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Contents

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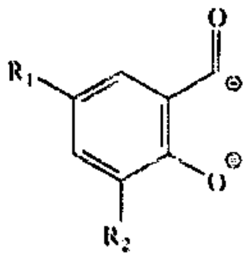
1. Introduction

This review covers the coordination chemistry of nickel published in 1995. Reviews for years 1990–1995 have appeared in this series. Classification is by ligand donor atom type alone, rather than by metal oxidation state, since the latter is often almost a formalism in nickel chemistry. Relevant references were obtained from the BIDS database using the term nickel* as a keyword and also searching for the occurrence of the exact term "Ni(II)" as an additional check. The years 1995–1996 (April) were searched, but only references dated 1995 are included. Since the BIDS database is now capable of searching titles, abstracts and keywords, independent checking of journals has not been performed this year. The growth in the number of papers continues year upon year, and this review is not intended to be exhaustive. In particular, complexes containing metal-carbon bonds are specifically excluded (except in cases where the complexes are judged to be of special significance to coordination chemists). Likewise, many papers appear each year where nickel–phosphine complexes are used as catalysts in organic reactions, and these too are generally excluded. Papers in which nickel complexes of classical ligands, characterised solely by non-structural methods, are described have not all been included.

Nickel-containing hydrogenases are attracting much attention at present, and because a key question in the mode of action of these is the nature of the Ni(II) site, these are included specifically, in the section on mixed nitrogen and sulfur donor ligands. All $E_{1/2}$ values are quoted with respect to the saturated calomel electrode except where otherwise stated.

2. Complexes with group IV donor ligands

Two reviews detailing, respectively, the syntheses and characterisation of nickel carbonyl clusters, and structural studies of these, have appeared [1,2]. The first homoleptic aminomethyl-transition metal complexes $\{Li(OEt_2)\}_2[Ni(CH_2NR_2)_4]$ ($R_2N = Me_2N$, $C_5H_{10}N$), made by treating $[NiCl_2(PBu_3)_2]$ with $LiCH_2NR_2$, have been reported; the crystal structure of the NC_5H_{10} complex shows square planar geometry at Ni(II) (Ni-C 2.023(4), 2.032(4) Å) with the lithium ions showing interaction with two of the N lone pairs and a significantly short Ni–Li distance (2.592(2) Å) [3]. Organonickel(IV) species are of obvious interest in considering mechanisms for Ni-catalysed coupling reactions, and another remarkable complex reported this year is a bis(acylphenolato) complex of Ni(IV). Reaction of $[Ni(L)(PMe_3)_3]$ (L^{2-} = (1)) with CH_2I_2, I_2 or diiodoethane at −70°C results in a dismutation reaction with formation of $[Ni(L)_2(PMe_3)_2]$ and $[NiI_2(PMe_3)_2]$ [4]. The Ni(IV) complexes are thermally stable and surprisingly air-stable. X-Ray crystallography shows the two phosphine ligands mutually trans, the acyl groups mutually cis. Interestingly, while the precursor Ni(II) complexes are acid-sensitive, the Ni(IV) complex is not. In the enantiopure square planar complex [Ni(L)Br] (L = (2)), Ni(II) is coordinated to aryl C and both tertiary amine donors, with the carbonyl oxygens lying above and below the plane but not coordinated. The [Ni(L)Br] has been investigated as a chiral catalyst for the addition of CCl_4 to alkenes [5]. This was unsuccessful, but an unusual complex $[Ni(L)Cl]_2[NiCl_4]$ was obtained, in which the six-coordinate Ni(III) is coordinated to aryl C (1.900(5) Å), both tertiary amine donors (2.092(4), 2.074(4) Å) and the carbonyl oxygens (2.052(4), 2.063(4) Å). The complex $[Ni(L)Br]_2[CuBr_4]$ was also obtained on $CuBr_2$ oxidation of [Ni(L)Br].



$R_1 = Me, R_2 = {}^tBu$
$R_1 = {}^tBu, R_2 = {}^tBu$
$R_1 = H, R_2 = OMe$

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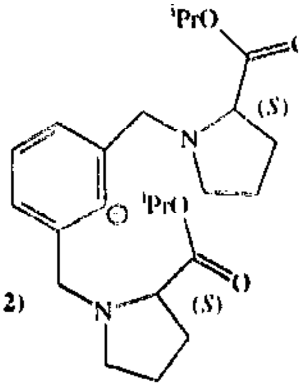


(2)

Absorption and emission spectra of endohedral nickel-containing fullerenes have been reported [6].

3. Complexes with halide and pseudohalide ligands

3.1. Halide ligands

The thermodynamically unstable fluorides NiF_4 and NiF_3 have been obtained by the addition of F^- acceptors to solutions of $[NiF_6]^{2-}$ in anhydrous HF at low temperature [7,8]. At −65°C, the tan solid NiF_4 is precipitated; this is converted back to $[NiF_6]^{2-}$ quantitatively on treatment with F^- donors (XeF_6 or KF). Dry

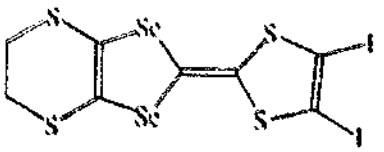
NiF_4 decomposes above −60°C to black NiF_3 with loss of F_2. When $K_2[NiF_6]$ is the precursor, a pyrochlore form, $K_{0.1}NiF_3$ is obtained. Suspensions of NiF_4 in anhydrous HF decompose to a rhombohedral form of NiF_3. When K^+ is present, at 20°C, a tungsten bronze form of NiF_3 is precipitated. The forms of NiF_3 differ in thermal stability, the pyrochlore form being the most stable (it loses F_2 at 138°C). NiF_4 is an extremely powerful oxidant; it converts $[MF_6]^-$ to MF_6 (M=Pt, Rh), while NiF_3 fluorinates perfluoropropene and oxidises Xe to XeF_6. Solutions of $[NiF_6]^{2-}$ in anhydrous HF, when treated with three equivalents of BF_3, give yellow solutions with extreme oxidising power; these probably contain solvated Ni(III) [9]. High valent nickel fluorides are probably intermediates in the electrochemical synthesis of new N,N′-bis(trifuoromethyl) perfluoroalkanesulfonamides [10], and probably in similar electrochemical fluorinations using nickel anodes.

The reaction of NiO with pyridine/HF/H_2O at 150°C yielded $Ni_3F_6(py)_{12}.7H_2O$, the structure of which consisted of discrete *trans*-$[NiF_2(py)_4]$ units linked by water molecules hydrogen bonded to the fluoride ligands [11]. The electron deformation density map for K_2NiF_4, determined from an accurate X-Ray structural determination, has been discussed [12]. The crystal structure of $NaNiZr_2F_{11}$ has been reported; the Ni(II) ion is in a slightly compressed octahedral environment (Ni–F 1.989(2), 2.026(1) Å) [13]. Turning to chloro-complexes, the density and electrical conductivity of $NiCl_2$ and its solution in molten NaCl have been determined [14]. Crystals of (3-chloroanilinium)$_8NiCl_{10}$ have been studied using X-ray diffraction; the Cu(II) analogue was previously suggested to be a rare example of Jahn–Teller axial compression in a d^9 ion. However, the Ni environment is also a compressed octahedron (Ni–Cl 2.383(2), 2.492(2) and 2.487(2) Å) [15].

