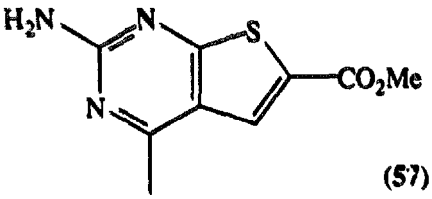
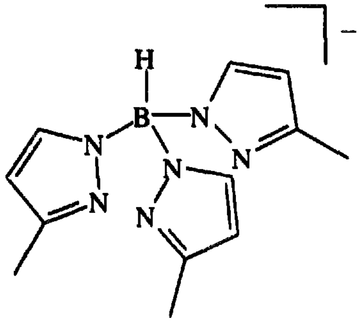


(57)

Benzotriazoles are renowned for their anti-corrosion properties, and this stimulates interest in their coordination chemistry. With nickel(II) nitrate in ethanol in the presence of $(EtO)_3CH$, methylbenzotriazole (**55**) (L) gave *cis*-$[Ni(NO_3)_2(L)_2]$, characterised crystallographically [181]. In acetone-water, $[Ni(NO_3)(H_2O)(L)_2](NO_3)$ or *trans*-$[Ni(H_2O)_4(L)_2](NO_3)_2$, the latter also characterised crystallographically, was the product, depending on the concentration of water. Under anhydrous conditions in acetone, a mixture of *mer*-$[Ni(NO_3)_2(L)_3]\cdot CH_3COCH_3$ and *trans*-$[Ni(NO_3)_2(L)_4]$ formed. Also isolated were *trans*-$[NiX_2(methanol)_2(L)_2]$ (X = NCS, Br), *trans*-$[NiX_2(L)_4]$ (X = NCS, Br) and polymeric $[NiCl_2(L)]_n$ and $[NiX_2(L)_2]_n$ (X = Cl, Br), showing the versatility of this ligand, which always bonds *via* N_3. The complex $[Ni(L)Cl_2]$ [L = **(56)**; nitrogens in bold involved in coordination sphere] is distorted trigonal bipyramidal, with the two chloride ligands and the phosphazene ring nitrogen atom in the equatorial plane, and two axial pyrazolyl nitrogen donors [182]. The corresponding bromide was also isolated, but not structurally characterised.

Ligands **(57)** afforded complexes analysing as $[Ni(L)_2X_2]$ (X = Cl, Br) [183]. These were assigned tetrahedral geometries on the basis of their magnetic moments and electronic spectra. The ligands probably coordinate *via* N_1 (shown in bold), according to IR spectroscopic data. The interesting new lipophilic ligands 5,5'-di-^{t}Bu-2,2'-dipyrimidine and 5,5'-dihexyl-2,2'-dipyrimidine have been prepared using Ni(0)-catalysed coupling reactions [184]. The thermally stable complex $[Ni(\mathbf{58})_2]$ has been characterised crystallographically [185]. There were two distinct Ni sites within the crystal; one was almost ideally octahedral, the other rather distorted. The bite angle of this ligand is greater than either tris(pyrazolyl)borate or tris(3,5-dimethylpyrazolyl)borate.



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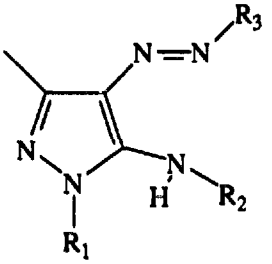


(59)

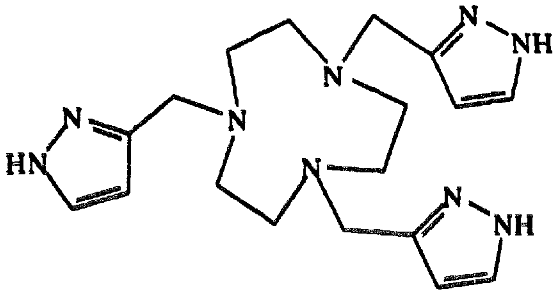
The complexation behaviour of a series of pyridinecarbaldehyde-pyridylhydrazone ligands with Ni(II) has been explored [186], and the effect of bulky groups upon complexation equilibria and ligand field parameters tested. Complexes of some azopyrazoles have been described [187,188]. The complexes $[Ni(L)_2]$ [HL = **(59)**; R_1,R_2, R_3 = various aryl or alkyl groups] were tetrahedral when R_2 = aryl, but one complex with R_2 = H was square planar [187]. The complexes were characterised using electronic spectra and magnetic measurements and, further, by paramagnetic ^1H NMR spectroscopy. The crystal structure of one example ($R_1 = {}^iPr$, $R_2 = p\text{-}MeOC_6H_4$, $R_3 = p\text{-}C_6H_4Me$) was obtained. The rates of interconversion of *R* and *S* forms were slow on the NMR spectroscopic timescale. Some complexes of Ni(II) with 4-arylazopyrazoles have also been described [188]. However, the observation of apparently diamagnetic ^1H NMR spectra for the complexes contradicts the assignment of electronic spectral bands in terms of tetrahedral geometries, leaving the formulation of the complexes open to question.

Finally, the crystal structure of $[Ag(NH_3)_2]_2[Ni(L)_2]\cdot 6H_2O$ ($L^{2-} = {}^{-}HNC(O)NHC(O)NH^{-}$) has been determined, the first Ni(II) complex of the biuretato ion to be structurally characterised [189]. The complex is square planar (centrosymmetric; mean Ni–N 1.868(4) Å).

6.9 COMPLEXES WITH MACROCYCLIC AMINE LIGANDS

6.9.1 Complexes with triazamacrocycles

The mechanism of the oxidation of excess thiocyanate by $[Ni(tacn)_2]^{3+}$ has been studied [190]. Under these conditions there is kinetic inhibition by the product $[Ni(tacn)_2]^{2+}$. In the presence of a spin trap the rate law is of the form $2k_1[SCN^-] + 2k_2[SCN^-]^2$. The k_1 term represents electron transfer to form Ni(II) and SCN radical, and the k_2 term to formation of Ni(II) and $(SCN)_2^-$ radical, with electron transfer concerted with S–S bond formation. The azide-bridged dinuclear complex $[Ni_2(dmptacn)_2(\mu\text{-}N_3)](ClO_4)_3$ (dmptacn = 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane) has been described; this is antiferromagnetic and has $J = -42.5\ cm^{-1}$, typical of singly end-to-end azide-bridged Ni(II) complexes [165]. A molecular mechanics study of ethylenediamine, tacn and pendant arm-substituted tacn ligands (including some not yet synthesised), of particular relevance to Ni(II) complexes, has been undertaken [191].



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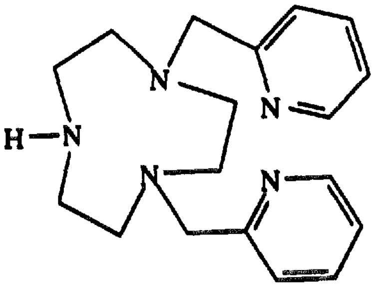
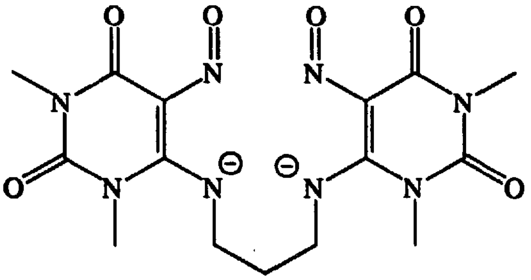


(61)

Fast atom bombardment mass spectrometry (FAB-MS) of complexes $[Ni(tacn)_2]X_2$ (X = Cl, NO_3, ClO_4) in different matrices establishes that the highest mass fragment, and base peak, is $[Ni(tacn)_2X]^+$ [192]. Subsequent matrix-assisted one-electron reduction with concomitant loss of the second anion produces $[Ni(tacn)_2]^+$, and successive oxidative dehydrogenations then give $[Ni(tacn\text{-}H)_2]^+$. The intensities of the latter fragments depended significantly on the reducing power of the matrix. The ligand **(60)** (L) has been synthesised, and the crystal structure of the complex $[Ni(L)](ClO_4)_2\cdot 0.5H_2O$ solved [193]. The complex $[\{Ni(L)\}_2(\mu\text{-}N_3)](ClO_4)_3$ [L = **(61)**], made by treating $[Ni(L)(H_2O)](ClO_4)_2$ with NaN_3 in aqueous methanol, has been described [165]. It is antiferromagnetic, indicating end-to-end azide bridging. The complex $[Cu(L)(H_2O)]\cdot 3H_2O$ [L^{2-} = **(61a)**] has been employed as a ligand in reactions with Ni(II)-macrocycle complexes [194]. With $[Ni(OH)(L_1)]_2(ClO_4)_2$ (L_1 = 2,4,4-Me_3-1,5,9-triazacyclododec-1-ene), $[Cu(ClO_4)(\mu\text{-}L')Ni(L_1)](ClO_4)\cdot H_2O$ formed, where L'^{2-} = **(61a)** with one CO molecule eliminated from a pyrimidine ring to give an imidazole. The Cu(II) is coordinated to the exocyclic nitrogens of the pyrimidine ring, to the NO oxygen and exocyclic nitrogen of the imidazole ring, and to one perchlorate ion; the NO oxygen also bridges to Ni(II). The Ni(II) ion has square pyramidal coordination geometry, with two of the L_1 nitrogens and two bridging NO oxygens in the basal plane and the third L_1 nitrogen axial. This complex is strongly antiferromagnetically coupled, with $J > 500\ \mathrm{cm}^{-1}$.

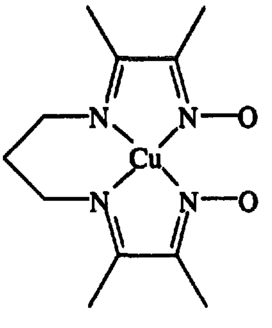


(61a)

6.9.2 *Complexes of tetraamine macrocyclic ligands*

6.9.2.1 *Cyclam and its derivatives*

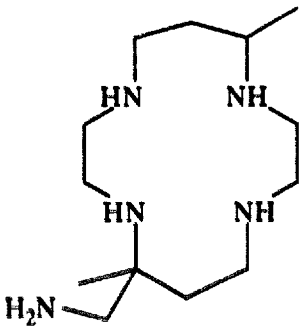
The violet transient that forms when acid $[\mathrm{Ni(cyclam)}]^{3+}$ solutions are added to water buffered at pH 7 ± 1 has been examined using diode array spectrophotometry [195]. The colour originates from a band at 539 nm, with a high extinction coefficient (1330 ± 100), assigned to a Ni(III) complex of monodeprotonated cyclam (pK_a of Ni(III)-cyclam secondary amine 7.1 ± 0.1). The latter undergoes decay by a second-order rate process, probably transfer of an electron from the amido nitrogen to a second Ni(III) centre, giving a Ni(II)-cyclam radical complex which undergoes loss of a proton to give a Ni(II) complex of the monoimine macrocycle. The FAB-MS spectra of $[\mathrm{Ni(cyclam)Cl_2}]$ and $[\mathrm{Ni(cyclam)}](\mathrm{ClO_4})_2$ have been recorded in different matrices [192]. The highest mass peaks were due to $[\mathrm{Ni(cyclam)X_2}]^+$; the most intense peaks were due to $[\mathrm{Ni(cyclam\text{-}H)}]^+$, formed by a mechanism identical to that for $[\mathrm{Ni(tacn)_2}]\mathrm{X_2}$.



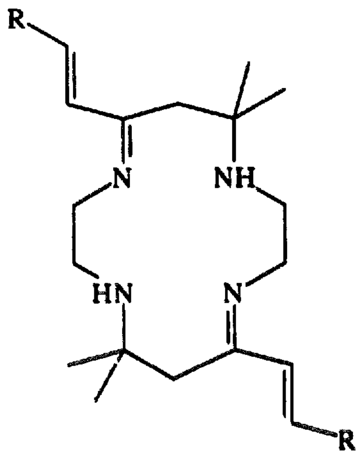
(62)

By treating $[\mathrm{Ni(cyclam)}]^{2+}$ with the Cu(II) complex (**62**), the heterodimetallic $[\mathrm{Cu(62)Ni(cyclam)}](\mathrm{ClO_4})_2\cdot\mathrm{H_2O}$ was produced [196]. The structure was not determined, but probably consists of Cu–Ni dimers, with Ni(II) coordinated to a *cis* cyclam and the two oximato oxygens. The complex shows strong antiferromagnetic coupling ($J = -204\ \mathrm{cm}^{-1}$).

There is continuing interest in the use of $[\mathrm{Ni(cyclam)}]^{2+}$ and related complexes in electrocatalysis. The electrocatalytic oxidation of alcohols using glassy carbon electrodes modified, in aqueous carbonate solutions, with adsorbed $[Ni(cyclam)]^{2+}$ has been studied [197]. At potentials just positive of the Ni(III)/Ni(II) redox wave, catalytic currents for oxidation of primary alcohols in aqueous solution were detected. Carbon paste electrodes (CPEs) modified with water-soluble $[Ni(cyclam)](ClO_4)_2$ and $[Ni(L)(H_2O)](ClO_4)_2$ [L = (63)], and hydrophobic $[Ni(L)](ClO_4)_2$ [L = (64), (65)], have been investigated for electrocatalytic oxidation of H_2O_2 [198]. The CPEs modified with the hydrophobic complexes showed no Ni(III)/Ni(II) redox process in aqueous electrolytes. Whereas CPEs modified with both the water-soluble complexes were redox-active, only CPEs modified with $[Ni(cyclam)](ClO_4)_2$ showed electrocatalytic ability, suggesting coordination of H_2O_2 to the Ni site at some point in the mechanism. In another paper, the crystal structure of $[Ni(L)(H_2O)](ClO_4)_2$ [L = (63)] was described, along with the modification of silica surfaces with the complex [199]. This was achieved by condensing the primary amine 'arm' with surface-bound γ-carboxypropylsilyl moieties.

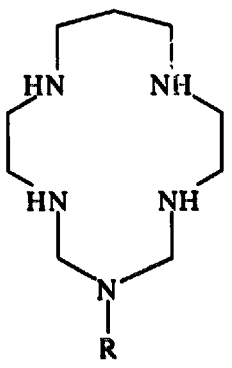


(63)



($R = n\text{-}C_{11}H_{23}$, Ph
Also corresponding
cis-diimine macrocycle)

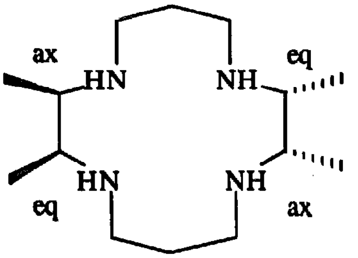
(64)



$R = n\text{-}C_{16}H_{33}$

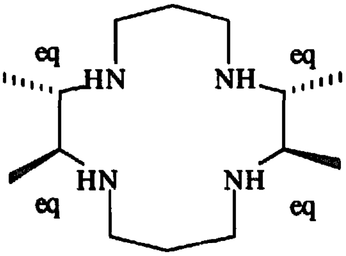
(65)

The outstanding catalyst for electroreduction of aqueous solutions of CO_2 to CO is $[Ni(cyclam)]^{2+}$, if a mercury working electrode is used; the complex is thought to adsorb to the electrode in a particular conformation favouring CO_2 binding. The isomers $[Ni(\mathit{RSSR}\text{-}L)](ClO_4)_2$ and $[Ni(\mathit{RRSS}\text{-}L)](ClO_4)_2$ [L = (66)] have been prepared by $NaBH_4$ reduction of the corresponding complex of the tetraimine, followed by repeated recrystallisations [200, 201]. Also examined were $[Ni(L')](ClO_4)_2$ [L' = (67)] (mixture of conformers). The complexes have been compared with $[Ni(cyclam)](ClO_4)_2$ as electrocatalysts in CO_2 reduction. Both $[Ni(\mathit{RRSS}\text{-}L)](ClO_4)_2$ and $[Ni(L')](ClO_4)_2$ were superior to $[Ni(cyclam)](ClO_4)_2$; the onset of electrocatalysis occurred at measurably more positive potential and the current enhancement was bigger. The binding constant for CO_2 in CH_3CN solution was also bigger for the better electrocatalysts. In contrast, although $[Ni(\mathit{RSSR}\text{-}L)](ClO_4)_2$ had marginally the most positive Ni(II)/Ni(I) couple it was a significantly less efficient electrocatalyst than $[Ni(cyclam)](ClO_4)_2$, and had the lowest binding constant for CO_2; the axial methyl group may sterically hinder CO_2 binding and Hg adsorption. The crystal structures of both isomers of $[Ni(L)](ClO_4)_2$, and of $[Ni(\mathit{RSSR}\text{-}L)](ClO_4)$, have been determined [201]. The arrangement of the nitrogen donor set for all complexes was *trans-III*. The Ni–N bond lengths for the Ni(I) complex (2.083(3), 2.053(3) Å) were significantly greater than for the corresponding Ni(II) complex (1.969(1), 1.948(2) Å). Binding constants and υ(CO) for the Ni(I) complexes with CO were determined; for $[Ni(\mathit{RRSS}\text{-}L)]^+$ the values were $9.0 \pm 2.0 \times 10^4$ and 1939 cm^{-1}, and for $[Ni(cyclam)]^+$ $2.8 \pm 0.6 \times 10^5$ and 1955 cm^{-1}.