3.2. Pseudohalide ligands

The complexation behaviour of Ni(II) in dimethylacetamide with thiocyanate ions has been investigated. In contrast to the very similar donor solvent dmf, in which six-coordinate $[Ni(NCS)_n(dmf)_{6-n}]^{(2-n)+}$ (n=1–4) sequentially form on addition of NCS^-, in dma there is some evidence for the formation of five-coordinate species $[Ni(NCS)_n(dma)_{5-n}]^{(2-n)+}$ (n=1–3) and tetrahedral $[Ni(NCS)_4]^{2-}$ [16]. The triflate ($CF_3SO_3^-$) anion is normally thought of as very poorly coordinating, but the crystal structure of $[Ni(bpy)_2(CF_3SO_3)_2]$ has been reported this year [17].

The molecular conductor $(DIETS)_4Ni(CN)_4$ (DIETS=(3)) has been synthesised by galvanostatic oxidation; it is a metal above 100 K and the crystal structure of the Pd(II) analogue (which is isostructural) shows a highly reticulated structure which seems to be determined by strong intermolecular CN…I contacts [18].



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The X-ray crystal structures of the complexes $[Cd(en)_3][Ni(CN)_4]$ and a series of $[Cd(H_2N(CH_2)_nNH_2)_2][Ni(CN)_4].xH_2O$ (n = 2–7 and 9; x = 0–2) have been determined [19]. This type of complex forms clathrate structures with aromatic guests, but on recrystallisation from water, guest-free complexes were obtained. Depending upon n, a variety of multidimensional infinite coordination structures with different topologies are found, ranging from one-dimensional chains to three-dimensional networks, with the diamine ligands and $[Ni(CN)_4]^{2-}$ ions bridging octahedral Cd(II) (except for $[Cd(en)_3][Ni(CN)_4]$). On attempting to produce a clathrate complex in this system using the ligand 1,4-diazabicyclo[2.2.2]octane (L), an unusual compound with the formula $[Cd(LH^+)_2\{Ni(CN)_4\}_2].4C_6H_5NH_3$ crystallised, the first 2:1 Ni:Cd complex of this kind [20]. The $[Ni(CN)_4]^{2-}$ units bridge *cis* positions at octahedral Cd(II) ions using two *trans* CN^- ligands, and the Cd(II) ions are coordinated by two *trans* monodentate LH^+ (the other nitrogen being protonated) and four nitrogens from $[Ni(CN)_4]^{2-}$ units. In the Prussian Blue analogue $Ni[Fe(CN)_6]$ the Ni(II) ions are coordinated by bridging cyanide nitrogens, and possibly by water. The progress of film growth, and ion fluxes on potential cycling, for films of $Ni[Fe(CN)_6]$ on gold electrodes in various electrolytes, have been studied using the electrochemical quartz crystal microbalance [21]. By using a 3,3′-thiodipropionic acid monolayer on gold, and adsorbing a monolayer of Ni(II) ions at the pendant carboxylate groups, it has been claimed that a monolayer of $Ni[Fe(CN)_6]$ could be deposited by redox cycling this electrode in aqueous $[Fe(CN)_6]^{3-}$ [22]. By irradiating electrodes modified with $\{\text{-}[(CN)_5Fe^{II}CNPt^{IV}(NH_3)_4NC]\text{-}\}_n$ in the intervalence charge transfer region, a two-electron transfer occurs and the Pt^{IV} is reduced to Pt^{II}, with cleavage of the Pt–NC bonds. When this process was carried out in the presence of Ni(II) ions, $Ni[Fe(CN)_6]$ could be formed within the film [23].

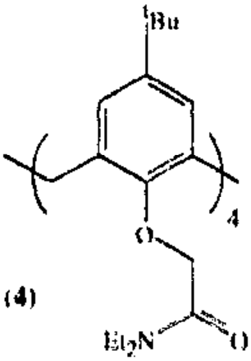
Tricyanomethanide complex of Ni(II) of formula $[Ni\{C(CN)_3\}_2L_2]$ (L = benzimidazole, 2-methylbenzimidazole) have been prepared [24]. The temperature dependence of the magnetic moment suggests that both antiferromagnetic and ferromagnetic coupling exist in these polymeric, six-coordinate complexes.

4. Complexes with oxygen donor ligands

4.1. Neutral ligands

The crystal structures of $[Ni(H_2O)_6][SnF_3]_2$ [25], $[Ni(H_2O)_6][MF_6]$ (M = Ti, Zr, Hf; prepared from equimolar amounts of the respective oxides in aqueous HF) [11], $[Ni(H_2O)_6]$(D-Camphor-10-sulfonate)$_2$ [26] and $[Ni(H_2O)_6]$(2,6-dichlorobenzoate)$_2$ [27] have been determined; the latter has an interesting structure in which layers of cations and anions, with hydrophilic and hydrophobic character respectively, alternate. Concerted tunnelling, induced by 'hole-burning' irradiation of the N–D modes, has been studied for a series of partially-deuterated Tutton salts $(NH_4)_2[Co_xNi_{1-x}(H_2O)_6](SO_4)_2$ (x = 0, 0.25, 0.5, 0.75, 1) [28]. The 'layered hydrogenselenite' $[Cu(HSeO_3)_2NiCl_2(H_2O)_4]$ has been described, which by analogy with its Mn(II) analogue is thought to have *trans*-octahedral [NiCl$_2$(H$_2$O)$_4$] units forming ···Cu···Cl–Ni–Cl···Cu bridges with the copper hydrogenselenite layers [29].

Turning to complexes of amides acting as O-donors, the calixarene (4) (L) reacts with [Ni(H$_2$O)$_6$](ClO$_4$)$_2$ in CH$_3$CN to afford [Ni(L)](ClO$_4$)$_2$, the X-ray crystal structure of which reveals distorted octahedral coordination of three of the four carbonyl oxygens (Ni–O 1.992(7), 2.003(8), 1.997(8) Å) and three ether oxygens (2.250(6), 2.315(6), 2.139(6) Å), with the fourth ether oxygen significantly further away (2.771(8) Å) [30]. An acetonitrile molecule is present as a guest species in the calixerene 'bowl'. Complexes [Ni(DA)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$·2DA, [Ni(DA)$_3$](ClO$_4$)$_2$ and [Ni(DA)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$ (DA = diacetamide) have been prepared, and the ESR spectra of Mn^{2+} ions 'doped' into the complexes have been studied [31]. The latter are consistent with NiO$_6^{2+}$ chromophores in all cases. A complex analysing as Ni(NO$_3$)$_2$(L)·H$_2$O (L = (5)) has been described; its electronic spectrum was consistent with 6-coordination, but crystals could not be obtained [32].