(*RSSR* isomer)

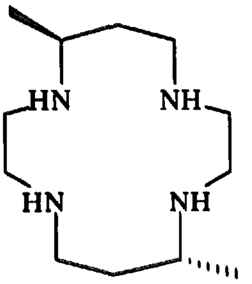
(66a)



(*RRSS* isomer)

(66b)

(ax = axial, eq = equatorial)



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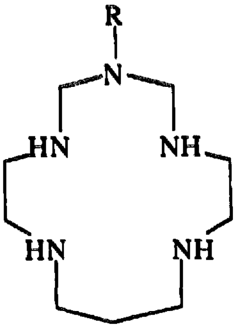
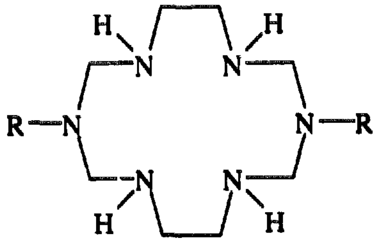


(R = Me, $-C_{16}H_{32}$, $-C(O)R$, $-SO_2R$)

(68)



R = $-(CH_2)_nX$; n = 2, 3; X = CN, OH, OAc. R = $-(CH_2)_nX$; n = 2, X = OAc)

(69)

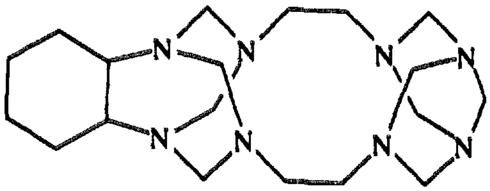
A series of Ni(II) complexes of amide- and sulfonamide-functionalised cyclam-like ligands (**68**) has been synthesised by Ni(II) template condensation of 2,3,2-tet with formaldehyde and the appropriate amide or sulfonamide [202]. Interestingly, the Ni(III)/Ni(II) and Ni(II)/Ni(I) redox potentials depend markedly on the substituent R. The structure of the complex $[Ni(\mathbf{68})](ClO_4)_2$ (R

= tolylsulfonamide) was determined; the sulfonamide nitrogen is planar. All the complexes were active for CO_2 electroreduction, and since the effect of the amido group is to make the Ni(II)/Ni(I) potential more positive, they reduce the overpotential for CO_2 reduction even more than does $[Ni(cyclam)](ClO_4)_2$.

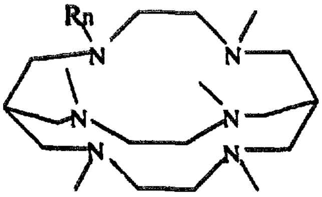
Similar condensations, employing amines in place of amides, have been used to make ligands L [L = (69)] [203]. Octahedral $[Ni(L)Cl_2]$ and square planar $[Ni(L)](ClO_4)_2$ were isolated for all ligands except R = $-CH_2CH_2CN$. In the latter case, $[Ni(L)](ClO_4)_2$ was octahedral and polymeric, with bridging *trans* pendant -CN coordination, characterised crystallographically (mean Ni–NH 2.058(5) Å, Ni–NC 2.162(4) Å). In aqueous or dmso solutions, the complex reverts to the square planar monomeric form.

The reactions of Li(tcnq) with $[NiCl_2L]$ where L is a ligand of the type 1,8-disubstituted-1,3,6,8,10,13-hexaazacyclotetradecane have been shown to lead to complete replacement of the chloride ligands by $tcnq^{\bullet-}$ [204].

Macrocyclic tertiary amines usually exert a weaker ligand field than the corresponding secondary amines. However, the ligand L [L = (70)] exerts a stronger ligand field in $[Ni(L)](PF_6)_2$ (λ_{max} 425 nm) than any other 14-membered ring tetraazamacrocyle [205]. The crystal structure of the complex shows unusually short Ni(low spin)-N(tertiary) bond lengths (mean Ni–N 1.904(7) Å), probably because N–N bite distances and angles of the six-membered chelate rings, constrained by the bicyclic structure, are fairly close to the values that would be expected for five-membered rings. The kinetics of electron transfer between *R,S,R,S*-$[Ni(L)]^+$ (L = 1,4,8,11-Me_4cyclam) and $[MeCo(dimethylglyoximate)_2(py)]$ have been studied; the reaction produces methane as the only organic product, and $[Co(dimethylglyoximate)_2(py)]^-$ [206].



(70)

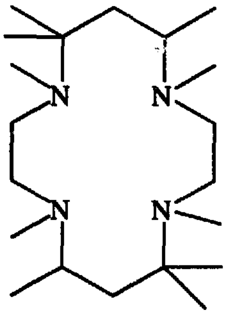


R = H, n = 1

R = Me, n = 1,2 (cation)

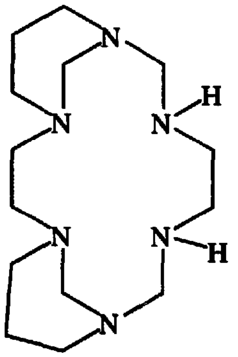
(71)

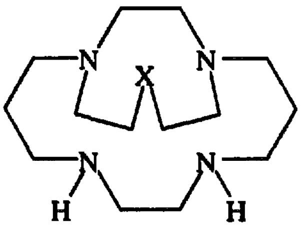
While dealing with tertiary amine donor macrocycles, it is convenient to include here mention of some complexes of ligands (71) [207]. Unlike their secondary amine analogues, which readily enclose Ni(II) forming octahedral complexes, these ligands are sterically prevented from forming other than square planar complexes, with the ligand adopting the *R,S,R,S*-configuration (all methyl groups on coordinated nitrogens facing in the same direction) and the remaining 'strap' uncoordinated. All three complexes $[Ni(L)](ClO_4)_2$ were crystallographically characterised. All complexes exhibited reversible Ni(II)/Ni(I) electrochemistry in water. An attempt has been made to use crystal structure data for Ni(II)-tetraazamacrocycle complexes to compute a force field to allow molecular mechanics calculations to be used to predict geometries of complexes [208]. However, relatively minor changes in parameters led to considerable variations in strain energies for different stereoisomers.



(72)

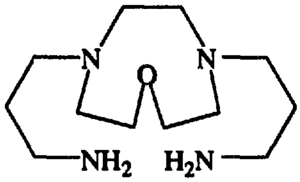
(73)



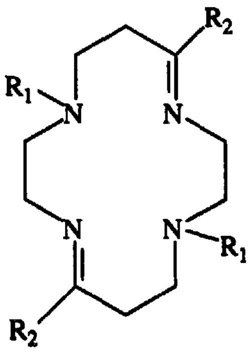


(X = O, S, NH)

(74)



(75)

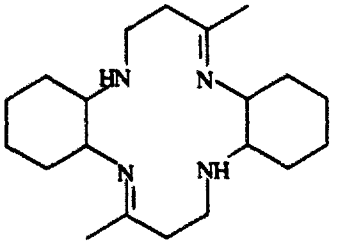


(76)

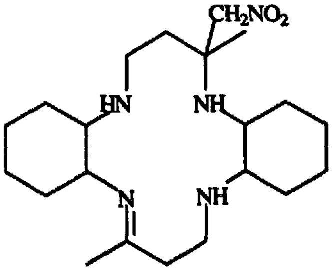
Tertiary amine macrocycles are often effective at stabilising Ni(I). Irradiation of solutions of $[Ni(L)]^{2+}$ and 0.01 M HCO_2Na (L = (72), (73)) with γ-rays or 3 MeV electrons afforded $[Ni(L)]^+$ [209]. Injection of methyl coenzyme M ($MeSCH_2CH_2SO_3^-$) gave methane; blank experiments without the Ni complexes did not. The Ni(II) coordination chemistry of the ligands (74) and of one of their precursors (75) has been explored [210]. The crystal structure of $[Ni(74)(CH_3CN)](ClO_4)_2$ shows that the ether oxygen is coordinated (Ni–O 2.189(12) Å) *trans* to one of the pendant amines, and the acetonitrile molecule is in the equatorial plane. However, in $[Ni(75)(ClO_4)]ClO_4$ (X = O), the ether oxygen (Ni–O 2.190(6) Å) is *trans* to the weakly-coordinated (Ni–O 2.373(7) Å) perchlorate ion and the nickel lies in the plane of the four macrocycle amine donors. The corresponding Ni(III) complexes could be generated in aqueous or non-aqueous media by oxidation with $Co^{3+}_{(aq)}$ or NO^+. The kinetics of reduction of all the Ni(III) complexes with outer-sphere electron transfer reagents, and the electron self-exchange processes have been studied.

Nickel(II) complexes of ligands (76) (R_1 = H, Me, R_2 = Et; R_1 = H, Me, Et, R_2 = Me) have been reported, and their complexes compared with the secondary amine analogues [211]. *N*-Alkylation reduces the ligand field and stabilises the Ni(I) oxidation state markedly.

The reaction of $[Ni(L)](ClO_4)_2$ (L = (**77**)) with nitromethane in the presence of triethylamine, followed by perchloric acid, afforded $[Ni(L')](ClO_4)_2$ (L' = (**78**)) [212]. The crystal structures of both complexes were determined; whereas $[Ni(L)](ClO_4)_2$ had conventional, undistorted square planar geometry, the steric crowding in $[Ni(L')](ClO_4)_2$ resulted in severe distortion, with the Ni atom considerably displaced from the N_4 plane. The ligand field exerted by L' was unusually low for this type of ligand.



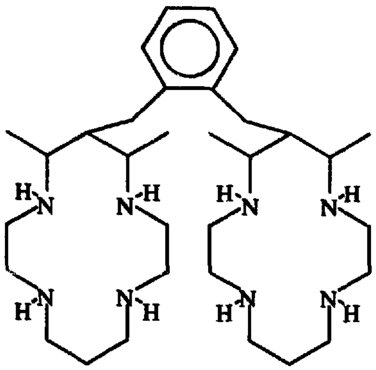
(77)



(78)

6.9.2.2 *Dinucleating macrocycles*

The ligand (**79**) forms $[Ni_2(\mu\text{-}Br)Br_2(L)]Br \cdot H_2O$; recrystallisation of this from 1 M aqueous $NaClO_4$ gave yellow $[Ni_2(L)](ClO_4)_4 \cdot 4H_2O$ [213]. When this, in turn, was recrystallised from 1 M aqueous NaCl, a complex of formula $[Ni_2Cl_2(L)](ClO_4)_2 \cdot 1.5H_2O$ was obtained, the crystal structure of which showed an unusual one-dimensional chain structure, consisting of alternating units of bis-octahedral $Ni_2Cl_2(\mu\text{-}Cl)(L)(ClO_4)$ and square planar-octahedral $(\mu\text{-}Cl)ClNi(L)Ni(ClO_4)_3$, such that for every pair of dimers, three Ni(II) ions are paramagnetic and six-coordinate and the fourth is square planar. Both the magnetic properties (antiferromagnetic; $J = -48.2(3)\ cm^{-1}$) and solid-state electronic spectrum were consistent with this. A method of selectively making heterodimetallic complexes of the ligand (**80**) has been described [214]. The square planar $[Ni(L)](ClO_4)_2$ [L = (**80**)] was prepared from L and $NiCl_2$ in dilute aqueous solution, in 37% yield after chromatography on Sephadex. This could be treated with Cu(II) to afford $[NiCu(L)](ClO_4)_4$ in good yield, or with $CoCl_2$ followed by aerial oxidation to afford $[NiCoCl_2(L)]^{3+}$. By selective removal of the labile Ni(II) by treatment with CN^-, followed by treatment with Cu(II), the Cu(II)-Co(III) dimetallic could be prepared. Another approach to dinucleating macrocycles has been described, in which tritosylated tetraamine macrocycles were reacted with bromoacetyl bromide, then with a further tritosylated tetraamine macrocycle, to give a $-C(O)CH_2-$ bridged dimacrocycle [215]. Subsequent borane reduction, followed by metal ion complexation, gave dinuclear metal complexes of ligands (**81**) – (**83**). Whereas it was not possible readily to prepare heterodimetallic complexes of (**81**) or (**83**), (**82**) (R = Me) was amenable to successive metallation reactions, the secondary amine cavity being metallated first.



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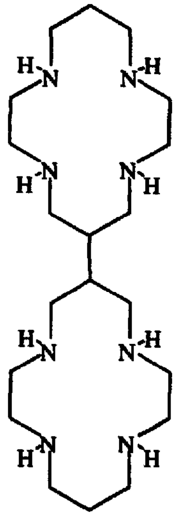
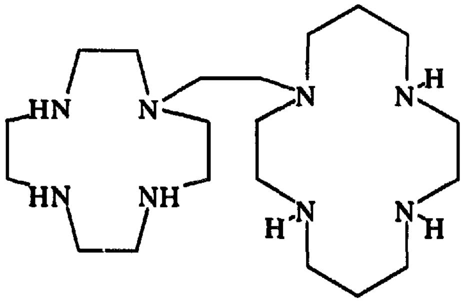
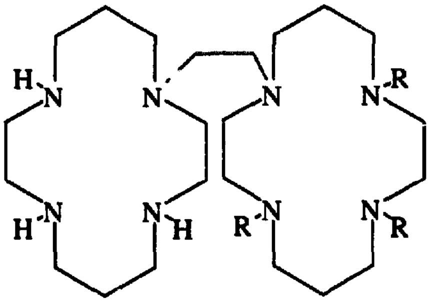


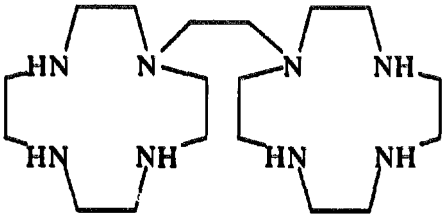
(80)



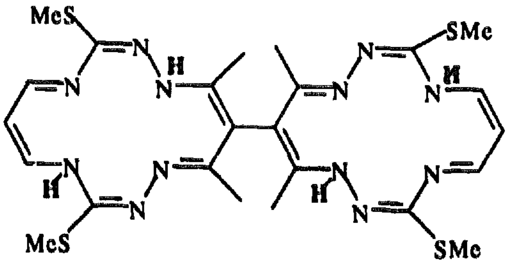
(81)



(82); R = H or Me



(83)

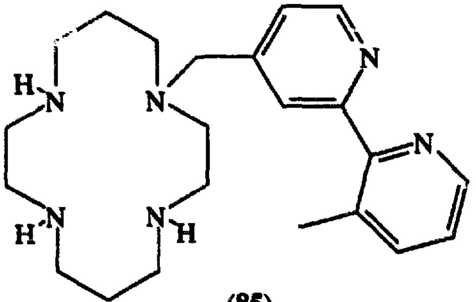


(84)

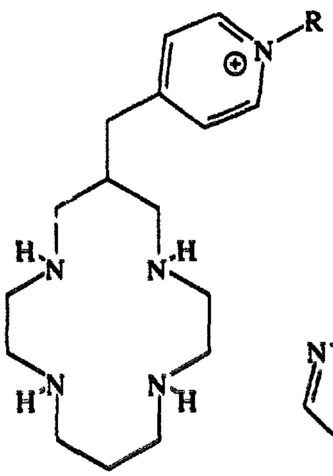
Template condensation of $[Ni_2(L_1)]$ (H_6L_1 = tetrakis[1-{3-methylisothiosemicarbazono}-ethyl]ethane) with 3-ethoxyacrylaldehyde in dmf afforded square planar $[Ni_2(L_2)]$ (H_4L_2 = **(84)**; H's in bold lost on complexation) [216]. NMR and electronic spectral data suggest little interaction between the two metal centres.

6.9.2.3 Macrocycles bearing pendant groups

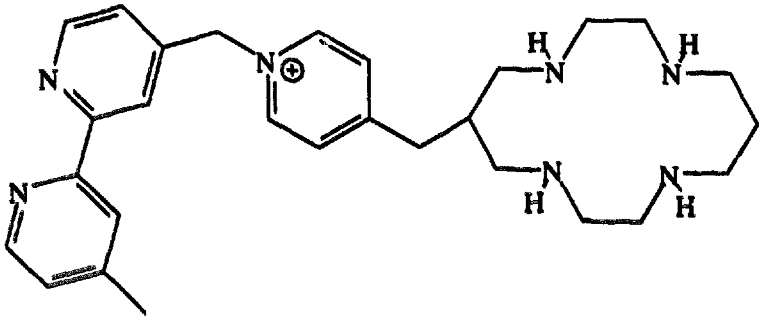
Several interesting examples of cyclam-like ligands bearing pendant groups have been described this year. Monobromination of 4,4'-Me_2-bpy followed by treatment with excess cyclam afforded the ligand **(85)** [217]. Treatment of this with $[RuCl_2(bpy)_2]$ followed by Ni(II) resulted in selective complexation of Ru(II) at the bpy site and square planar Ni(II) at the cyclam site. Although the emission frequency for the $Ru(bpy)_3^{2+}$ moiety was little affected by the $Ni(cyclam)^{2+}$, the emission intensity was greatly reduced by an intramolecular mechanism, probably energy transfer. The redox properties of the $Ni(cyclam)^{2+}$ moiety were greatly affected by the nearby dicationic Ru(II) centre; the Ni(II)/Ni(I) and Ni(III)/Ni(II) process occurred at more positive potentials than for $[Ni(cyclam)]^{2+}$ itself.



(85)

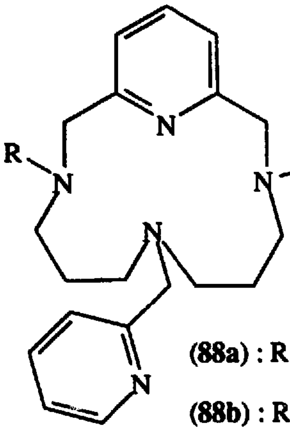


($R = Me, p\text{-}MeOC_6H_4, -CH_2Ph, p\text{-}O_2NC_6H_4$)



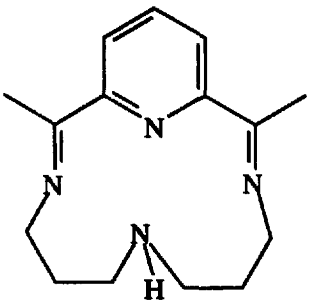
(86) **(87)**

Square planar Ni(II) complexes of the ligands **(86)** and **(87)** have been synthesised [218]. The intention was to use the pendant pyridinium group [in complexes of **(86)**] as electron acceptors for the photocatalytic reduction of CO_2 by the $Ni(cyclam)^{2+}$ moiety, with $[Ru(bpy)_3]^{2+}$ as photosensitiser. The one-electron reduction potential for all the pyridinium moieties was less than that of the Ni(II) centre. The yield of CO was increased by a factor of *ca.* 5 compared with $[Ni(cyclam)]^{2+}$ itself. By using supramolecule **(87)**, with the bpy unit coordinated to $Ru(bpy)_2^{2+}$ (photosensitiser) and linked to a $[Ni(cyclam)]^{2+}$ moiety *via* a pyridinium centre, a further factor of two improvement in CO yield was obtained, but the molecule itself was unstable to reductive photocleavage. A synthetic route to **(88a)** has been designed, allowing further functionalisation of the remaining secondary amines [219]. The Ni(II) complexes $[Ni(L)(H_2O)](BF_4)_2$ (L = **(88a)**, **(88b)**) were synthesised.



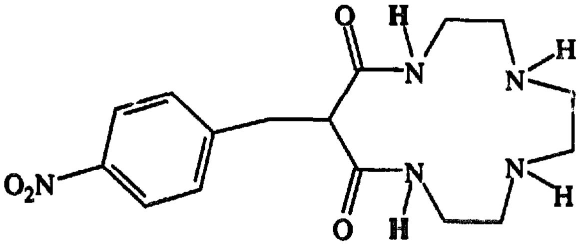
(88a) : R = H

(88b) : R = Me



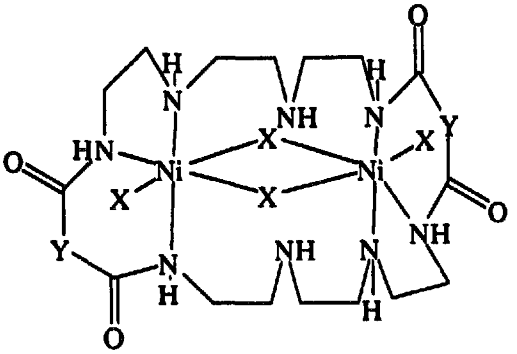
(89)

Thermodynamic and kinetic parameters for the square planar-octahedral equilibrium for the nickel(II) complex of the related ligand (**89**) in methanol have been characterised using variable temperature electronic spectroscopy and ultrasonic relaxation methods [220]. The rate constant for the square planar to octahedral reaction is nearly the same as that measured earlier by NMR spectroscopy for solvent exchange.



(90)

Turning now to amide macrocycles, the ligand (**90**) affords square planar [Ni(L)] (protons in bold lost on complexation) [221]. The binding constant is rather lower than for the ligand without the 4-nitrobenzyl substituent. While dealing with amide macrocycles, the acid hydrolysis of [Ni(L)] (H_2L = 5,7-dioxo-1,4,8,11-tetraazacyclotetradecane) has been investigated. The kinetic data suggested a two-stage protonation giving $[Ni(H_2L)]^{2+}$, which then dissociates [222].



Y = $-CH_2-$, $-CH_2CH_2-$,

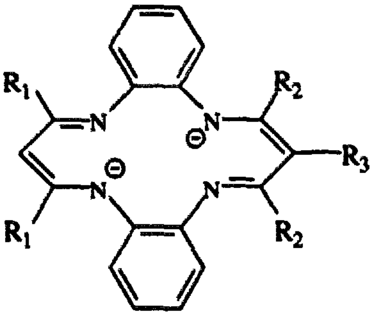
$-CH_2CH_2CH_2-$, $o-C_6H_4$

(91)

Finally, some dinuclear complexes $[Ni_2(L)X_4]$ (X = Cl, NO_3) have been reported, with structure (**91**) claimed on the basis of spectroscopic and analytical data [223].

6.9.3 Complexes of tetraaza[14]annulenes and related ligands

The reductive dehalogenation of alkyl halides to alkanes is catalysed by [Ni(L)] (L^{2-} = (**92a**), and related ligands bearing aryl Me or COOEt substituents), using $NaBH_4$ or $NaBH(OMe)_3$ in 10% ROH/diglyme [224]. Modified electrodes consisting of polymers of [Ni(L)] (L^{2-} = (**92a**)) were obtained on cycling the potential of a Pt electrode between −1.8 and +1.5 V in a solution of the complex in CH_3CN [225]. Controlled potential oxidation of the complex at the potential of the first oxidation wave leads to formation of the dimer (**93**), which is readily deprotonated to give the neutral dimer. The protonated dimer is the key intermediate in the electropolymerisation mechanism.

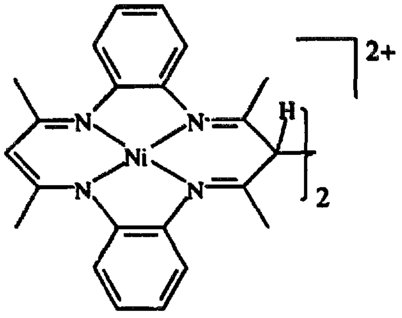


$R_1, R_2 = Me; R_3 = H$ (**92a**)

$R_1, R_3 = Me; R_2 = H$ (**92b**)

$R_1, R_2 = H; R_3 = Me$ (**92c**)

$R_1 = Me; R_2, R_3 = H$ (**92d**)

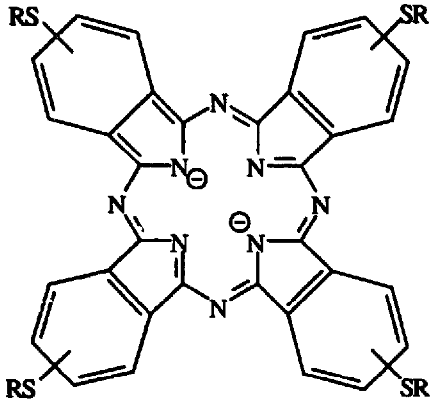


(**93**)

The synthesis of tetraazaannulene-Ni(II) complexes of (**92b–d**), and their electrochemical properties, have been reported [226]. By potential cycling essentially as described above for [Ni(**92a**)], polymer-modified electrodes were obtained, some of which were more durable to repeated redox cycling than poly-[Ni(**92a**)]. The syntheses of tetraazaannulenes analogous to (**92a**), but bearing four aryl methyl substituents, have been described, along with the square planar [Ni(L)] which are significantly more soluble [227]. A brief report of the *cis* and *trans* isomers of [Ni(L)] [L^{2-} = (**92a**); one methyl group on each acac residue replaced by a $-CF_3$ group), and of [Ni(L')] (L' = (**92a**); $R_1 = R_2 = CF_3$), has appeared [228]. The isomers of [Ni(L)] were not separated, but apparently have identical redox properties. Neither undergoes the electropolymerisation reaction.

6.9.4 Complexes of phthalocyanines and related ligands

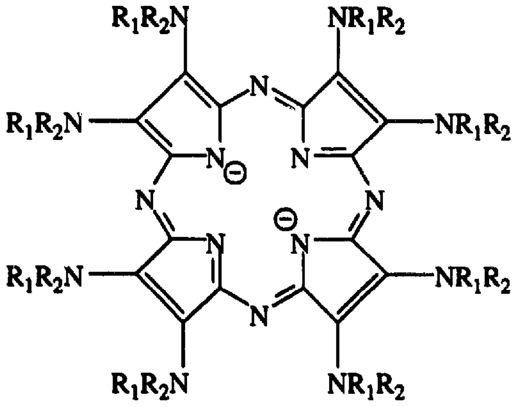
Phthalocyanines bearing exocyclic thioether functions [L^{2-} = (**94**)], and their complexes [Ni(L)] have been described [229]. The latter react with $AgNO_3$ or Na_2PdCl_4 to form complexes $[Ni(L)\{AgNO_3\}_2]$ and $[Ni(L)\{PdCl_2\}_2]$ which are oligomeric, with the other metals each coordinated to two thioether donors.



R = $-C_{12}H_{25}$, $-C_{16}H_{33}$

(94)

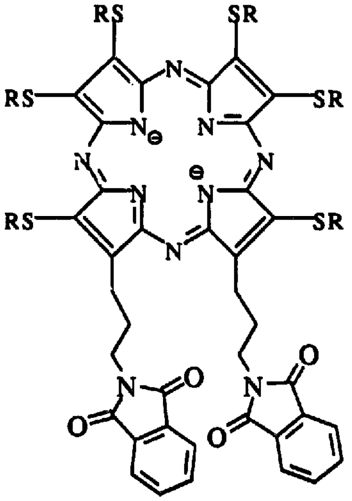
(mixture of isomers)



$R_1 = R_2 = Me$; $R_1 = R_2 = -CH_2Ph$

$R_1 = Me$, $R_2 = CH_2CH{=}CH_2$

(95)



R = octyl

(96)

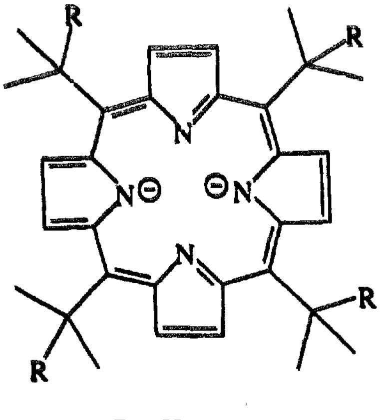
Statistical condensation of two different phthalonitriles is not usually a useful strategy for synthesising asymmetrically-substituted phthalocyanines because intermolecular interactions render separation of the isomers difficult. However, condensation of the bulky tetraphenylphthalonitrile with monoalkoxy- or monoalkyl-phthalonitriles in the presence of nickel acetate has been reported both to reduce the number of isomer possibilities and to render the intermolecular interactions negligible, enabling column chromatographic separation of the different possible products [Ni(L)] [230].

Langmuir-Blodgett mono- and multilayer films have been prepared from [Ni(*tetra*-^{t}Bu-phthalocyanine)] (mixture of isomers), and this material has been used to promote Langmuir-Blodgett film formation with poly(3-hexylthiophene) [231]. The nickel phthalocyanine molecules were found to stack in one dimensional arrays, with their rings perpendicular to the substrate surface. The complex [Ni(*octakis*{pentyloxy}phthalocyanine)] also forms Langmuir-Blodgett films with the molecules stacked with the rings perpendicular to the substrate [232]. Attempts have been made to intercalate [Ni(phthalocyanine)] into the superconductor $Bi_2Sr_2CaCu_2O_{8+\delta}$ [233].

Turning to porphyrazines, the new 'star' porphyrazines H_2L [L^{2-} = (**95**)] have been synthesised; with nickel acetate these give [Ni(L)] with Ni(II) exclusively within the macrocycle cavity [234]. The complex [Ni(**96**)] has been used to form molecular assemblies at the air-water interface, and Langmuir-Blodgett films [235]. The phthalimide moieties improve ordering by favouring edge-on orientation in these films.

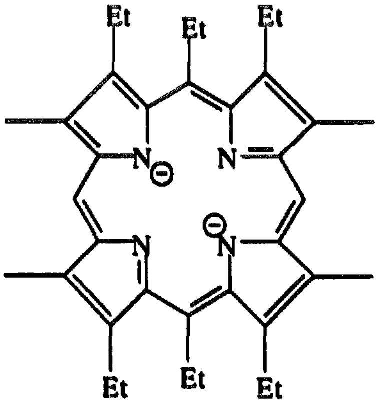
6.9.5 Complexes of porphyrins and related ligands

The state of knowledge on the biosynthesis of Coenzyme F-430, the nickel porphyrinoid involved in methanogenesis, has been reviewed [236]. The novel porphyrins (**97**) are greatly deformed from planarity, and on protonation, or with Cu(II) and Zn(II), exhibit very unusual chemistry [237]. However the complex [Ni(L)] [L^{2-} = (**97**); R = H], although distorted, can readily be prepared, and was characterised by X-ray diffraction. There is still considerable interest in the conformation of sterically crowded porphyrins, and the variation in resonance Raman spectroscopic lines with increasing deformation. Whereas changing the metal ion in [M(L)] (H_2L = tetracyclohexenyltetraphenylporphyrin) has little effect on the planarity of the macrocycle core, changing the size of the alkyl ring in the series [Ni(tetracycloalkenyltetraphenylporphyrin)] from pentyl to hexyl to heptyl causes an increase in non-planarity [238]. Correlations between resonance Raman spectroscopic frequencies and structural parameters (core size, C_α–N–C_α angle) for this series have been obtained. X-Ray crystal structures have been obtained of both the free ligand (H_2L) and [Ni(L)] [L^{2-} = (**98**)]; steric crowding in the latter is relieved by the porphyrin adopting a non-planar conformation [239]. Only one set of proton NMR spectroscopic signals could be observed for [Ni(L)] even at low temperatures.



R = H; R = Me

(**97**)

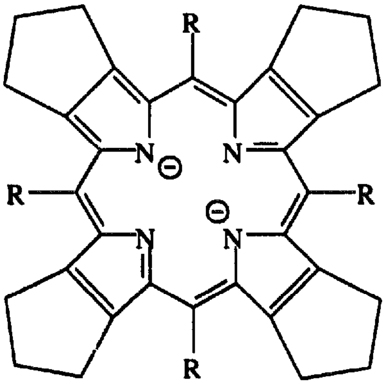


(**98**)

The electronic structures and affinity for additional axial ligands for a series of nickel porphyrin complexes with different degrees and kinds of deformation from planarity have been investigated using MCD spectroscopy [240]. For [Ni(OEP)], [Ni(**99**)] and [Ni(octaethyltetraphenylporphyrin)] the spectra were normal, indicating that neither the ruffled nor saddle-shaped conformation lifted the excited state degeneracies; D_{2d} symmetry is retained. The

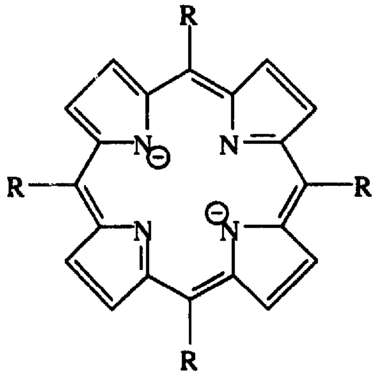
MCD spectra of Ni-reconstituted hemoglobin and myoglobin were indicative of no protein effect on the electronic energy levels. A correlation was noted between the relative intensities of the Soret Q and MCD bands and the coordination of additional axial ligands. Potential ligands such as cyanide, azide and fluoride did not bind the Ni in the reconstituted proteins.

The novel water-soluble porphyrin complex [Ni(**100**)]$^{4+}$ has been synthesised by reaction of [Ni(tetrakis{pentafluorophenyl}porphyrin)] with dimethylammonium hydrochloride in dmf, followed by methylation with methyl trifluoromethanesulfonate (triflate) in trimethyl phosphate [241]. The triflate and chloride salts are water-soluble. The fluorine substituents reduce the tendency to aggregation and adsorption to electrode surfaces often found for water-soluble porphyrins. However, the complex was not effective as an electrocatalyst for electroreduction of protons to H_2 above pH 4. A time-resolved resonance Raman spectroscopic study of the electronic excited states of [Ni(OEP)] and [Ni(TPP)] has been reported [242].