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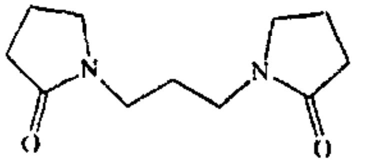

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4.2. Anionic ligands

4.2.1. Oxides and related systems

Nickel oxides are used as battery materials and as the anode material in tungsten oxide-based 'smart' windows. This stimulates efforts at their synthesis and characterisation; a further stimulus is the synthesis of Ni analogues of cuprate superconductors. Beginning with materials containing Ni(III), an EXAFS study of LiNiO$_2$ revealed two different bond lengths; Ni–O bonds of 1.91 Å (4) and 2.09 Å (2) were resolved, a consequence of the Jahn–Teller effect for this low-spin d^7 environment [33]. The thermal stability of the perovskite nickelates MNiO$_3$ (M = La, Pr, Nd, Sm, Eu) has been investigated; these decompose to M$_2$NiO$_4$ (M = La, Pr, Nd) or M$_2$O$_3$ and NiO (M = Sm, Eu) [34,35]. Thermal stability in air decreases with decreasing radius of M^{3+}. Nickel K-edge XANES data obtained for LaNiO$_3$, NdNiO$_3$, Nd$_{1-x}$La$_x$NiO$_3$ and NdNi$_{1-x}$Fe$_x$O$_3$ have been interpreted in terms of a large mixing of 3d^7 and 3d^8 configurations in the ground state [36]. Reduction of LaNiO$_3$ with aluminium gave LaNiO$_{2.6}$ as a single-phase, semiconductive and ferromagnetic material, with octahedrally-coordinated Ni(III) and square planar Ni(II) environments deduced from magnetic measurements [37]. Tetragonal K$_2$NiF$_4$-type phases LnSr$_5$Ni$_3$O$_{11}$, isostructural with the previously reported YSr$_5$Ni$_3$O$_{11}$, have been prepared for

Ln = Dy, Ho, Er and Tm [38]. These are stoichiometric Ni(III) oxides, and show Curie–Weiss behaviour from 6 to 300 K. Phases $(A,A')_2M_{0.5}Ni_{0.5}O_4$ (A,A′ = alkali, alkaline earth metal respectively; M = Mg, Zn, Ti, Al, Ga), prepared under high oxygen pressure, have been characterised using XRD, ESR and IR spectroscopies; the Ni(III) site is six-coordinate and Jahn–Teller distorted [39]. A quaternary cerium strontium nickel oxide, $CeSr_7Ni_4O_{15}$ has been prepared; this has K_2NiF_4-type structure with Ce^{4+} and Sr^{2+} disordered over the K sites, and is a metallic conductor [40]. The solid solution series $NdSr_{(1-x)}M_xNiO_4$ (M = Ca; $0.0 \leq x \leq 1.0$; M = Ba: $0 \leq x \leq 0.6$) crystallise in tetragonal space groups (except $NdCaNiO_4$; orthorhombic), and contain low spin Ni(III) [41]. When $x \geq 0.4$, the materials were semiconductors, but were metallic when $x \leq 0.4$. Several studies detailing the behaviour of sputter-deposited NiO films on indium-doped tin oxide electrodes have appeared this year; these materials are oxidised to ill-defined phases containing Ni(III) on electro-oxidation, and recently even Ni(IV) has been suggested as being involved [42,43].

The ferrimagnetic Ni(II) mixed oxide $Sr_3Sb_2NiO_9$ has been reported; this contains high-spin Ni(II) [44]. Large single crystals of the oxygen-rich phase $La_2NiO_{4+\delta}$ ($\delta = 0.12$–0.19) have been prepared. Variations of the unit cell with δ have been interpreted in terms of the formation of peroxide ions in the lattice.

An unusual number of papers this year describe Ni(I) coordinated to oxide ligands in various environments. Heating the mixed oxide $K_2Na_4CdO_4$ in a nickel container at 520°C for 47 days gave crystalline $KNa_2[NiO_2]$. X-Ray crystal structure determination and infrared spectroscopic evidence show that the $[NiO_2]^{3-}$ ion is significantly distorted from centrosymmetric, and the ESR spectra suggest a $^2E_g(d_{z^2})$ symmetry [45]. Nickel(I) ions in various glasses have been studied by ESR spectroscopy [46]. Nickel(I) can also be generated in nickel-exchanged silicoaluminophosphates Type 5 (SAPO-5) [47,48] and Type 11 (SAPO-11) [48,49] by gamma-irradiation, hydrogen reduction or heating. In the case of SAPO-5, Ni(I) in both extraframework or framework positions can be made. Treatment with ammonia or ethylene gave distinct Ni(I) complexes which could be characterised by ESR spectroscopy. It is also possible to perform this chemistry with MCM-41-type molecular sieves [50].

4.2.2. Complexes of oxyanion ligands

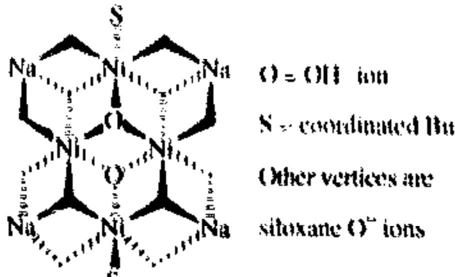
The synthesis of a nickel(II) orthoperiodate, $NiH_3IO_6 \cdot 6H_2O$, has been described [51]. The crystal structure of *trans*-$Rb_2[Ni(CO_3)_2(H_2O)_4]$ has been reported [52]. The pillaring, by metavanadate ions, of the nickel–aluminium double hydroxide layer compound $[Ni_{1-x}Al_x(OH)_2](CO_3)_{x/2}$ has been studied [53].

Neutron powder diffraction has been used to determine the crystal structure of the canted antiferromagnet $ND_4NiPO_4 \cdot D_2O$. The NiO_6 coordination sphere is severely distorted, having point symmetry C_{2v} [54]. The crystal structure of calcium nickel orthophosphate, $Ca_{8.5}Ni_{9.5}(PO_4)_{12}$ [55] and of new diphosphates $K_2NiP_2O_7$ and $K_6Sr_2Ni_5(P_2O_7)_5$ [56], have been determined The structure of nickel ultraphosphate, NiP_4O_{11}, has also been solved [57]; this contains rings of six and fourteen PO_4 units sharing corners, and the nickel is octahedrally coordinated. The coordination environment in nickel(II)—containing pyrophosphate glasses has been studied by X-ray and neutron diffraction and electronic spectroscopy; distorted octahedral coordination was found [58]. Replacement of the two symmetrically unrelated Ti^{4+} ions by a Ni^{2+} and a W^{6+} in the non-linear optical crystal $KTiOPO_4$ leads to the new compound $K_2NiWO_2(PO_4)_2$, which has helical chains of NiO_6 and WO_6 octahedra connected by phosphate groups [59].