R = pentyl

(99)

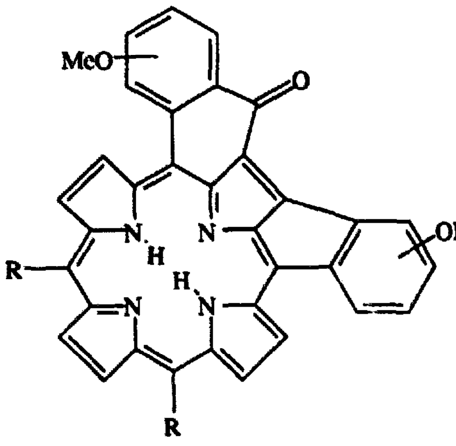


R = $-C_6F_4NMe_3^+-4$

(100)

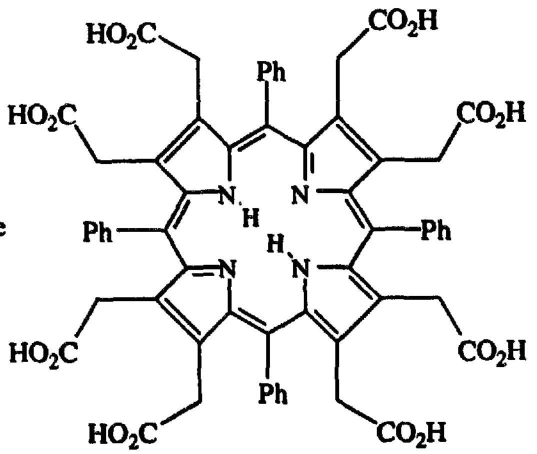
Turning to bridged diporphyrin ligands, McMurray coupling of [Ni(5-formyl-OEP)] gives the corresponding ethene-bridged bisporphyrin complex [243]. Surprisingly, the main product of the reaction was the *cis* isomer. This undergoes acid-catalysed rearrangement to the *trans* isomer. The structure of the *cis* isomer shows strong intramolecular interaction, with the two rings almost coplanar; both isomers show strong intermolecular interaction as well. The identity of the *trans* isomer was confirmed by independent synthesis using another route. Unusually, a hydroxymethyl-bridged dimer was obtained when [Ni(2-formyl-OEP)] was subjected to similar coupling conditions, one carbon unit being lost in the reaction. The crystal structure of a [Ni(OEP)] analogue bridged in the *meso* position by a 2,5-bis(ethynyl)thiophene moiety has been determined [244]. That there is strong π–π interaction across the conjugated bridge is indicated by the near-planarity of the C_{meso}–C≡C–thiophene–C≡C–C_{meso} unit. Additionally, the B-band splitting ($\Delta\nu = 2785$ cm^{-1}) was very similar to the corresponding butadiyne-bridged complex, indicating little interruption of conjugation by insertion of the thiophene ring.

There is strong interest in the chemistry of functionalised porphyrin ligands. The nickel(II) complex of β-formyl-*meso*-tetraphenylporphyrin undergoes intramolecular cyclisation, with the formation of a naphthoporphyrin derivative, on attempted demetallation with strong acid. When analogues bearing electron-releasing aryl methoxy groups were treated with H_2SO_4-CF_3COOH, a second cyclisation, resulting in a fused naphthoindenyl pyrrole as part of the porphyrin skeleton, occurred, giving demetallated (**101**) (mixture of isomers) [245]. Attempts to elucidate the mechanism of this process by using milder conditions (10% CF_3COOH in CH_2Cl_2) were also described.



R = 3-$MeOC_6H_4$

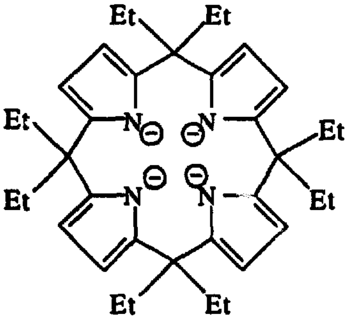
(**101**)



(**102**)

Nickel complexes of a new type of water-soluble porphyrin, (**102**) and its derivatives, the octa(methyl ester) (**102a**), octakis(hydroxyethyl)tetraphenylporphyrin (**102b**) and octakis(acetic acid)tetrakis(4-nitrophenyl)porphyrin (**102c**), have been studied [246]. The complexes are highly non-planar as indicated by resonance Raman and NMR spectroscopic experiments. Consistent with this, EXAFS measurements show short Ni–N bond lengths (1.92(2) Å for [Ni(**102a**)], 1.89(2) Å for [Ni(**102c**)]). Unlike [Ni(uroporphyrin)], which undergoes aggregation in low pH (<3) or high ionic strength media, these complexes remain unassociated, probably because of the degree of distortion from planarity. By reaction of the peripheral pyridine moieties with $[RuCl(bpy)_2]^+$, a tetraruthenated derivative of [Ni(tetra-*meso*-{4-pyridyl}porphyrin)] has been prepared [247]. This is soluble in polar organic solvents. Five redox waves, one ascribed to Ru(III)/Ru(II), one to a bpy/bpy$^{\cdot -}$ process, and two to successive reductions of the porphyrin moiety, were observed in cyclic voltammetry experiments. The oxidation of $TMPH_2$ and $TPPH_2$ with peracids results in oxidation of one pyrrole nitrogen to an amine oxide. These ligands can be metallated to afford, respectively, [Ni(TMP–N–*O*)] and [Ni(TPP–N–*O*)], with three porphyrin nitrogens and the oxygen as the donor set; the interaction of these complexes with acids has been examined [248]. Protonation with trifluoroacetic acid (TFA) results in protonation of the oxygen followed by rapid homolysis giving a Ni(III) porphyrin-trifluoroacetate complex. This undergoes protonation, possibly followed by loss of TFA, giving a Ni(II)-porphyrin cation radical complex. Use of trifluoromethylsulfonic acid resulted in a different mechanism, giving an unusual Ni(I)-(porphyrin dication) product.

Treatment of the complex $\{Li_2(thf)_4\}[Ni(L)]$ [L = (**103**)] with ≥ 2 mole equivalents of benzoquinone gave the unusual complex (**104**) containing a cyclopropyl ring, characterised crystallographically [249]. This reaction could be reversed by treatment of **(104)** with Li/biphenyl. There has been considerable interest lately in the porphycenes, structural isomers of the porphyrins. An electrochemical study of complexes [Ni(**105**)] has been reported [250]. These undergo two one-electron reversible reductions and two oxidations, all of which appeared ligand-centred. Thus, these ligands behave electrochemically much like bacteriochlorins; smaller potential differences between the first oxidation and reduction waves are found than for porphyrins.



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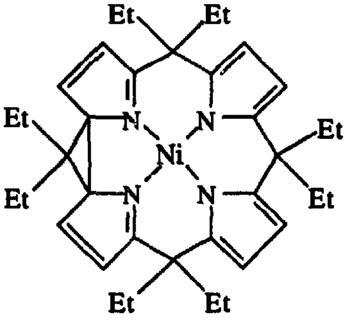

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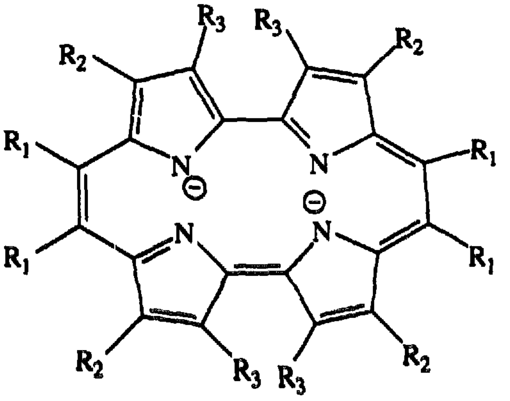


$R_1 = -CH_2CH_2CH_3$; $R_2 = R_3 = H$: **(105a)**

$R_1 = R_3 = H$; $R_2 = -CH_2CH_2CH_3$: **(105b)**

$R_1 = H$; $R_2 = R_3 = Et$: **(105c)**

$R_1 = H$; $R_2 = CH_2CH_2CH_3$; $R_3 = Br$: **(105d)**

The complex [Ni(L)] [L^{2-} = **(105)**; $R_1 = R_2 = R_3$ = Me], on electro-oxidation gave a partially-oxidised material $[Ni(L)]_{2.5}(BF_4)_2 \cdot C_{10}H_7Cl$, characterised crystallographically [251]. This has a columnar arrangement of stacked metallomacrocycles. The intermolecular spacing (< 3.4 Å) suggested π-overlap, and ESR spectroscopic measurements showed the oxidation to be ligand-centred. The material has an intermolecular charge transfer band at *ca.* 3000 cm^{-1}. Similarly, chemical oxidation of [Ni(L)] [L^{2-} = **(105b)**] with iodine afforded $[Ni(L)I_{1.67}]$ [252]. The complex consisted of $[Ni(L)]^{0.33+}$ cations packed in a slipped stack along the *b* axis, and surrounded by disordered chains of iodine, identified as I_5^- by Raman spectroscopy. Again, the oxidation was identified as ligand-based. The complex [Pt(L)] [L^{2-} = **(105b)**] has been characterised and compared with the Ni analogue [253]. As part of this work, extended Hückel calculations on [Ni(L)] were performed.

6.10 COMPLEXES WITH MIXED NITROGEN-OXYGEN DONOR LIGANDS

6.10.1 *Amino acid, peptide, nucleotide and related ligands*

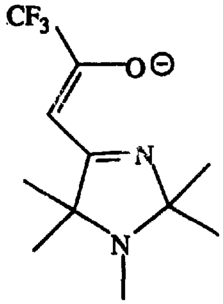
Equilibria for the binding of Ni^{2+} to synthetic double-stranded polyribonucleotides poly(A)·poly(U), poly(I)·poly(C) and poly(G)·poly(C) have been investigated spectrophotometrically [254]. Whereas Mg^{2+} binds only electrostatically, Ni^{2+} undergoes inner-sphere reaction, and the kinetic data are interpretable as due to coordination of the purine base N_7 and a phosphate oxygen atom.

The cyclodextrin βCDpn (βCDpn = 6^I-(3-aminopropylamino)-6^I-deoxycyclomaltaheptose) binds the tryptophan anion without any chiral discrimination, but the complex between βCDpn and Ni(II) selectively binds (*S*)-tryptophan anion, presumably with the amine and carboxylate groups coordinated [255]. Treatment of [Ni(glycinate)$_2$] with acetamide and formaldehyde afforded a complex of the product of Mannich aminomethylation, $HO_2CCH_2N(CH_2NHC\{O\}CH_3)_2$, characterised crystallographically [256]. The Ni(II) ion is coordinated to the two residues *via* the glycine carboxylate oxygen, the amine, and one amide oxygen, all pairs of these donors being mutually *trans*. The tripeptide Gly-Gly-*L*-His is thought to bind Ni(II) in a square planar fashion *via* two deprotonated amide nitrogens, the terminal amine and the histidine ring Nδ, and the complex catalyses the oxidative cleavage of DNA by oxygen. It has been shown that the reaction proceeds *via* a Ni(III) intermediate, and the structure of the product complex has been determined by crystallography to be [Ni(Gly-Gly-α-hydroxy-*D,L*-Histamine^{2-})] [257]. Thus racemisation, decarboxylation and hydroxylation of the terminal histidine have occurred. Metastable ion decomposition mass spectrometry of the interaction between Ni^{2+} and peptides containing hydrocarbon side-chains revealed that the gas-phase and aqueous phase chemistries are essentially the same [258].

Turning to enzymes containing Ni(II) in N,O donor sites, EXAFS has been employed to study superoxide dismutase in which Ni(II) is substituted for Zn(II) [259]. Tetrahedral coordination of Ni(II) is excluded. The results best fit five-coordination through didentate coordination of Asp 81, which is monodentate in the native (Zn_2Cu_2) enzyme. Similarly, Ni(II) substitution for tetrahedral Zn(II) in human carbonic anhydrase results in an increase in coordination number, as judged from X-ray crystallographic data, to six [260]. The nickel binding protein NiKA from *E. coli* has been the subject of preliminary X-ray crystallographic measurements [261]. An interesting bromoperoxidase enzyme from *Pseudomonas putida*, with Co, Ni, Zn and Fe(III) but no heme prosthetic groups, has been isolated [262]. The active site of the dinickel metalloprotein urease, from both jack bean and Klebsiella aerogenes, have been studied using nickel K-edge XAS and EXAFS [263]. No significant differences between the animal and plant enzymes were found. The data suggest five-coordinate [Ni(imidazole)$_x$(N,O)$_{5-x}$], with x = 2 or 3. In the presence of the inhibitor 2-mercaptoethanol, one of the non-imidazole donors is replaced by a thiolate and a new peak appears consistent with Ni...Ni interaction, suggesting that a thiolate bridges the two nickel ions.

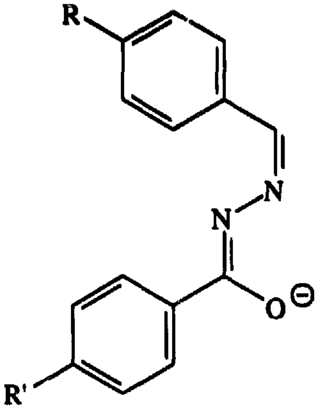
6.10.2 Amine- and imine-carbonyl and related ligands

On removal of coordinated alcohol from all-*trans*-[Ni(L)$_2$(ethanol)$_2$] [L$^-$ = **(106)**] by heating *in vacuo*, and subsequent recrystallisation from either CH_2Cl_2-heptane, or pure CH_2Cl_2 respectively, two modifications of [Ni(L)$_2$] were obtained [264]. X-Ray crystallography revealed that these are both polymeric, six-coordinate species, coordinated by enamineketone oxygens and nitrogens of the two ligands, and, in addition, the N–O oxygens of two adjacent molecules. However, the first modification has *trans* geometry and the second *cis*. This gives rise to purely antiferromagnetic interactions in the *trans* isomer ($J = -69.4$ cm^{-1}), but both antiferromagnetic ($J \approx -115$ cm^{-1}) and ferromagnetic ($J \approx 9.8$ cm^{-1}) in the *cis* isomer. A theoretical investigation of these properties is also reported.



(106)

A range of Ni(II) complexes of *N*-alkylidene- and *N*-arylalkylidene-aroylhydrazinato complexes of Ni(II), bearing long alkyl chains, has been synthesised to test their behaviour as potential metallomesogens [265]. Square planar complexes [Ni(L)$_2$] of ligands **(107)** (with the *E,E* stereochemistry) showed no mesomorphic behaviour, but similar complexes of **(108)** (R = $C_{12}H_{25}$) did show a crystal to smectic C transition at 126.2 °C. The analogues also showed nematic and/or smectic C phase formation.

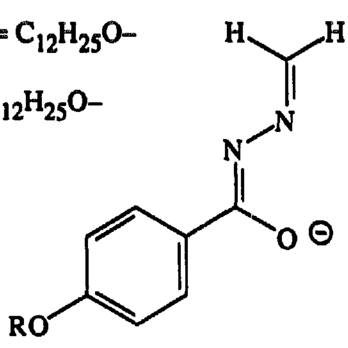


R = $C_{12}H_{25}O$–, R' = H

R = H, R' = $C_{12}H_{25}O$–

R = R' = $C_{12}H_{25}O$–

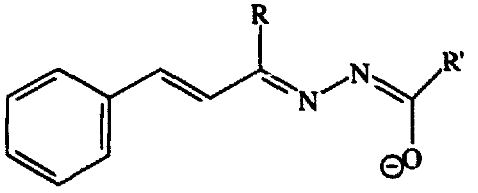
(107)



R = C_4, C_6, C_8, C_{10}, C_{14}, C_{20}, C_{22} alkyl

(108)

The reaction of Ni(OAc)$_2$ with HL [L$^-$ = **(109)**; R = H, Me; R' = various aryl] gave green, pseudo-octahedral [Ni(L)$_2$(H$_2$O)$_2$], which, on dehydration gave square planar α-[Ni(L)$_2$] [266]. *In situ* reaction of cinnemaldehyde and aroylhydrazines with Ni(OAc)$_2$ gave orange β-[Ni(L)$_2$] (R = H); based upon spectroscopic data, these two forms are *trans* and *cis* isomers respectively. The latter did not form when R = Me because of unfavourable steric interactions. The thermodynamics of complexation of the isomers with pyridine is reported. The complexes $Ni(L)_2 \cdot H_2O$ [L^- = **(110)**] have been briefly described [267]. They are paramagnetic.



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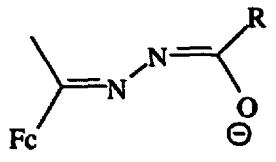
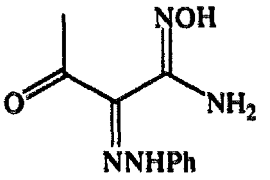


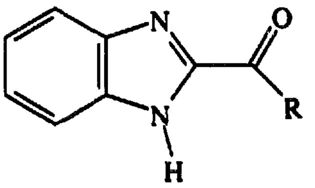
Fc = ferrocenyl; R = 3- or 4-pyridyl

(110)

The ligand **(111)** reacts with $NiCl_2$ in HOAc to afford an octahedral complex analysing as $[Ni(L)_2(H_2O)_2](OAc)Cl \cdot H_2O$ [268]. It is suggested that the ligand chelates *via* the hydrazone nitrogen and carbonyl oxygen. Treatment of Ni(II) salts in ethanol with 2-acetylbenzimidazole or 2-benzoylbenzimidazole **(112)** gave complexes $[Ni(L)_2Cl]Cl$ and $[Ni(L)_2(H_2O)_2]X_2$ (X = Br, NO_3, ClO_4) [269]. Infra red data suggests coordination *via* imidazole nitrogen and carbonyl oxygen.

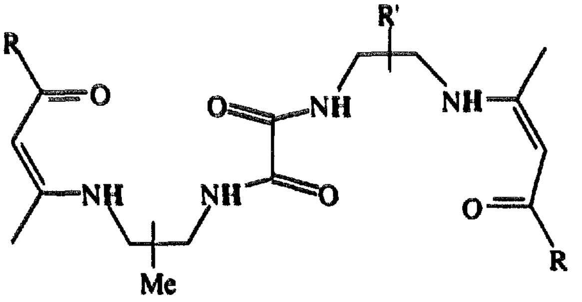


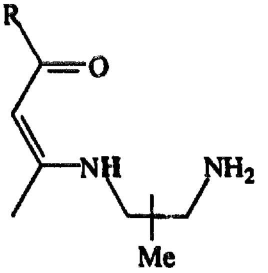
(111)



R = CH_3, Ph

(112)



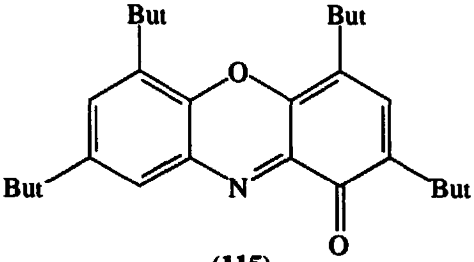


R = Me, Et; R' = H, Me

(113) **(114)**

All but one of the possible geometric isomers of the square planar complexes $[Ni_2(L)]$ of ligands H_4L **(113)** (protons in bold lost on complexation) have been synthesised [270]. Further, the existence in solution of the different enantiomers has been established by ^1H and ^{13}C NMR spectroscopy. The coordination of the corresponding terdentate ligand **(114)** (HL) has also been investigated [271]. When the crude ligand (consisting of a mixture of isomers) reacts with Ni(II) salts, only two of the possible geometrical and optical isomers of square planar [Ni(L)X] or

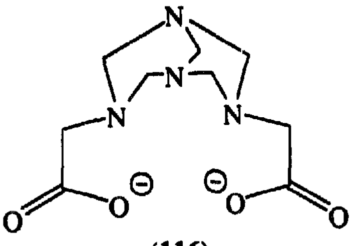
$[Ni(L)(py)]ClO_4$ are formed. In both isomers, the methyl group is remote from the imino nitrogen and is equatorial. The X-ray crystal structure of $[Ni(L)N_3]$ is reported.



(115)

On treatment of $Ni(NO_3)_2{\cdot}6H_2O$ with the iminoquinone ligand **(115)** in ethanol, the complex $[Ni(L)_2(NO_3)]NO_3$ was obtained [272]. X-Ray crystallography of the dichloromethane solvate revealed a didentate nitrate ion, and the two iminoquinone ligands coordinated with similar donor atoms mutually *trans* (Ni–O = 1.998(7), 1.968(4) Å; Ni–N 2.116(7), 2.075(6) Å). Reduction with cobaltocene gave the unusual red, tetrahedral $[Ni(L^{\cdot-})_2]$ (Ni–O 1.896(5), 1.913(6) Å; Ni–N 1.913(7), 1.904(6) Å); the ligand is reduced to the semiquinone form. Although tetrahedral, the complex is diamagnetic due to strong antiferromagnetic coupling of the unpaired electrons on the ligand with those of the metal. The semiquinone complex, in dichloromethane, showed two reversible reductions and two quasi-reversible oxidations, all ligand-based.

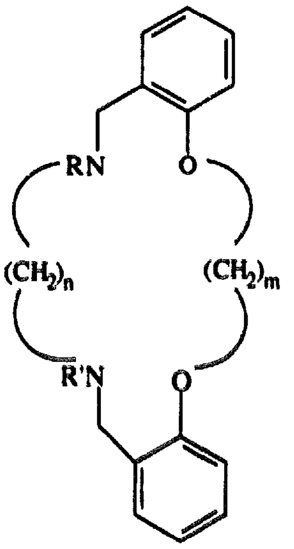
The complexation of $[Ni(nta)]^-$ with bpy and phen has been examined [273]. Ternary complexes are unstable; the product is $[Ni(diimine)_3]^{2+}$, but a complex $[Ni(nta)(diimine)]^-$ forms at low [diimine]. Similarly, the formation of ternary complexes of Ni(II) with di- and tricarboxylic acids (H_2L, H_3L'), and *N*-(2-acetamido)iminodiacetic acid (H_2ADA) [274] or bpy and phen [275], have been explored. Octahedral complexes assigned as $Na_2[Ni(L)(ADA)(H_2O)]{\cdot}nH_2O$ and $Na_3[Ni(L')(ADA)]{\cdot}nH_2O$ were isolated, and stability constants were determined. Neutral complexes $[Ni(ADA)(diimine)(H_2O)]$ were isolated and characterised spectroscopically. Long-chain 2-carboxy-5-alkoxypyridines (together with the corresponding aldoximes) have been investigated as ligands for removal of Ni(II) from aqueous media by extraction into micelles, and subsequent ultrafiltration [276]. Rates of Ni(II) complexation were 2-3 orders of magnitude slower by these ligands in micelles than by corresponding short-chain analogues in aqueous solution, and depended strongly on the nature of the surfactant. The crystal structure of the complex [Ni(**116**)] has been re-determined in the centrosymmetric space group *Pnma*; it had previously been solved in the non-centrosymmetric space group $Pna2_1$ [277].



(116)

The coordination chemistry of methylhydrazinecarboxylic acid (HL_1) and 1,1-dimethylhydrazinecarboxylic acid (HL_2) with various metals, including Ni(II), has been examined [278]. Complexes analysing as $Ni(L_1)_2(H_2O)_3$·methylhydrazine and $Ni(L_2)_2(H_2O)_2$ were isolated by treating ethanol solutions of the hydrazine and Ni(II) salts with CO_2. Infrared data and analogy with structurally characterised complexes suggests that the ligands are *N,O*-didentate and the geometry is all-*trans*.

On treatment of $NiSO_4 \cdot 6H_2O$ with 2-acetylpyrrole (HL) in $BuNH_2$, all-*trans*-$[Ni(L)_2(BuNH_2)_2]$ was isolated, and characterised crystallographically [Ni–O 2.126(2) Å, Ni–N(pyrrolyl) 2.060(2) Å, Ni–N(amine) 2.118(2) Å] [279]. However, when the reaction was performed in $^iPrNH_2$, the centrosymmetric dimer $[Ni_2(L)_4(^iPrNH_2)_2]$ was isolated. The coordination about each Ni consists of one amine donor and two mutually *cis* acetylpyrrolyl moieties, one of which bridges the neighbouring metal ion through the carboxyl oxygen. Finally, dimethyl(aminomethyl)phosphine oxide (L), used in the preparation of polyurethane foams, reacts with $Ni(NCS)_2$ in ethanol to afford a complex $[Ni(SCN)_2(L)_2]$ in which the ligands are probably chelating through the amine nitrogen, and oxygen [280].



m	n	R, R'
2	2	CH_2CH_2OH **(117a)**
2	3	CH_2CH_2OH **(117b)**
3	3	CH_2CH_2OH **(117c)**
4	3	CH_2CH_2OH **(117d)**
2	3	R = H, R' = CH_2CH_2OH **(117e)**
2	2	$CH_2CH_2CONH_2$ **(117f)**
2	3	$CH_2CH_2CONH_2$ **(117g)**

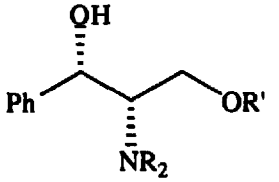
Turning now to amide complexes, new pendant arm macrocycles (**117f**, **117g**) and their Ni(II) complexes [Ni(**117f**)]$(NO_3)_2 \cdot 4.5H_2O$ and [Ni(**117g**)]$(NO_3)_2 \cdot 0.5H_2O \cdot 0.5$ethanol have been synthesised, and the latter complex characterised crystallographically [281]. All macrocycle ring donors are coordinated, and the pendant arms are coordinated *via* the carbonyl oxygens, mutually *trans*. These ligands were too insoluble for stability constant studies.

The reaction of $[(L)Ni(\mu\text{-}OH)_2Ni(L)]$ (L^- = hydrido-tris(3,5-diisopropylpyrazol-1-yl)borate] with $4\text{-}O_2NC_6H_4NHC(O)Me$ (HL') gave the five-coordinate complex [Ni(L)(L')], with the deprotonated amido group chelating via N and O [282]. Complexes analysing as $[Ni(H_2L)_2X_2]$ (X = Br, NCS, ONO_2) and $K_2[Ni(L)_2] \cdot 2H_2O$ (H_2L = $H_2NC(O)CH_2C(O)NH_2$] were prepared from H_2L and the metal salt in acetic acid, or H_2L and $NiCl_2$ in 8M KOH, respectively [283]. Spectroscopic evidence supports all-*trans* coordination, of the carbonyl oxygens in $[Ni(H_2L)_2X_2]$

and the deprotonated amide nitrogens in $K_2[Ni(L)_2]\cdot 2H_2O$. Direct electrochemical oxidation of nickel metal in a solution of benzoylglycine or ethylphthaloylglycine (L) gave complexes containing L coordinated *via* amide nitrogen and ester carbonyl, of uncertain composition [284].

6.10.3 Amine- and imine-alcohol and -ether ligands

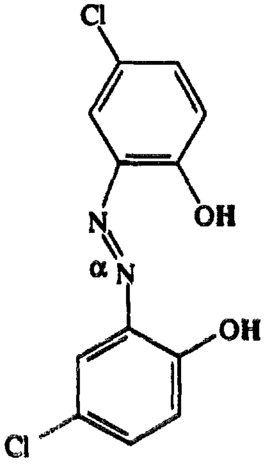
The nickel(II) nitrate complexes of ligands (**117a–e**) have been prepared, and most of them structurally characterised [281]. The complex [Ni(**117a**)(NO_3)]NO_3 has both macrocycle nitrogens, and both pendant arm hydroxy groups, coordinated. The macrocycle ether oxygens are not coordinated, and the pseudo-octahedral coordination sphere is completed by a didentate nitrate ion. The complexes [Ni(**117b**)(NO_3)]NO_3 and [Ni(**117c**)(NO_3)]NO_3 are very similar. The nickel(II)-ROH bond lengths (2.030 – 2.075 Å) are normal. In [Ni(**117e**)(H_2O)]$(NO_3)_2$, however, the Ni(II) is coordinated to all four macrocycle ring donor atoms, and the pendant alcohol. In solution, the stability constant for Ni(II) with (**117a–d**) are higher than for the corresponding ligands without the pendant alcohols, suggesting that the latter are involved in coordination in solution as well as in the solid state.



(**118**)

The ligands (**118**), when employed in the presence of catalytic amounts of [Ni(acac)$_2$], catalyse asymmetric 1,4-addition of organozinc reagents to *trans*-PhCH=CHC(O)Ph [285]. Best results (> 90% e.e) were obtained with R' = benzyl, R_2 = $-CH_2CH_2OCH_2CH_2-$ in CH_3CN. Derivatives of 8-hydroxyquinoline bearing long alkyl chains at C11 have been tested as ligands for the extraction of Ni(II) from aqueous media into micelles of cetyltrimethylammonium bromide/1-butanol [286]. The stoichiometry of the complexes was determined by Job's method, and their dissociation kinetics were examined using stopped-flow methods. A detailed one- and two-dimensional ^1H and ^{13}C NMR spectroscopic study of the square planar complexes [Ni(L)(py)] [H_2L = (**119**) - (**121**)] has been reported [287]. The ^{13}C NMR chemical shifts in particular are sensitive probes of isostructurality among the complexes; all the ligands coordinate *via* N_α and the deprotonated OH groups; the corresponding Pd(II) and Pt(II) complexes are isostructural.

Treatment of $[Ni_2(L)(CH_3OH)_2(ClO_4)_2]\cdot 2NHEt_3ClO_4$ [H_2L = (**122**)] with NaNCS, followed by recrystallisation, yielded $[Ni_2(L)(NCS)_2(H_2O)_2]\cdot 2Me_2NCHO$, the crystal structure of which was determined [288]. The complex has a centre of inversion; each Ni(II) is coordinated by two nitrogens and two bridging phenolate oxygens from the macrocycle, one *N*-bound NCS^- and one water molecule. The magnetic properties of this, together with those of the six-coordinate complexes $[Ni_2(L)(H_2O)_4](ClO_4)_2\cdot 4H_2NC(O)NH_2$, $[Ni_2(L)(CH_3OH)_2(ClO_4)_2]\cdot 2NHEt_3ClO_4$, five-coordinate $[Ni_2(L)(L')_2](ClO_4)_2$ (L' = pyridine or imidazole), and $[Ni_2(L)(\mu\text{-}O_2CCH_2NH_3)(H_2O)_2](ClO_4)_2\cdot 2H_2O$ were determined as a function of temperature. The size of J for these complexes varied from -1 cm^{-1} to -67 cm^{-1}; increased tetragonal distortion gave increased magnetic interaction, and the five-coordinate species showed the most interaction. The crystal structure of $[Ni_2(L)(imidazole)_2](ClO_4)_2$ was later determined [289]. The cation is centrosymmetric and each Ni(II) is five-coordinate, with an apical distortion towards the secondary amine donor of the imidazole ligand. A correlation was noted between the degree of antiferromagnetic interaction and the Ni–O–Ni angle in the former series of complexes of L^{2-}; the larger the angle, the greater the antiferromagnetism. By treating $[Ni_2(L)(CH_3OH)_2(ClO_4)_2]\cdot 2NHEt_3ClO_4$ with excess carboxylic acid, mixed carboxylate- and phenolate-bridged dinickel complexes $[Ni_2(L)(\mu\text{-}O_2CR)(H_2O)_2]ClO_4$ (R = H, Me, Et, Pr, Ph) were obtained [290]. These all undergo reversible one-electron oxidations at +0.8 V, with a further quasi-reversible oxidation at *ca.* +1.0 V in some cases. The crystal structure of the complex $[Ni_2(L)(\mu\text{-}O_2CR)(H_2O)_2]ClO_4$ (R = Me) shows a distorted octahedral arrangement. Adjacent macrocycle donor atoms, in the equatorial plane, are alternately displaced above and below the mean planes, and the metal centres are not coplanar; there is no centre of symmetry in the molecule. The Ni–O (phenolate) bonds [2.059(4)–2.158(4) Å] are rather long.