The structure of $NiV_2O_6 \cdot H_2O$ shows dimeric moieties $[Ni_2O_8(H_2O)_2]$, each dimer being surrounded by four different metavanadate chains [60]. The magnetic properties of $Ni_4Nb_2O_9$ have been studied as a function of temperature [61], and the layered, network compound $Ni(ReO_4)_2$ has been shown to have a 3D-ferromagnetic ground state [62].

4.2.3. *Complexes of RO^- and related ligands*

Beginning with siloxanolate and antimony alkoxide ligands, an interesting paper reports the crystal structures and magnetic properties of two Ni(II)–siloxanolate sandwich complexes. In $Na_2[(PhSiO_2)_6Na_4Ni_4(OH)_2(O_2SiPh)_6] \cdot 4BuOH$, the geometry is as shown in (**6**). In $Na[(PhSiO_2)_6Ni_6(O_2SiPh)_6Cl] \cdot 12MeOH \cdot H_2O$, the Ni(II) ions are located at the vertices of an almost regular hexagon in tetragonally distorted octahedral environments [63]. The Ni(II) ions in the first complex are weakly coupled ferromagnetically, but in the second complex the chloride ion, which occupies a site inside the Ni_6 core, apparently mediates an antiferromagnetic interaction. The crystal structure of the nickel antimony alkoxide, $Ni_2Sb_4(OEt)_{16}$, revealed the coordination geometry outlined in (**7**) (bridging ethoxy groups abbreviated 'O'; average Ni–O 2.08(4) Å) [64].



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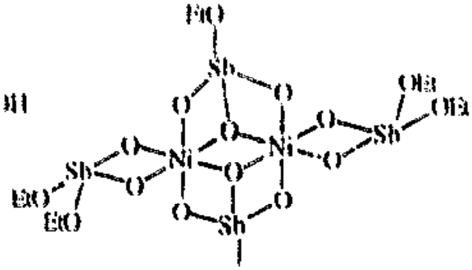


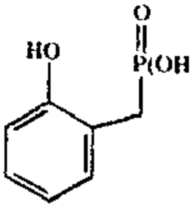
(**7**)

Whereas ligand (**8**) does not complex with Ni(II) in aqueous solution, the doubly-deprotonated form of (**9**) does do so, at pH > 6 [65]. Treatment of the catecholate ligand (**10**) (H_4L) with nickel(II) nitrate in the presence of CsOH gave an air-sensitive, square planar Ni(II)-catecholate $Cs_2[Ni(L)]$, the first such complex to be characterised crystallographically (Ni–O 1.87(1) Å) [66].

The crystal structure of all-*trans*-$[Ni(L)_2(MeOH)_2]$ (HL = *N*-nitroso-*N*-phenylhydroxylamine) has been reported [67].

4.2.4. *Carboxylic acid, amide and related ligands*

The complex $[Ni(HL)_2(H_2O)_2]$ ($H_2L = H_2NC(O)CH_2COOH$) has been prepared; its X-ray powder pattern shows it to be isostructural with the *trans*-$[Zn(HL)_2(H_2O)_2]$ characterised crystallographically, the ligands chelating



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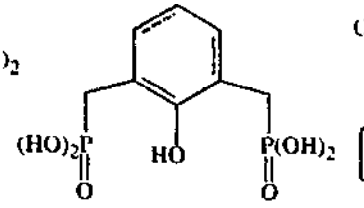

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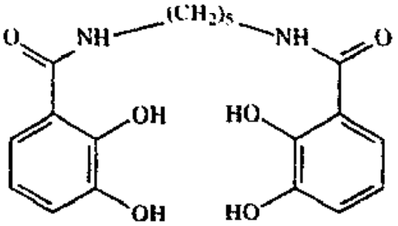

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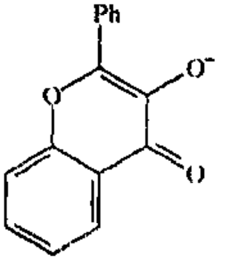
through the deprotonated carboxylate oxygen and the amide oxygen [68]. Reaction of $NiCl_2.6H_2O$ with the triethylammonium salt of (**11**) (L^-) gave *trans*-$[Ni(L)_2(H_2O)_2]$, which on reflux in pyridine gave *trans*-$[Ni(L)_2(py)_2]$, characterised crystallographically (Ni–O^- 2.023(2) Å, Ni–O(carbonyl) 2.067(2) Å) [69]. Oxamic acid ($H_2NCOCOOH$) reacts with $NiCl_2$ to form a complex $[Ni(L)_2(H_2O)_2]$; spectroscopic data were interpreted in terms of an all-*trans* structure with the oxamate chelating through the deprotonated carboxylate and the amide carbonyl [70]. Reaction of oxamide ($H_2NC(O)C(O)NH_2$) with $Cu(NO_3)_2$ in basic dmso solution, followed by addition of $Ni(ClO_4)_2.6H_2O$ gave a dimetallic, ferrimagnetic complex [71].

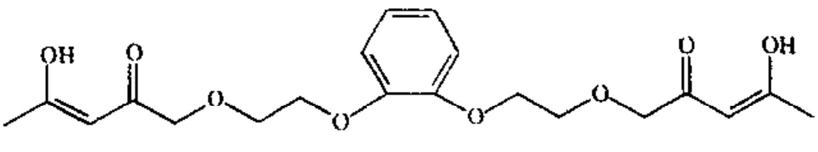


(**11**)

The coordination chemistry of nickel(II) carboxylates with 2-chloropyridone (Hchp) and 2-methylpyridone (Hmhp) ligands involves the formation of polynuclear complexes. Thus, $[Ni(OAc)_2(H_2O)_4]$ with Hchp in MeOH gives the linear centrosymmetric trimer $[Ni_3(chp)_4(OAc)_2(MeOH)_6]$, with the central Ni(II) bridged to the external Ni(II) ions by pairs of pyridonate oxygens and a 1,3-acetate ion; the coordination spheres of the external Ni(II) ions are completed by MeOH molecules [72]. Using nickel(II) trichloroacetate results in a complex $[Ni_4(\mu_3\text{-}OMe)_4(\eta\text{-}chp)(chp)_3(MeOH)_7]$ which has a Ni_4O_4 cube at its core. With Hmhp and $[Ni(OAc)_2(H_2O)_4]$, the cluster $[Ni_{11}(\mu_3\text{-}OH)_6(\mu\text{-}O_2CMe)_6(mhp)_9(Hmhp)_2\text{-}(O_2CMe)]$ was isolated; whereas Hchp only binds *via* oxygen, the Hmhp ligand in the cluster binds through both N and O.

4.2.5. *β-Diketonato and related ligands*

When the ligand (**12**) (H_2L) was treated with Ni(II) salts under high dilution conditions, intramolecular coordination of the two β-diketonate groups to Ni(II) occurred; the corresponding Cu(II) complex behaved, in alkali metal picrate extraction experiments, as a pseudo-crown ether [73]. The complex [Ni(L)] (H_2L=(**13**)), whose electronic spectrum is consistent with square planar geometry, is also assigned a mononuclear structure as it shows a molecular ion in FAB-MS studies [74].



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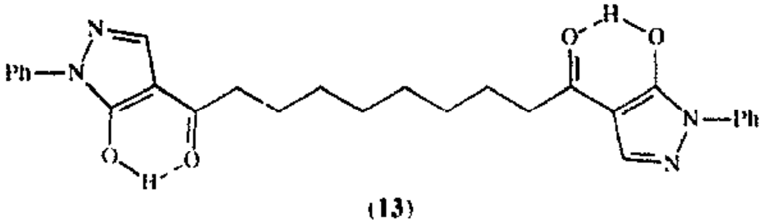

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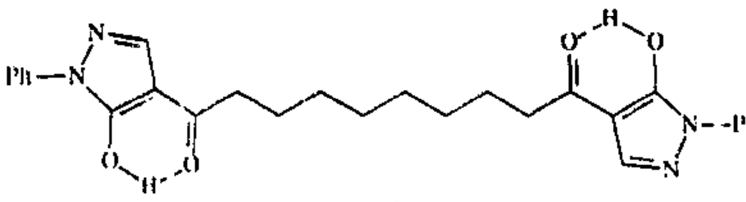
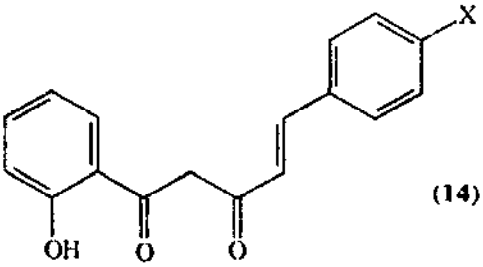


(13)

The crystal structure of bis(3-methylpyridine)bis(4,4,4-trifluoro-1-{2-thienyl}-1,3-butanedionato)nickel(II) has been determined: equivalent oxygen donors are mutually *cis* in this pseudo-octahedral complex, with *trans* pyridines [75]. In contrast, the pyridine donors are mutually *cis* in bis(4-methylpyridine)bis(4,4,4-trifluoro-1-{2-thienyl}-1,3-butanedionato)-nickel(II) [76]. Reaction of $[Ni(OAc)_2(H_2O)_4]$ with Na(dbm) (Hdbm = dibenzoyl-methane) affords green $[Ni_4(OMe)_4(dbm)_4(MeOH)_4]$, which has a $Ni_4(OMe)_4$ cubane structure with each Ni(II) coordinated to three bridging MeO^- ions, a chelating dbm anion and one terminal MeOH [77]. In the presence of NaN_3 in EtOH a similar reaction yields $[Ni_4(N_3)_4(dbm)_4(EtOH)_4]$, the first example of a paramagnetic molecule with triply end-on bridging azide ions [78]. The magnetic behaviour of the first complex is described well by a two-*J* model ($J_1 = -3.4\ cm^{-1}$, $J_2 = 12.2\ cm^{-1}$) but the second complex can be modelled with one *J* value, $+11.9\ cm^{-1}$, in spite of the distortion to D_{2d} symmetry observed. The complex $[Ni_5(OH)(L)_5(acac)_4(H_2O)_4]$ was isolated in low yield from a reaction between $[Ni(acac)_2(H_2O)_2]$ and benzotriazole (L) [79]. This consists of four six-coordinate Ni(II) ions in a distorted tetrahedron around a fifth Ni(II). Each of the five μ_3-benzotriazole ligands spans an edge of the Ni_4 tetrahedron and coordinates to the fifth Ni(II) through the central nitrogen.

Nickel(II) complexes, $[NiL_2]$ (HL = (14); X = H, Cl, Me, MeO) have been described; these have pseudo-octahedral polymeric structures [80]. Monomeric adducts with water and pyridine were also isolated. The crystal structures of [Ni(hfacac)$_2$(PhHNCH$_2$CH$_2$NHPh)] [81] and [Ni(hfacac)(NO$_3$)(PhHNCH$_2$CH$_2$NHPh)] [82] have been determined.



(14)

5. Complexes of sulfur, selenium and tellurium donor ligands

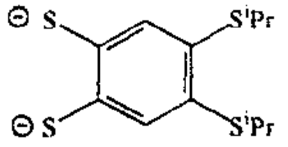
5.1. Complexes of xanthate, dithiocarbamate and related ligands

Crystal structure determinations have been reported for the complexes Ni(*O,O'*-di-R-dithiophosphate)$_2$(L)$_2$] (R = Et, L = isoquinoline [83]; R = Bu, L = 4-methylpyridine [84]). The latter are both *trans* isomers. A redetermination of the crystal structure of [Ni(Et$_2$NCS$_2$)$_2$] has also been reported [85]. Mixed ligand complexes [Ni(i-prxa)$_2$(L-L)] and [Ni(i-prxa)$_2$(L)$_2$] (i-prxa = isopropylxanthato anion; L-L = en, bpy, phen, 5-nitro-1,10-phenanthroline; L = 3-methylpyridine, benzothiazole) have been described, and the crystal structures of [Ni(i-prxa)$_2$(phen)], [Ni(i-prxa)$_2$(bpy)] and [Ni(i-prxa)$_2$(benzothiazole)$_2$] have been determined [86–88]. The monodentate amine adducts are *trans* octahedral and the diimine adducts are *cis* octahedral. Complexes [M^{II}(L-L)$_3$][Ni(1,1-dicarboethoxy-2,2-ethylenedithiolate)$_2$] (M = Zn, Ni, Co, Cd, Fe; L-L = en, bpy, phen) have been synthesised, and characterised spectroscopically [89]. These are semiconductors with conductivities 10^{-6} to $10^{-5}\,\Omega^{-1}\,\mathrm{cm}^{-1}$. The enthalpy of formation of [Ni(S$_2$CNMe$_2$)$_2$] (-146.1 ± 10.9 kJ mol^{-1}) has been measured [90]. Complexes [Ni(S$_2$CNHR)$_2$] (R = CH(CH$_2$Ph)CO$_2$H, CH(Ph)CO$_2$H) have been synthesised; these are square planar, apparently with NiS$_4$ donor sets [91]. Similar complexes have been made using tetrahydroquinoline dithiocarbamate and tetrahydroisoquinoline dithiocarbamate [92].

Mixed ligand complexes [NiX(S$_2$COR)(PPh$_3$)] (X = Cl, Br, I, NCS; R = Et, ^{i}Pr) have been synthesised [93]. These are square planar, as exemplified by the crystal structure of [NiCl(S$_2$CO^{i}Pr)(PPh$_3$)], and infrared evidence suggests that the NCS$^-$ is N-bonded.

5.2. Complexes of dithiolenes and related ligands

The resonance Raman spectra of salts containing the anion [Ni(S$_2$C=C{CN}$_2$)$_2$]$^{2-}$ suggest that there is less delocalisation than for the isomeric [Ni(mnt)$_2$]$^{2-}$ [94]. Complexes [Bu$_4$N][Ni(L)$_2$] (L = (**15**), (**16**)) have been synthesised by I_2 oxidation of the corresponding dianionic complexes; they have low conductivities and ESR spectra typical of complexes of this type [95]. A partially-oxidised derivative $[Bu_4N]_{0.29}[Ni(L)_2]$ (L = (**16**)) has also been made [96].