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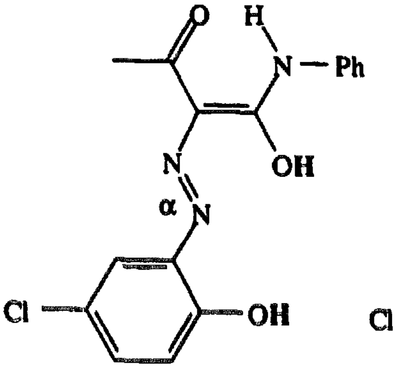

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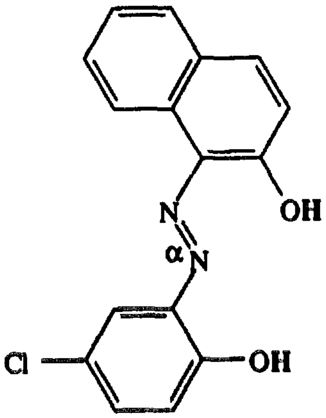

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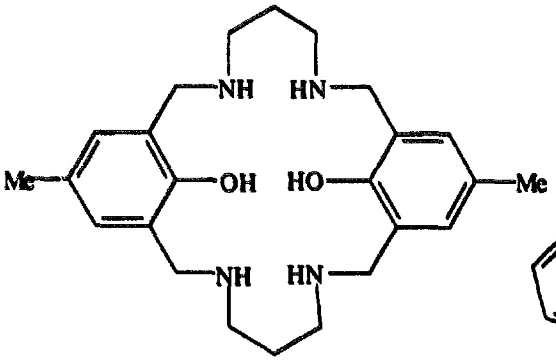
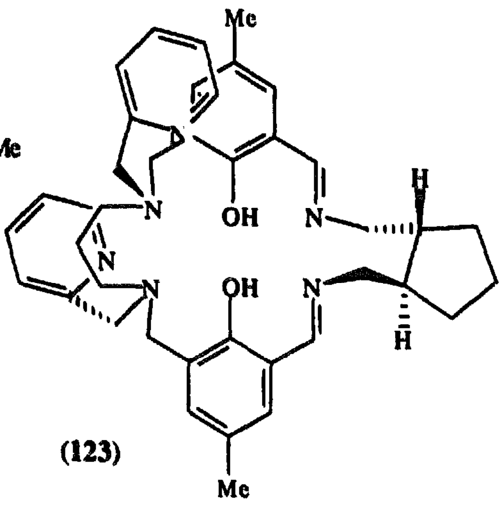


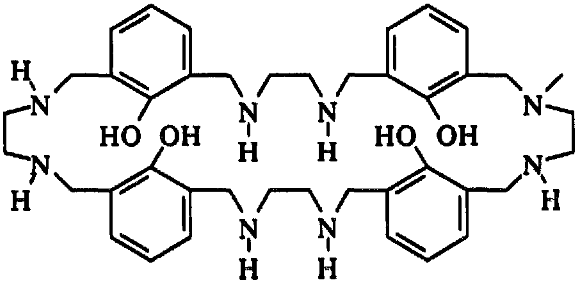
(122)



(123)

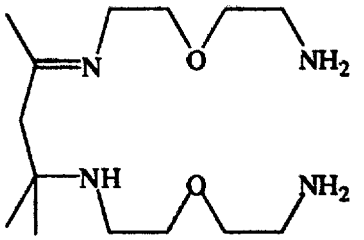
Complexes $[Ni^{II}(S,S\text{-cypim})(H^+)_2](PF_6)_2$, $[Ni^{II}(S,S\text{-cypim})Ni^{II}Cl](PF_6)$, $[Co^{III}(S,S\text{-cypim})Ni^{II}Cl](PF_6)_2$ and $[Ni^{II}(S,S\text{-cypim})Cu^{II}](PF_6)_2$ [S,S-cypim^{2-} = **(123)**] have been synthesised as part of a wider study of the interaction between the 'closed site' (octahedral) and 'open site' (four coordinate) metal centres [291]. The protonated monometallic complex is high-spin, and the ligand adopts the C_2 symmetric geometry illustrated, so that the pyridine nitrogens coordinate the axial sites of the metal. Electronic spectral data suggest that in all the complexes where Ni(II) occupies the 'open' site, it is five–coordinate (high spin). Interestingly, the homodimetallic complex apparently has both Ni(II) ions in five-coordinate high-spin environments. ESR spectra indicated that the NiCu species was a spin doublet with metal-metal interaction.

The Mg^{2+}-templated condensation of 2,6-diformyl-4-methylphenol (1 equiv.) and ethylenediamine (1 equiv.), followed by BH_4^- reduction, gave a novel octaamino-tetraphenol macrocyclic ligand **(124)** [292]. On reaction with $Ni(ClO_4)_2{\cdot}6H_2O$ and NEt_3 in methanol, this afforded the tetranuclear complex $[Ni_4L(\mu_3\text{-}OH)(\mu\text{-}H_2O)_2(ClO_4)](ClO_4)_2{\cdot}2MeC(O)Me{\cdot}H_2O$ after recrystallisation from acetone. The crystal structure of this complex shows the four non-planar Ni(II) ions in distorted octahedral environments; each is coordinated to two amine nitrogens and two bridging phenoxide oxygens. Each pair of metals is bridged by water molecules, while three of the metals are capped by the hydroxide ion and the fourth metal is bonded to a perchlorate ion.



(124)

Whereas condensation of ethylenediamine with acetone (either in the presence of Ni(II) ions or protons) yields the same macrocyclic product, condensation of 3-oxa-1,5-diaminopentane with acetone alone gave the Schiff base $(Me_2C{=}NCH_2CH_2)_2O$ [293]. However, with acetone and Ni(II) the product was a complex of the ligand **(125)**, formed evidently by a metal templated condensation of two diamine with two acetone molecules. The corresponding Co(II) complex was crystallographically characterised. The ligand adopts a helical geometry about the distorted octahedral metal ion, with the ether oxygens coordinated and the two amine nitrogens *trans* disposed; their coordination presumably prevents further Schiff base formation. Finally, complexes $[Ni(L)X_2]{\cdot}nH_2O$ (X = Cl, NO_3) of the potentially tridentate ligands bis(2-benzimidazolylmethyl)ether and bis(2-benzimidazolylmethyl)sulfide with Ni(II) have been prepared, and their ^1H and ^{13}C NMR spectra recorded [294]. Contact shift data suggest the two benzimidazole rings are equivalent. It is suggested that the complexes are five-coordinate in the solid state and six-coordinate in solution.

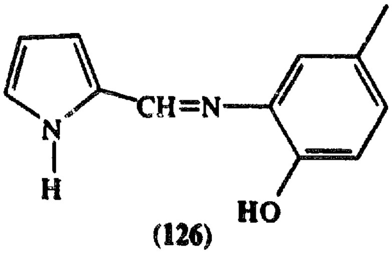

(125)

6.10.4 Schiff base and related ligands

6.10.4.1 Complexes with a single Schiff base donor

The Schiff bases derived by condensation of 3-chlorobenzaldehyde [295] or 2-chlorobenzaldehyde [296] with glycine (HL) act as a didentate ligand (through the imine nitrogen and carboxylate oxygen) to Ni(II), in '$[Ni(L)_2]\cdot H_2O$'; the antifungal activity of these were tested. No conclusions as to structure were drawn. The complexation of Ni(II) by other amino acid Schiff bases, those formed by condensation of L-phenylalanine, L-leucine, L-histidine or L-tryptophan with salicylaldehyde, *o*-hydroxynaphthaldehyde, pyruvic acid, *o*-vanillin or isatin, has also been examined [297]. The bromination and cyanobromination of (among others) Ni(II) complexes of salicylaldimine and salicylethylenediamine, followed by decomplexation of the brominated ligands with H_2S, has been tested [298]. The non-linear optical properties of various bis(salicylaldiminato)nickel(II) complexes substituted with both electron donating and electron withdrawing substituents have been examined; sizeable second-order NLO responses were obtained [299]. Some ferrocene-substituted Schiff base complexes (HL), prepared by condensation of formyl- or acetylferrocene with *o*-phenylenediamine, *o*-aminophenol or *o*-aminobenzoic acid, have been prepared, and complexes $[Ni(L)_2]$ have been described [300]. The extraction of Ni(II) into hexane using 5-nonylsalicylaldoxime has been studied [201]. The main factor governing the rate of extraction is the adsorptivity of the neutral form of the ligand, and the rate data are consistent with the initial step being reaction of the deprotonated oxime hydroxy group with Ni(II) on the aqueous side of the liquid-liquid interface.

Electrooxidation of nickel in a solution of (**126**) (HL) and phen afforded $[Ni(L)_2(phen)]$, a crystal structure of which established that L^- was bonded to Ni(II) *via* the imine nitrogen and deprotonated phenol oxygen only [302]. The oxygens were mutually *trans*, and significant intramolecular hydrogen-bonding was observed in the complex, between the coordinated oxygen and the pyrrole NH of the neighbouring L^-.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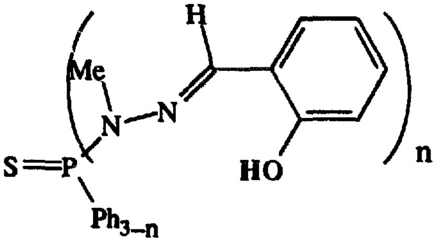
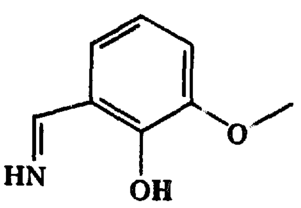


n = 3; **(127)**

n = 2; **(128)**



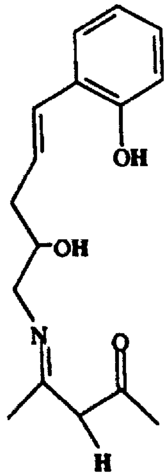
(129)

The reaction of the ligand **(127)** (H_3L) with $Ni(OAc)_2 \cdot 4H_2O$ gave a brown product, which X-ray diffraction (after recrystallisation) established was an unusual trinuclear complex $[Ni_3(L)_2]$ [303]. The central Ni(II) ion was located on an inversion centre, and surrounded by an almost perfect octahedron of phenolate oxygens, three from each ligand, forming bridges to the two outer Ni(II) ions whose coordination was completed by the three imino nitrogens. The corresponding phosphonodihydrazone **(128)** (H_2L') with $Ni(OAc)_2 \cdot 4H_2O$ gave square planar, mononuclear $[Ni(L')]$, with Ni(II) coordinated by two phenolate oxygens and two imine nitrogens. However, a second, minor, product was obtained. This was a trinuclear species $[Ni_3(L')_2(OAc)_2(CH_3CN)_2]$, with a structure rather similar to that of $[Ni_3(L)_2]$; the central Ni(II) this time was coordinated to two phenolate oxygens from each ligand in a plane, bridging to the two outer Ni(II), and axially to two acetate ions, each bridging to an outer Ni(II). The outer Ni(II) ions were coordinated to two imine nitrogens and the two phenolate oxygens in a plane, the bridging acetate and an acetonitrile solvent molecule.

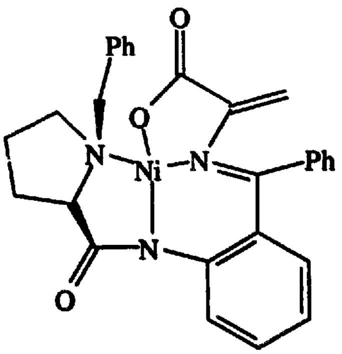
The condensation of $[Ni(L)_2(H_2O)_2]$ (HL = *o*-vanillin) with ammonia gave square planar $[Ni(L')_2]$ [HL' = **(129)**] [304]. Treatment of this in acetone with MX (M = Na, Li, X = ClO_4; M = K, X = I) afforded $[Ni(L')_2M(H_2O)](X)$. The sodium perchlorate adduct was characterised crystallographically; the Ni(II) ion is *cis*-coordinated by the imine and phenolate oxygens, and is almost perfectly planar. The sodium cation has an unusual coordination sphere consisting of two phenolate oxygens, two methoxy oxygens and a water molecule, all roughly equatorial, and an axial perchlorate ion, giving approximate pentagonal pyramidal geometry. Interestingly, the complex is monomeric; there are no short intermolecular distances. The complex $[Ni(L')_2]$ showed greater affinity for Na^+ compared with the other alkali metal cations.

The unsymmetrical ligand H_3L **(130)**, with $Ni(ClO_4)_2 \cdot 6H_2O$ and pyrazole, or 3,5-dimethylpyrazole, affords dinuclear complexes $[Ni_2(L)(\mu\text{-pz})]$ or $[Ni_2(L)(\mu\text{-3,5-Me}_2pz)]$ respectively, in the presence of KOH [305]. These are square planar and have been characterised by ^1H and ^{13}C NMR spectroscopy and ($[Ni_2(L)(\mu\text{-pz})]$) X-ray crystallography. Comparison of voltammetric data with that obtained for corresponding symmetrical dinuclear complexes suggests that the first reduction process occurs at the nickel-salicylidene end of the molecule.

The asymmetric radical addition of alkyl halide to the exocyclic $C{=}CH_2$ of **(131)**, initiated by Bu_3SnH, has been investigated [306]. A diastereomeric mixture with a 40-90% excess of (*S,S*) over (*S,R*) form resulted. Subsequent work-up of the product with HCl resulted in the hydrolysis of the imine group. The enantiomerically pure β-substituted α-aminopropanoic acid, and the ketone chiral auxilliary, could then be recovered.

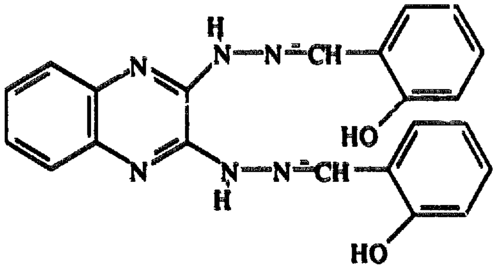


(130)



(131)

The ligand (132) reacts with $NiCl_2 \cdot 6H_2O$ to afford polymeric, octahedral $[Ni(L)]_n$ [307]. The complexation of Ni(II) with 2-aminomethylbenzimidazole (L) has been investigated [308]. In the presence of salicylaldehyde (HSal), a mixed ligand complex $[Ni(L)(Sal)(H_2O)_n]^+$ forms, although the presence of the coordinated amine reduces the equilibrium constant for Sal^- complexation. The $[Ni(L)(Sal)(H_2O)_n]^+$ slowly undergoes intramolecular Schiff base condensation to give a complex $[Ni(L')(H_2O)_n]^+$ [HL' = (133)].



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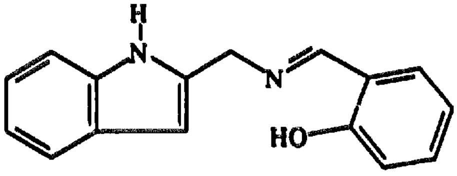
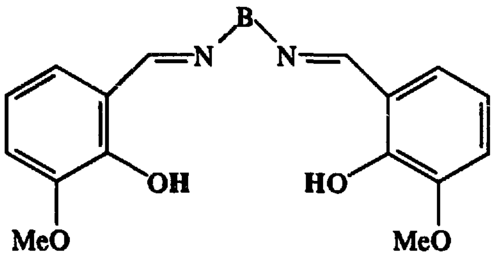


(133)

6.10.4.2 Complexes with salen and related Schiff base donor ligands

The effect of transition metal-salen complexes (including Ni(II)) on the fluorescence spectra of europium(III) and terbium(III) has been explained in terms of the formation of heteronuclear complexes in solution [309]. The reaction of $[Ni(L)] \cdot H_2O$ [H_2L = (134); B = $(CH_2)_n$; n = 3,4] with $SnMe_2(NCS)_2$ or $SnBu_2(NCS)_2$ results in NCS^- transfer from Sn to Ni, affording complexes $[SnR_2][Ni(L)(NCS)_2]$ [310]. Crystal structures of three of the complexes were obtained; the Ni(II) is coordinated by the L^{2-} donor atoms and *trans* axial *N*-coordinated NCS^- ions, and the Sn(IV) coordination is best described as skew trapezoidal bipyramidal, with short Sn–O(phenolate) bonds and long Sn–O(methoxyl) bonds. The adduct formed between $[SnPh_2(NCS)_2]$ and $[Ni(L)] \cdot H_2O$

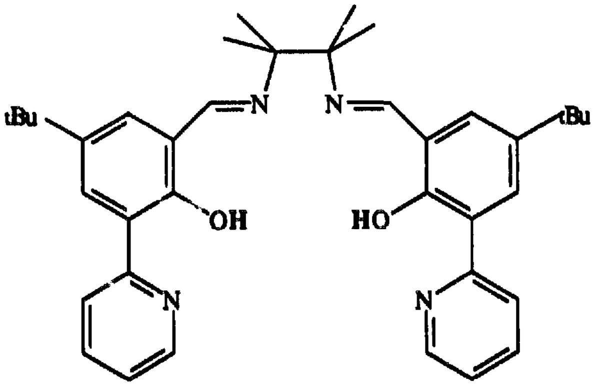
[H_2L = (134); B = $(CH_2)_3$] in CH_3CN, however, is [$SnPh_2(NCS)$][Ni(L)(NCS)(MeCN)], in which the tin has pentagonal bipyramidal geometry with *trans* phenyl groups.



B = $(CH_2)_n$; n = 2,3,4.
B = o–C_6H_4
B = $CH(CH_3)CH_2$

(134)

Although triphenyl- and tribenzyltin(IV) chlorides do not react with [Ni(salen)] and related complexes, in the presence of water they do form 1:1 adducts with [Ni(L)]·H_2O [H_2L = (134); B = $(CH_2)_n$; n = 2,3; B = o-C_6H_4; B = $CH(CH_3)CH_2$] [311]. The X-ray crystal structures of [$SnPh_3Cl{\cdot}H_2O$][Ni(L)·xH_2O] [B = $(CH_2)_n$; n = 3; x = 0,1] show that when x = 0, a trigonal bipyramidal [$SnPh_3Cl{\cdot}H_2O$] unit hydrogen-bonds through the coordinated water to a square planar [Ni(L)] through the phenoxy- and methoxy-oxygens. When x = 1, the same arrangement pertains, except that the Ni(II) is high spin and square-based pyramidal, and the water coordinated to Ni(II) is involved in further hydrogen-bonding, forming a dimeric arrangement with a neighbouring [Ni(L)].