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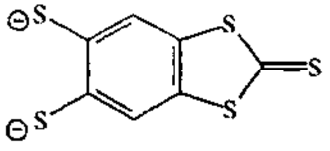
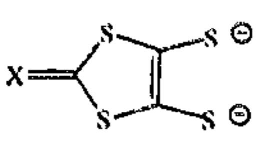
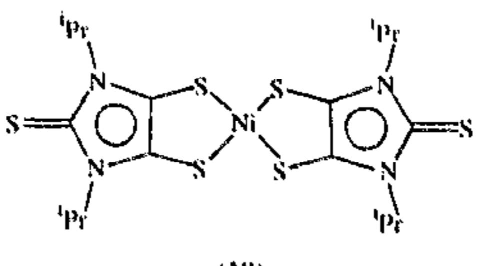


(**16**)

The complex $Ph_4P\{[Ni(dmit)_2]_3$ (dmit = (**17**); X = S) prepared by electrocrystallisation, has been described [97]. It has an unusual crystal structure, with two of the three anions forming columns and the remaining anion filling the spaces between the columns. The conductivity along the *b* axis is $10\,\Omega^{-1}\,cm^{-1}$ at room temperature, and is highly one-dimensional. The structures of $[guanidinium][Ni(dmit)_2]_2$ and $[1,1\text{-dimethylguanidinium}][Ni(dmit)_2]_2$, prepared by electro-oxidation of $[Bu_4N][Ni(dmit)_2]$ in presence of a large excess of the appropriate guanidinium tetrafluoroborate, have been published [98]. In the first compound, two independent anions lie in a head-to-tail orientation, forming two different sheets of units in the *ab* plane. In the second compound, two crystallographically independent anions lie in a face-to-face orientation, thereby forming one anionic sheet in the *ab* plane. Both behave as semiconductors from 100–300 K, with E_a 0.12 and 0.13 eV, respectively. The complexes $[Me_3NH][Ni(dmise)_2]_2$ (dmise = (**17**); X = Se) and $[EDT\text{-}TTF][Ni(dmise)_2]$ (EDT-TTF = ethylenedithiotetrathiafulvalene) have been electrosynthesised using $[Bu_4N][Ni(dmise)_2]$, and their electrical behaviour assessed: replacement of S by Se in the dmise ligand compared with dmit promotes significantly stronger intermolecular interactions in the former complex [99].



X = S: dmit
(**17**)
X = Se; dmise

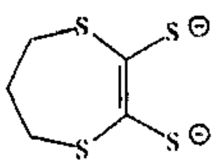


(**18**)

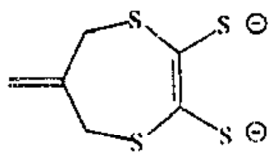
The crystal structure of $[Fe(Cp^*)_2][Ni(L)_2]\cdot CH_3CN$ (L = (**17**); X = O) has been reported [100]; its magnetic behaviour is dominated by ferromagnetic interactions. The ligand 2-dicyanomethylene-1,3-dithiole-4,5-dithiolate ((**17**); C=X replaced by $C(CN)_2$)) has been prepared, together with $[Bu_4N]_x[Ni(L)_2]$ (x = 1,2) and $[[Fe(Cp^*)_2][Ni(L)_2]$ [101]. The crystal structure of the complex (x = 1) shows it to be almost planar; face-to-face stacking of the anions with alternating Ni–Ni distances results in a columnar structure of dimeric anions, with antiferromagnetic coupling within the dimers. Complexes of ligands of type (**17**) with C=X replaced by dicyanomethylene, [1,2,5]thiadiazolo[3,4*b*]pyrazine and 2-(2-propylidene) moieties have been reported [102]. The complex $[Bu_4N][Ni(L)_2]$ (L = 2H-1,3-dithiole-4,5-dithiol) has been prepared from $[Bu_4N]_2[Zn(dmit)_2]$, and its crystal structure determined [103]. The $[Ni(L)_2]^-$ unit is significantly distorted from planarity. Treatment of 1,3-diisopropylimidazolidine-thione-4,5-dione with Lawesson's reagent in the presence of $NiCl_2$ in refluxing toluene afforded the neutral complex (**18**), which has a surprisingly strong ($\epsilon = 80\,000\ \mathrm{l\ mol^{-1}\ cm^{-1}}$) near-IR absorption band [104].

Turning now to maleonitriledithiolate (mnt) and related ligands, the electronic absorption and resonance Raman spectra of [Ni(mnt)(baba)] (baba = bisacetylbisaniline) have been studied [105], and the lowest energy excited state assigned as a ligand to ligand electron transfer from the mnt to the baba moiety. The crystal structure of the salt [6,7,8,9-tetrahydrodipyrido[1,2*a*-2,1-*c*]-[1,4]-diazocinium]$[Ni(mnt)_2]$ has been published [106]. The dimetallic complex $[Ni(mnt)_2\{Ag(PBu_3)_2\}_2]$ has been prepared; this does not appreciably dissociate in solution [107]. Comparable Pd(II) and Pt(II) complexes have structures in which each square planar dianion has two silvers, chelated by the sulfur donors of each ligand, one above and the other below the square plane. Coordination of Ag(I) raises the oxidation potential of the dianion.

The salt [2-(*p*-dimethylaminostyryl)pyridylmethyl]$[Ni(L)_2]$ (L = (**19**)) has been prepared and characterised; intermolecular contacts are rather large, consistent with the semiconducting behaviour ($1.3 \times 10^{-9}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature) [108]. Complexes $[Bu_4N]_x[Ni(L_2)]$ (x = 1 [109], 0 [110]; L = (**20**)) have been described. In the monoanion structure there are two crystallographically distinct anions and no significantly short intermolecular contacts. Cyclic voltammetry shows that there is a large difference between the two redox waves (dianion↔monoanion↔neutral) for this ligand. These facts suggest less charge delocalisation than in comparable ligands (e.g. dmit), making it unsuitable for promoting high electrical conductivity in partially-oxidised materials. Complexes $[Bu_4N][Ni(L_2)]$ (L = (**21**)) have been described; these are similar to the complexes of (**19**) and (**20**) in exhibiting long intermolecular distances and semiconducting ($10^{-8}\ \Omega^{-1}\ \mathrm{cm}^{-1}$ at room temperature) behaviour [111].



(**19**)



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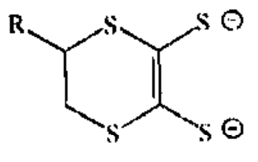


(R = Me, Ph)

(**21**)

Two papers describe dithiooxalato (dto) complexes this year. The synthesis, characterisation and thermal decomposition of $(Ph_4P)_2[Ni(dto)_2]$ [112] and of [2-aminopyridinium]$[Ni(dto)_2]$ [113] have been described.