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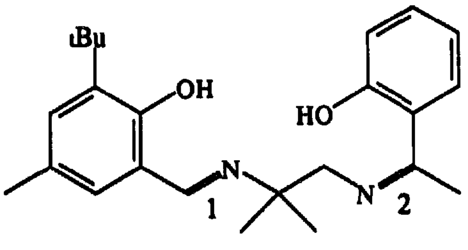
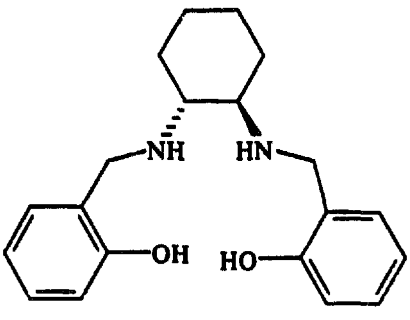


Bonds 1 and 2 -CH_2NH- **(136)**

Bond 1 -CH=N-, bond 2 -CH_2NH- **(137)**

Bonds 1 and 2 -CH=N- **(138)**

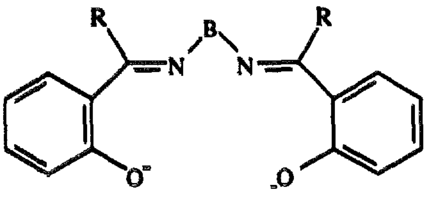


(139)

Continuing the theme of dinucleating ligands, metallation of **(135)** (H_2L) with $Ni(OAc)_2$ in ethanol affords the diamagnetic [Ni(L)], with the Ni(II) coordinated to the imine and phenoxy oxygens [312]. Further treatment of this with $Ni(OAc)_2$ or $Cu(OAc)_2$ in ethanol/CH_3CN followed by ion exchange affords the dinuclear, isomorphous $[Ni(L)M(HOEt)_2](PF_6)_2$ (M = Cu, Ni), in which the second metal ion is coordinated by bridging phenoxy oxygens, the pyridyl ligands and two axial ethanol molecules. The complexes have good solubility in organic solvents, unusual with this class of ligands.

Complexes of asymmetric derivatives of salen, dihydrosalen and tetrahydrosalen **(136–139)** have been described [313]. The complex [Ni(L)] [H_2L = **(136)**] reacts with O_2 in acetone to give [Ni(L')] [H_2L' = **(137)**].

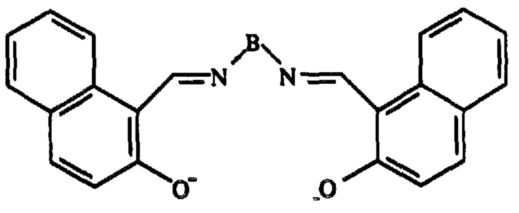
Turning to electrochemical studies, the Ni(II)/Ni(I) and Ni(III)/Ni(II) redox processes of complexes of *N*,*N'*-bis(salicylaldehyde)-*o*-phenylenediamine, and *N*,*N'*-bis(2-hydroxy-1-naphthaldehyde)-*o*-phenylenediamine, have been studied using *in situ* electronic spectroscopy [314]. An additional electrochemical reduction, of a ligand-based orbital, was observed for the naphthaldehyde derivative. The catalytic reduction of iodoethane and 2-iodopropane at a carbon electrode coated with an anodically-electropolymerised layer of [Ni(salen)] has been examined in acetonitrile solution [315].



B = $-(CH_2)_3-$, R = H; B = $-(CH_2)_3$, R = Me

B = $-CMe_2CMe_2-$, R = H; B = $o-C_6H_4$, R = H

(140)

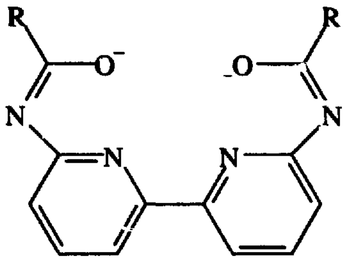


B = $-(CH_2)_3-$; B = $-(CH_2)_3$

B = $-CMe_2CMe_2-$; B = $o-C_6H_4$

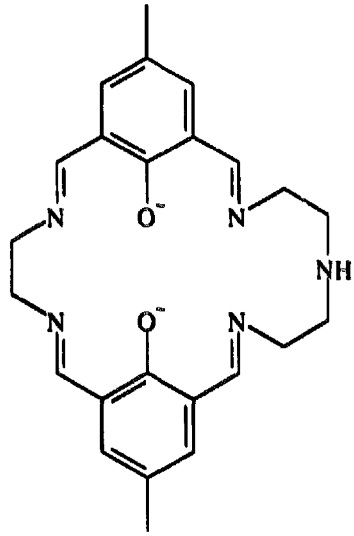
(141)

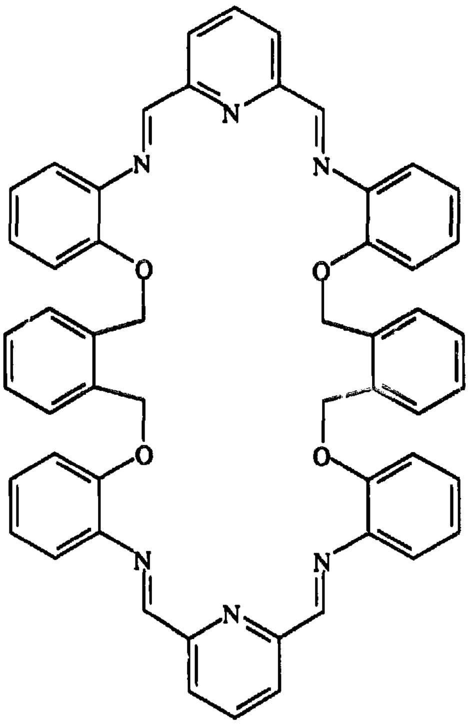
The electrochemical and chemical (iodine) oxidation of complexes [Ni(salen)] and [Ni(L)] [L^{2-} = **(140)**, **(141)**] in dmso yields Ni(III) complexes $[Ni(L)(dmso)_2]^+$ [316]. Cyclic voltammetry of the Ni(II) complexes [Ni(salen)] and [Ni(L)] in dmso revealed a single, one-electron quasi-reversible oxidation wave at between +0.7 V and +1.0 V. ESR spectra of the electrochemically-oxidised complexes in frozen matrices showed rhombic patterns characteristic of Ni(III), $[Ni(L)(dmso)_2]^+$. In some instances, another band at $g = 2.00$, characteristic of a ligand radical cation-Ni(II) complex, could also be observed, for instance with the $-CMe_2CMe_2-$ backbone. The kinetics of decomposition of the Ni(III) complexes were studied, and it is suggested that the decomposition path involves intramolecular electron transfer to give a Ni(II)-(ligand radical cation) intermediate. A similar study of the reductive and oxidative chemistry of the complexes [Ni(L)] [L^{2-} = **(140)**; R = Me, B = $-CH_2CH_2-$; **(I)** L^{2-} = **(140)**, R = Me; B = –1,2-*cis*-cyclohexane–; **(II)**), and **(III)** [Ni(*N*,*N'*-1,2-benzene-1,2-diyl-(bis(3,5-dichlorosalicylideneiminate)] showed that whereas **I** and **II** were reduced to Ni(I) species with a d_{xy} ground state, **III** gave a Ni(II)-(ligand radical anion) species [317]. Oxidation of all three complexes in dmso is metal-centred, as discussed for the related complexes above. Scanning tunnelling microscopy has been used to characterise monolayers of a dodecyl-substituted salen complex of Ni(II), deposited by the Langmuir-Blodgett technique onto highly oriented pyrolytic graphite [318].



R = Ph, 4–^{t}BuPh
(142)

Two papers concerning salen analogues based on substituted bpy have appeared. The complexes [Ni(L)] [L^{2-} = (**142**)] have been shown to catalyse the epoxidation of alkenes and, in particular, are better catalysts than [Ni(salen)] for electron-deficient substrates [319]. The new ligand 6,6'-bis(2-hydroxyphenyl)-2,2'-bipyridine (H_2L) forms neutral square planar [Ni(L)] [320]. This can readily be electropolymerised potentiostatically at + 1.05 V on Pt electrodes. The polymer films are electroactive, and can be demetallated by treatment with 5 M HCl, making metal exchange possible.





(143) (above)

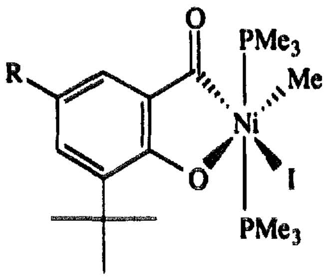
(144) (right)

The heterodimetallic complex [NiPb(L)]$(ClO_4)_2 \cdot H_2O$ [L^{2-} = (**143**)] has been prepared by the template reaction of [Ni(*N*,*N'*-ethylenebis{3-formyl-5-methylsalicylideneiminate})] with $Pb(ClO_4)_2$ and dien in methanol [321]. This undergoes transmetallation reactions with 3d metal salts to give complexes of the type [NiM(L)]$(ClO_4)_2$ (M = Mn, Fe, Co, Ni, Cu, Zn). Spectroscopic and magnetic data suggest that the Ni(II) ion occupies the 4-coordinate (square planar) site in all the complexes. A Ni(II)/Ni(I) redox process is seen at *ca.* –1.0 V, with (in the case of the dinickel complex) a further wave at –1.23 V. The macrocycle (**144**) results from (2+2) condensation of the appropriate diamine and pyridine-2,6-dicarbaldehyde in the presence of $AgClO_4$, affording the $[Ag_2(L)](ClO_4)_2$ complex [322]. On treatment of this with $Ni(ClO_4)_2{\cdot}6H_2O$, the monometallic $[Ni(L)](ClO_4)_2$ forms; this has a very distorted octahedral NiN_6 coordination, with each pyridinediimine unit adopting *fac* geometry, giving a helical structure. Interestingly, the Zn^{2+} analogue has D_2 symmetry (^1H NMR spectroscopic evidence) and the methylene protons are diastereotopic, indicating the retention of a helically chiral structure in solution.

6.11 COMPLEXES WITH PHOSPHINES AND RELATED LIGANDS

6.11.1 Monodentate phosphines and related ligands

The first examples of organonickel(IV) complexes to be isolated and characterised have been described. The complex $[Ni(L)(PMe_3)_3]$ undergoes oxidative addition with MeI in Et_2O to afford six-coordinate $[Ni(Me)I(L)(PEt_3)_2]$ (**145**) [323]. X-Ray crystallographic study of two dimorphic crystals of the latter (R = ^{t}Bu) confirmed that the phosphine ligands are mutually *trans* and the methyl group is *trans* to the phenolate oxygen. Significant differences in bond lengths and angles between the two structures are ascribed to packing effects; the bond lengths are not greatly different from typical values for corresponding Ni(II) complexes. The complexes are surprisingly stable, surviving at room temperature under argon for days. Their decomposition in solution (with C–C bond formation between the methyl and acyl groups) is catalysed by $[Ni(PEt_3)_4]$.



R = CH_3, $C(CH_3)_3$

(**145**)

The first X-ray crystal structure of a homoleptic Ni(0)-trialkylphosphine complex, $[Ni(PEt_3)_4]$, has been reported [324]. The geometry is considerably distorted from tetrahedral, with Ni–P bond lengths of 2.210(1) Å and 2.215(1) Å, and P–Ni–P angles ranging from 102.4(2)° to 111.6(1)°. This is due to steric interactions, the cone angle for this ligand being 132°. Treatment of $[Ni(cod)_2]$ with $R_2P(C_6Cl_5)$ (R = Ph, Et), alone or in the presence of other phosphines PR'_3 (R' = Et, CH_2Ph, Ph) or PMe_2Ph afforded complexes $[Ni(C_6Cl_4PR_2)_2]$ and $[NiCl(C_6Cl_4PR_2)PR'_3]$ containing *o*-metallated perchlorophenylphosphine ligands, and $[NiCl(C_6Cl_4PR_2)(PR'_3)_2]$ where the four-membered chelate ring of the *o*-metallated phosphine is opened by the additional PR'_3 [325]. The $[NiCl(C_6Cl_4PR_2)PR'_3]$ complexes are unstable in solution, reacting to form $[NiCl_2(PR'_3)_2]$ and $[Ni(C_6Cl_4PR_2)_2]$, while treatment with more PR'_3 gives $[NiCl(C_6Cl_4PR_2)(PR'_3)_2]$. When didentate phosphine ligands are employed in the oxidative addition reaction, five-coordinate $[NiCl(C_6Cl_4PR_2)(L–L)]$ (L–L = dppe, dppp) are obtained, but dppm acts as a monodentate ligand and gives five-coordinate $[NiCl(C_6Cl_4PR_2)(dppm)_2]$. With L (L = CO or PR'_3), $[Ni(C_6Cl_4PR_2)_2]$ react to give five-coordinate $[Ni(C_6Cl_4PR_2)_2(L)]$ without disruption of the four-membered rings. The crystal structures of $[Ni(C_6Cl_4PEt_2)_2]$, $[NiCl(C_6Cl_4PPh_2)(P\{CH_2Ph\}_3)_2]$ and $[Ni(C_6Cl_4PR_2)_2(PEt_3)]$ are reported. The reaction of Ni(II) salts with ethane-1,2-dithiolate (edt) in the presence of PR_3 (R = Et, Ph) in methanol gives $[Ni_2(edt)_2(PR_3)_2]$, $[Ni_2(tpdt)(PPh_3)]$ and $[Ni_2(tpdt)_2]$ (tpdt = 3-thiapentane-1,5-dithiolate) [326]. The crystal structures of $[Ni_2(edt)_2(PEt_3)_2]$ and $[Ni_2(tpdt)_2]$ are reported. The former shows two distorted square planar Ni(II) ions coordinated to one PEt_3 and the two thiol sulfur atoms of an edt (one of which bridges to the neighbouring Ni(II)). The tpdt complexes were obtained in greater yield in the presence of air, suggesting that the mechanism of formation of tpdt from edt involves oxidation of coordinated RS^- to coordinated RSO_2, followed by excision of SO_2 and coupling to a further edt. The reaction of $PhP(NCS)_2$ with $NiCl_2$ in the presence of Zn powder is reported to give zerovalent $[Ni(PhP(NCS)_2)_2]$, with the ligand apparently chelating *via* the sulfur atoms [327]. With $[NiCl_2(PPh_3)_2]$, a red diamagnetic product assigned as $[Ni_2(PPh_3)_4(PhP(NCS)_2)_2]Cl_2$, a Ni–Ni bonded dimer, is obtained.

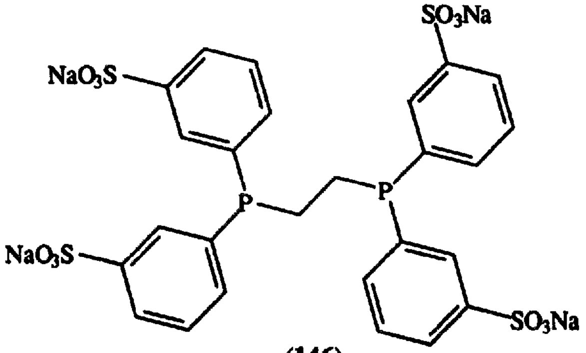
The thermal decomposition of complexes $[NiX_2(PPh_3)_2]$ (X = Cl, Br, I, NO, NCS) has been studied [328]. The crystal structure of $[Ni(Me_2PhCCO_2)_2(PPh_3)]_2$ establishes that this complex has the classical 'Cu(II) carboxylate' structure; two nickel ions are bridged by four carboxylate ligands, and the PPh_3 ligands complete square pyramidal coordination at Ni(II) [51].

The bonding in clusters $M_8(\mu_4\text{-}E)_6L_n$, a class of compounds that includes, *inter alia*, $[Ni_8(\mu_4\text{-}PPh)_6(PPh_3)_4]$ (112 metallic valence electrons, MVEs) and $[Ni_8(\mu_4\text{-}PPh)_6(PPh_3)_4(CO)_4]$ (120 MVEs), has been examined theoretically, using extended Hückel and self-consistent field multiple-scattering $X\alpha$ calculations [329]. Results indicate that 120 MVEs is the optimum number with electronegative metals and / or terminal π-acceptor ligands. The rather strong M–M bonds are due mainly to through-space interactions, but also to through-bond M–E interactions. A delocalised bond picture is therefore necessary to account for the electronic structure of these molecules. The M–M bonding is strengthened upon depopulation of the top of the d-band. The slight antibonding or nonbonding nature of the top of the metallic d-band accounts for the large range of electron counts (from 99 to 120 observed so far).