5.3. *Complexes of pentane-2,4-dithionate and related ligands*

An electrochemical study of $[Ni(sacsac)_2]$ revealed a one-electron quasi-reversible reduction at −1.09 V and an irreversible four-electron oxidation at +1.09 V (acetone, 0.1 M Bu_4NBF_4) [114]. The product of the reduction reacts with H_2O, CO, CO_2, CH_3I and $C_{12}H_{25}SH$. The ligand $NH(SPPh_2)_2$ reacts with nickel carbonate to give $[Ni(N\{SPPh_2\}_2)_2]$ [115], but no complex could be isolated for the analogous $NH(SePPh_2)_2$. The crystal structure of $[Ni(N\{SPPh_2\}_2)_2]$ shows a distorted tetrahedral arrangement, and the complex is deep green in solution.

5.4. *Chalcogenide cluster and related complexes*

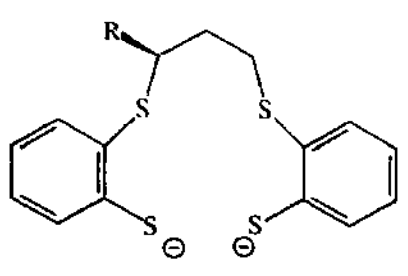
Reaction of $NiCl_2$ with NaSMe in the presence of Me_4NCl gives $[Ni_3(\mu_3\text{-}S)(\mu_2\text{-}SMe)_3]$, but when $[NiCl_2(PPh_3)_2]$ is reacted with NaSeMe, the cluster $[Na_2(P\{O\}Ph_3)_6][Ni_{20}Se_{12}(SeMe)_{10}]$ forms in 10% yield [116]. The anion consists of a pentagonal antiprism of Ni atoms at the core, with a Ni_2 unit located over each triangular face of the antiprism. Two Se atoms are μ_5 and cap the top and bottom faces of the antiprism. Remaining Se atoms are μ_4, and the $MeSe^-$ ligands bridge the Ni atoms of the external Ni_2 units. The novel iron cluster $[Fe_6(CO)_{12}S_6]^{2-}$ can react as a $[Fe_2(CO)_6S]^{2-}$ transfer unit, reacting with NiL_4 (L = CO, PPh_3) to give $[NiFe_4(CO)_{12}S_4]^{2-}$ [117] in an oxidative addition-type reaction. Each Ni(II) is coordinated to four sulfurs in a planar arrangement, each of which also bridges two $Fe(CO)_3$ moieties. In a manner reminiscent of 1,2-dithiolene complexes, this cluster undergoes a quasi-reversible one-electron reduction at −0.02 V.

The 'incomplete cubane' $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with metal powders, including nickel to give $[NiMo_3S_4(H_2O)_{10}]^{4+}$ [118]. In this cluster, the nickel appears best described as Ni(II), and is coordinated by three μ_3 S^{2-} ions and a water molecule in a tetrahedral arrangement. It reacts with L (L = CO, C_2H_4, C_2H_2) to give $[Ni(L)Mo_3S_4(H_2O)_9]^{4+}$. Complexes $[Ni(en)_3][MoS_4]$, $[Ni(dien)_2][MoS_4]$ and $[Ni(phen)_2(MoS_4)]\cdot 2H_2O$ have been described [119]. Chemical oxidation of $[Ni(en)_3][MoS_4]$ affords $[Ni(en)(MoS_4)]_2SO_4$. Finally, the compound $KNiPS_4$ has been described, and its infrared and Raman spectra interpreted [120].

5.5. *Complexes with thioether and thioether–thiolate ligands*

The chiral dithioether–dithiol ligands (**22**) (R = Me, $HO(CH_2)_6$, $PhCH_2$) were formed on reaction of $Na_2[Ni(1,2\text{-}S_2C_6H_4)_2]$ with the appropriate dibromides [121]; the ligands could be displaced for complexation to other metals upon treatment with aqueous HCl. Upon treatment of $Na_2[Ni(1,2\text{-}S_2C_6H_4)_2]$ with 2,3-dibromo-1-propanol, however, rearrangement of the carbon skeleton of the ligand occurred and the complex [Ni(L)] (L = (**23**)) formed instead [122].

Complexes $[Ni(L)](ClO_4)_2$ of the ligands (**24**) and the *S,O*-mixed donor (**25**), together with $[Ni(L)_2](ClO_4)_2$ (L = (**26**)), have been synthesised, and in the case of complexes of (**24**) and (**26**), characterised crystallographically [123]. The complex $[Ni(\mathbf{24})](ClO_4)_2$ is optically active as the two six-membered chelate rings are *gauche*



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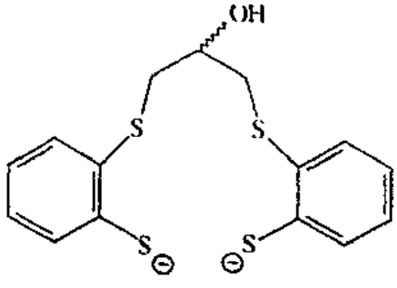
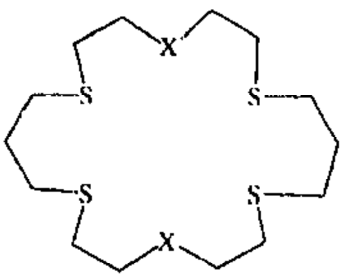


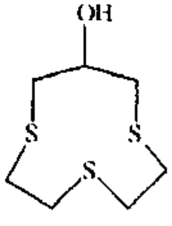
(23)

with respect to each other. There are four molecules (two *d* and two *l*) per unit cell. In $[Ni(\mathbf{26})_2](ClO_4)_2$ the two six-membered rings are *anti* with respect to each other. All three complexes have six-coordination, and replacement of S by O donors considerably weakens the ligand field.



X = S (**24**)

X = O (**25**)



(**26**)