6.11.2 Di- and multidentate phosphine donors

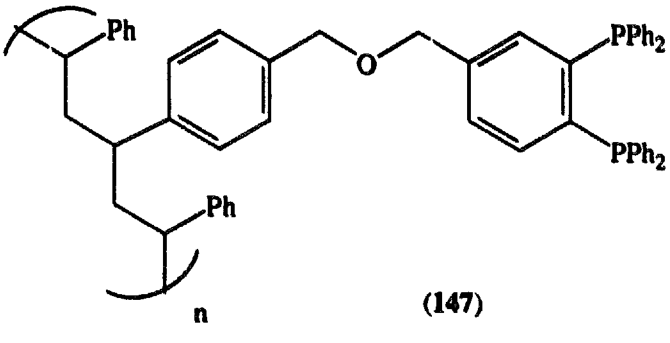
The key role played by diverse nickel complexes in the development of CO_2 coordination chemistry and CO_2 electroreduction catalysts has been highlighted in a review [330], sparked by the earlier publication of the photochemical activation of CO_2 by $[Ni_3(\mu\text{-dppm})_3(\mu_3\text{-}I)_2]$ [331]. The complex $[NiCu(CO)_2(\mu\text{-dppm})_2(CH_3CN)_2]ClO_4$ is the product when $[Ni(CO)_2(\eta^1\text{-dppm})_2]$ is treated with $[Cu(CH_3CN)_4]ClO_4$ in CH_3CN [332]. The ^{31}P NMR spectrum is AA'XX' and typical of dppm-bridged heterodimetallics, and both metals are presumed to be tetrahedral, with CO coordinated to Ni(0) and CH_3CN to Cu(I). Treatment of this with $NaBH_3CN$ gives $[NiCu(CO)_2(\mu\text{-dppm})_2(BH_3CN)]$, which can also be prepared in a 'one-pot' reaction, reduction of $NiCl_2{\cdot}6H_2O$ with $NaBH_3CN$ under CO in the presence of dppm, followed by treatment with $CuCl_2{\cdot}2H_2O$.

X-Ray crystallography reveals that the Ni(II) is approximately tetrahedral, and the dppm ligands adopt a 'cradle' arrangement; the geometry at Cu(I) is trigonal planar, with the BH_3CN ion coordinated through the lone pair on the nitrogen.



(146)

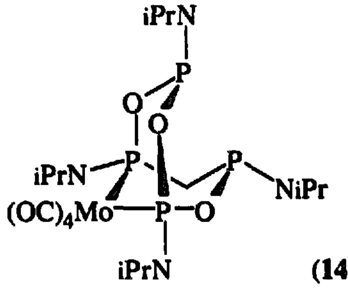
There is much interest at present in the coordination chemistry of water-soluble phosphine ligands. Direct sulfonation of dppe gives a complex mixture of products, from which **(146)** can be isolated in 30% yield by fractional crystallisation [333]. This reacts with $[Ni(CO)_4]$ in aqueous THF to give $[Ni(CO)_2$**(146)**$]$. The sulfonated diphosphine is less electron-donating than dppe; the CO stretching frequencies in this complex are at higher wavenumber than those of $[Ni(CO)_2(dppe)]$. Treatment of $[NiCl_2(vdp)]$ (vdp = *cis*-1,2-bis{diphenylphosphino}ethene) with $SnCl_2{\cdot}2H_2O$ gives $[Ni(SnCl_3)(vdp)]$ [334]. The complexes $[Ni(L–L)_2]^{2+}$ and $[Ni(L–L)_2X]^+$ [L–L = vdp, *o*-$C_6H_4(PPh_2)_2$, *o*-$C_6H_4(PPh_2)(PMePh)$, *o*-$C_6H_4(PPh_2)(PBuPh)$; X = Cl, Br] have been prepared and characterised [335]. For the complex $[Ni\{o\text{-}C_6H_4(PPh_2)(PBuPh)\}_2](ClO_4)_2$, the ^{31}P NMR spectrum shows the existence of only two of a possible four stereoisomers. Electrochemical studies of these complexes, and of complexes $[NiL_4]^{2+}$ (L = $PMePh_2$, $PBuPh_2$) generated *in situ*, have been performed. For $[Ni(L–L)_2]^{2+}$, two successive one-electron metal-based reductions are observed. The $[Ni(L–L)_2X]^{2+}$ lost halide upon reduction to give the stable $[Ni(L–L)_2]^+$. The Ni(I)/Ni(II) potentials varied according to the nature of the chelate bridge (no link < ethene < ethane < *o*-phenylene). The Merrifield resin-supported *o*-phenylenediphosphine **(147)** (L–L) has been synthesised from 1,2-bis-diphenylphosphino-4-hydroxymethylbenzene, and its interaction with various metal centres, including $NiCl_2$, examined [336]. Although the polymer-supported metal complex has an electronic spectrum similar to that of square planar $[NiCl_2(L–L)]$, fluorescence EXAFS data suggest additional coordination of an oxygen donor in the polymer-bound complex, probably from thf or water.



(147)

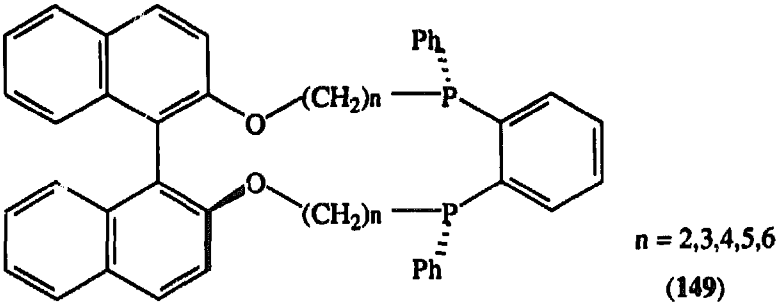
The reaction of [$NiCl_2$(L–L)] (L–L = dppe, dppp) with NaOR gives [Ni(L–L)$_2$], Ni(OR)$_2$ and aldehyde or acetone in a 1:1:1 ratio (R = Me, Et, ^{i}Pr), as well as NaCl [337]. When L–L = 1,2-bis(dicyclohexylphosphino)ethane (dcpe), the product is [Ni_2(dcpe)$_3$] or (with additional diphosphine present) [Ni(dcpe)$_2$]. Under CO, corresponding [Ni(CO)$_2$(L–L)] are formed in high yield. Unstable alkoxo(diphosphine) complexes were observable at low temperature in the reaction mixtures by ^{31}P NMR spectroscopy, but only with dcpe did it prove possible to isolate and characterise [Ni(OMe)$_2$(dcpe)]. The mechanism probably involves β-hydride transfer to give an unstable Ni(II)-hydride(η^2-aldehyde) alkoxy complex, which then reductively eliminates ROH.

A full paper has appeared detailing the reactions of the metallo-ligand Mo(CO)$_4$[^{i}Pr$_2$NPO]$_4$ (**148**) with $NiBr_2$·dimethoxyethane (among other transition metal complex precursors) [338]. The complex [$NiBr_2$(**148**)] has approximate C_{2v} symmetry at Ni(II), with a large Br–Ni–Br (128.9(1)°) and small P–Ni–P (85.7(1)°) angle. The Br–Ni–P angles, in contrast, are almost tetrahedral. Reaction of the MoNi(II) complex with Fe(CO)$_5$ in refluxing hexane gives [Ni(CO)$_2$(**148**)], which reacts with I_2 or SO_2Cl_2 to give [NiX_2(**148**)] (X = I or Cl respectively).



(148)

The complex [$NiCl_2$(L–L)] [L–L = (**149**); n = 2] has been prepared, and partial assignment of ^{1}H, ^{13}C and ^{31}P NMR spectra on the basis of 2D experiments has been made; the poor solubility of the complex prevented full assignment [339]. The related *S,S* chiral ligands (**149**; n = 3,4,5,6) are the main products (along with small amounts of other stereoisomers in the cases where n = 4,5,6) of the reaction of 1,2-bis(lithiomethyldiphenylphosphino)benzene with the appropriate ditosylate under high dilution conditions [340]. Their complexes [$NiCl_2$(L–L)] have also been described. In these cases too, insolubility hampered full characterisation, although crystal structures were obtained for [$NiCl_2$(L–L)] (L–L = (**149**); n = 5; two structures of different diastereomeric forms, that shown in the drawing (*S,R*), and the (*S,S*) form, L–L = (**149**); n = 6; (*S,R*) form).



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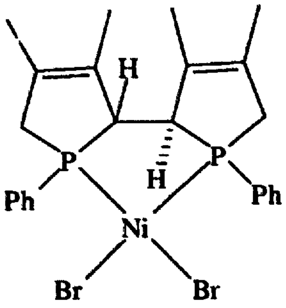
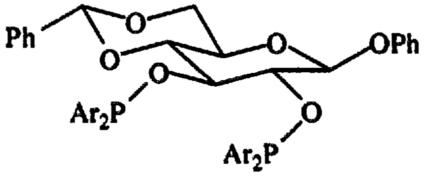


(150)

The phosphole complex (**150**), which is synthesised as a racemic mixture of the diastereoisomer shown, reacts with $AgBF_4$ in CH_3CN with disproportionation, to give *meso-* and *racemic-*[Ni(L–L)$_2$]$(BF_4)_2$, $[Ni(CH_3CN)_6](BF_4)_2$ and (in low yield) a single diastereomer of [Ni(L–L)$_2$Br](BF_4) [341]. These compounds were all separated by fractional crystallisation, and *meso-* and *racemic-*[Ni(L–L)$_2$]$(BF_4)_2$ characterised crystallographically.



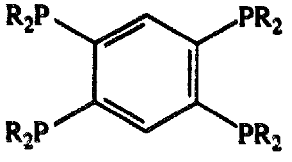
Ar = 3,5-$(F_3C)C_6H_3$; 3,5-$F_2C_6H_3$

C_6H_5; 3,5-$Me_2C_6H_3$

(151)

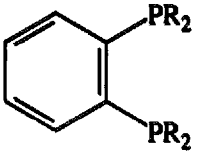
Several novel catalytic reactions utilising Ni-phosphorus donor complexes have been described this year, among them the use of Ni(0) complexes of the phosphinites (**151**), prepared *in situ* from the ligand and $[Ni(cod)_2]$, for the asymmetric hydrocyanation of arylolefins [342]. The highest enantiomeric excesses were obtained with electron-withdrawing substituents, particularly 3,5-bis(trifluoromethyl)phenyl. A route to chiral 2,2'-bis(diphenylphosphino)-1,1'-binaphthyl in one step from the readily-available triflate of 2,2'-dihydroxy-1,1'-binaphthyl using $[NiCl_2(dppe)]$-catalysed coupling with excess Ph_2PH has been described [343].

Turning now to complexes of ligands with three or more phosphorus donors, the reactions of $[Ni(tdpme)Cl_2]$ (tdpme = 1,1,1-tris(diphenylphosphinomethyl)ethane) with some tin compounds have been described [344]. With $Ph_3SnH/NaBH_4$ an apparently diamagnetic complex, formulated $[Ni(tdpme)(SnPh_3)]$ but having a sharp ^{31}P NMR spectroscopic signal, is the product. With $SnCl_2$, the complex $[Ni(tdpme)(\mu\text{-}Cl)_2SnCl_2]\cdot CH_2Cl_2$ is isolated.



R = Ph (**152a**)

R = Me (**152b**)



R = Ph (**153a**)

R = Me (**153b**)

R = ^iPr (**153c**)

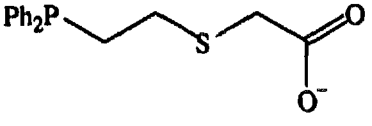
Two interesting papers this year describe the syntheses, characterisation and redox properties of Ni(II) complexes of (**152**) [345,346]. Treatment of [Ni(L–L)Cl_2] (L–L = (**153a**)) with HBF_4 and (**152a**) gives [Ni(**152a**)(L–L)]$(BF_4)_2$, which can be reacted further with HBF_4 and [M(L–L)Cl_2]

(M = Ni, Pd, Pt) to give [(L–L)Ni(**152a**)M(L–L)]$(BF_4)_4$, bridged by (**152a**) [345]. The polymeric $\{[Ni(\mathbf{152a})](BF_4)_2\}_n$ was also prepared, and n estimated as 37 ± 7 by integration of coordinated to uncoordinated P atoms after 'end-capping' the polymeric complex with excess (**152a**). The [(L–L)Ni(**152a**)Ni(L–L)]$(BF_4)_4$ undergoes a reversible, two-electron reduction to the Ni(I)Ni(I) state, followed by two one-electron reductions to Ni(I)Ni(0) and Ni(0)Ni(0), at –0.20, –0.47 and –0.56 V respectively. The heterodimetallic complexes, in contrast, undergo first two one-electron reductions (to Ni(I)M(II) and Ni(0)M(II) respectively), then a two-electron reduction to Ni(0)M(0). The Ni(0)M(II) complexes exhibit intervalence charge transfer transitions at 602 nm (M = Pd) or 618 nm (M = Pt) in CH_2Cl_2. A Marcus-Hush analysis of the energies of these bands as a function of solvent showed that the degree of coupling is very weak, and this is consistent with the very low conductivities (10^{-8} – 10^{-10} $\Omega^{-1}cm^{-1}$) found for partially-reduced solid samples of $\{[Ni(\mathbf{152a})](BF_4)_2\}_n$. Similar conclusions were reached regarding the complexes [(L–L)Ni(**152b**)M(L–L)]$(BF_4)_4$ (L–L = (**153b**) or (**153c**); M = Ni, Pd or Pt) and $\{[Ni(\mathbf{153b})](BF_4)_2\}_n$ (n = 48 ± 7) [346].

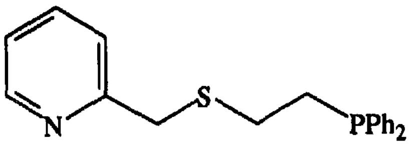
The complex [Ni(triphos)(P_3)]BF_4 reacts with [Pt$(PPh_3)_2(C_2H_4)$] to give (after metathesis) [(triphos)Ni(P_3)Pt$(PPh_3)_2$]BPh_4, in which insertion of the Pt$(PPh_3)_2$ moiety into one of the P–P bonds of the triangular P_3 unit has occurred, as revealed crystallographically [347]. The variable temperature ^{31}P NMR spectroscopic data is interpreted in terms of a 'ring whizzing' motion of the Pt moiety around the P–P edges.

6.11.3 *Complexes of mixed donor ligands including phosphorus*

In an interesting piece of work aimed at producing mixed donor ligands that stabilise a range of Ni oxidation states, the complexes [Ni$(L)_2$] (L^- = (**154**)) and [Ni$(L')_2$]$(BF_4)_2$ (L' = (**155**)) have been synthesised [348]. Both have been characterised crystallographically. The first has octahedral geometry, with *cis*-arranged phosphorus and sulfur donors arranged equatorially (mean Ni–P 2.390(3) Å, mean Ni–S 2.459(3) Å), and *trans* axial carboxylate oxygens (mean Ni–O 2.029(7) Å). The second has an all-*trans* distorted octahedral arrangement and is centrosymmetric (Ni–P 2.523(2) Å, Ni–S 2.419(3) Å, Ni–N 2.103(6) Å). In methanol, [Ni$(L)_2$] undergoes a reversible oxidation at +0.66 V (Ni(III)/Ni(II)). The Ni(III) cation can be generated chemically by Ce(IV) oxidation; it retains the stereochemistry of the Ni(II) species and has a d_{z^2} ground state. However, [Ni$(L)_2$] cannot be reversibly reduced. In contrast, [Ni$(L')_2$]$(BF_4)_2$ in propylene carbonate undergoes three one-electron redox steps, at +0.93 V (Ni(III)/Ni(II); reversible), –0.47 V (Ni(II)/Ni(I); quasi-reversible) and –1.01 V (Ni(I)/Ni(0); reversible). The quasi-reversibility of the Ni(II)/Ni(I) couple is ascribed to a geometry change (6- to 4-coordinate) which accompanies it.



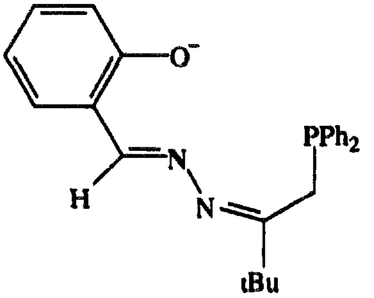
(**154**)



(**155**)

When $[Ni(CH_3CN)_6](BF_4)_2$ in thf is treated with 4 equivalents of tris(2,4,6-trimethoxyphenyl)phosphine, the orange diamagnetic complex $[Ni(P–O)_2]$ (P–O = **(156)**) forms [349]. This has a remarkably mild Ni(III)/Ni(II) couple at *ca* 0.0 V, and the Ni(III) complex is readily prepared by ferrocenium oxidation in acetone. The crystal structure of the Ni(II) complex shows square planar coordination (Ni–P 2.232(3) Å; Ni–O 1.856(5) Å), with a centre of inversion at Ni. Two of the methoxy oxygens reside above and below the plane, but the Ni–O distances preclude any bonding interaction. However, the Ni(III) complex has distorted octahedral geometry with these methoxy oxygens coordinated (mean Ni–P 2.223(3) Å; mean Ni–O⁻ 1.918(5) Å; mean Ni–OMe 2.192(1) Å).

Treatment of $NiX_2{\cdot}nH_2O$ (X = Cl, Br) with the ligand HL (L^- = **(156)**) in acetone gives square planar [NiX(L)], characterised by ^1H NMR spectroscopy [350]. This has L coordinated through phosphorus, the nitrogen shown in bold, and the phenoxy oxygen. Treatment of $Ni(OAc)_2{\cdot}4H_2O$ with two equivalents of HL gives a green non-electrolyte tentatively formulated as octahedral $[Ni(L)_2]$ - the second example of octahedral Ni(II) coordinated to $-PPh_2$ donors to be reported this year.



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