6. Complexes of ligands with mixed N,S-donor sets

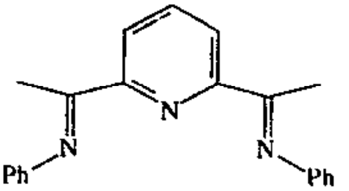
6.1. Metalloenzymes and related systems

The nickel-containing carbon monoxide dehydrogenases (CODH), thought to have sulfur or sulfur–nitrogen coordination environments, continue to attract attention. The enzyme from *Clostridium thermoaceticum* has been investigated using resonance Raman spectroscopy with assignment aided with ^{54}Fe and ^{64}Ni enrichment [124]. Evidence was obtained that there are Ni atoms at both the A centre (where the synthesis of acetylCoA from CO takes place) and the C centre (where the transformation of CO to CO_2 occurs). On the basis of changes in far-infra red bands on exposure of the enzyme to CO as a function of time, it appears that a Ni–Me complex is an intermediate at the A site, together with an Fe–CO complex [125]. Work by the same group has established that azide ion binds to the C site, probably to the metal centre that undergoes reduction in the catalytic cycle [126]. Butyl isocyanide binds to site A 105 times as slowly as CO and also inhibits CO oxidation at site C (with methylviologen as oxidant) [127]. The enzyme from *Clostridium* *thermoaceticum* has an '$\alpha_3\beta_3$' structure, and the 'α' subunit has been successfully isolated without apparent loss of activity [128]. It contains one Ni and approximately 4 Fe atoms. The Ni centre is ESR-silent and is therefore Ni(II). EXAFS measurements are consistent with an S_2N_2 donor set (Ni–S 2.19 Å, Ni–N 1.89 Å), with approximate D_{2d} symmetry. The Ni is evidently not part of a cubane-type cluster, and it was not possible to discern whether it was bridged to such a unit. In related studies, the breakdown of the enzyme by sodium dodecylsulfonate, and subsequent electrophoresis of the fragments, was examined [129]. The CODH from the thermophilic organism *Pyrococcus furiosus*, which is optimally active at 100°C, has been studied using XAS ($L_{2,3}$-edge) [130]. At 20°C, the Ni site is apparently not redox-active since the reduced and thionine-treated (oxidised) forms have essentially the same spectrum. In the reduced form at 80°C the spectrum is consistent with 5- or 6-coordinate high-spin Ni(II), while the spectrum of the oxidised form at this temperature is said to be consistent with a charge distribution of two holes on Ni and an additional hole significantly delocalised onto the ligand framework, which would imply high-spin Ni(III), something not previously suggested.

The first crystal structure of a hydrogenase enzyme, from *D. gigas* in the Ni–A state, has been published [131]. It appears that the Ni is in a dinuclear metal site, ligated by four cysteinyl sulfurs in a highly distorted geometry roughly approximating a square pyramid lacking a basal ligand. Two of the sulfurs bridge to the second metal ion, most probably iron, which is additionally coordinated to three non-protein ligands, modelled as waters. This work has been highlighted in reviews [132–135]. Two of these [132,135] suggest that the results of the crystal structure, taken together with biophysical studies, provide no evidence for redox or coordination chemistry at the nickel site playing a role in the catalytic cycle. Stoichiometric redox titrations of *D. gigas* hydrogenase have been performed by adding aliquots of H_2-saturated water to thionine-oxidised samples while monitoring the ESR spectrum, and electronic absorption at 410 nm [136]. The results were described by a model in which a 2-electron change occurs on reduction from the resting state (Ni(III)) to the active Ni–C form. An argument was advanced that this could be a Ni(I)-dithiol complex.

While dealing with nickel-containing hydrogenases, it is worth discussing work with the complex $[Ni(Me)_2(bpy)]$, which reacts with arenethiols to afford $[Ni(SR)(Me)(bpy)]$ [137]. These readily undergo thiolate ligand exchange. Reaction of one example with CO yielded $[Ni(COCH_3)(2,6\text{-}C_6H_3Cl_2S)(bpy)]$. With excess CO, thioesters RSCOR' and the complex $[Ni(bpy)(CO)_2]$ are formed. That this is intramolecular was shown by the reaction of $[Ni(SCH_2CH_2)(bpy)]$, which afforded γ-thiobutyrolactone quantitatively. In another attempt to model [NiFe] and [NiFeSe] hydrogenases, the reaction of $[Ni(terpy)Cl_2]$ with $2,4,6\text{-}(Me)_3C_6H_2Se^-$ (L^-) in acetonitrile ethanol afforded $[Ni(terpy)(L)_2]$, while $[Ni(DAPA)Cl_2]$ (DAPA = (**27**)) with PhS^- or $PhSe^-$ in ethanol or acetonitrile afforded $[Ni(DAPA)(EPh)_2]$ (E = S, Se) [138]. All three complexes have distorted trigonal bipyramidal NiN_3E_2 donor sets, characterised crystallographically. The $[Ni(terpy)(L)_2]$ is reduced by aqueous dithionate to a Ni(I) complex, which displays reversible CO binding, and also reacts with H^-; oxidation to Ni(III) gives low yields of an unstable species. Stable $(d_z^2)^1$

Ni(III) species are produced by ferricyanide oxidation of the DAPA complexes, in contrast; these do not bind CO or react with H^-. Remarkably, the DAPA complexes both react with BH_4^- to give hydride adducts, and react with H_2 in the presence of base to give the same hydride adducts, mimicking the activation of H_2 by hydrogenases.



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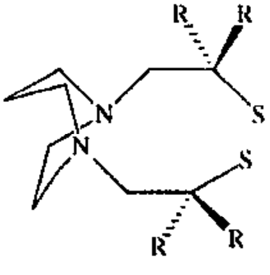
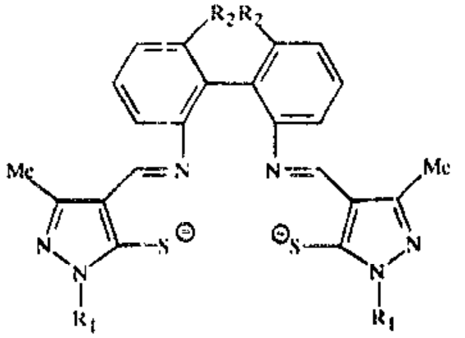
6.2. *Nitrogen–thiolate and related donor sets*

Further studies have been reported of the oxygenation of the thiolate–amine complex [Ni(L)] (L^{2-} = (**28**), (**29**)) [139–141]. This undergoes consecutive reactions with dioxygen in solution to form monosulfinatethiolate (sulfinate = $RS(O)_2^-$), then disulfinate complexes; the nickel(II) remains coordinated to sulfur. However, with hydrogen peroxide, the ligand undergoes oxidation affording coordinated monosulfenatethiolate (sulfenate = $RS(O)^-$), disulfenate then sulfinatesulfenate ligands; all complexes were characterised crystallographically, and the data show that the bond distances are in the order Ni–S(O)R (2.167(5) Å) > Ni–SR (2.159(3) Å) > Ni–$S(O)_2R$ (2.127(3) Å). Interestingly, electrochemical data reveal that oxygenation of the ligand makes the Ni(I)/Ni(II) couple less cathodic. Complexes [Ni(L)] (L = (**28**), (**29**)) also react with SO_2 to give stable adducts with the SO_2 bound to the thiolate via the sulfur, and react with SO_2/O_2 mixtures to afford SO_4^{2-} in a reaction which can be made catalytic by the addition of a sacrificial electron donor such as PhSH; in the latter case, simple salts like $NiCl_2$ and $NiSO_4$ are more effective catalysts [142].



R = –CH_3 (**28**)
R = –H (**29**)

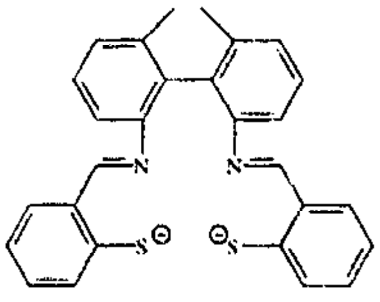
The complex [$Ni(aet)_2$] (aet = 2-aminoethanethiolate) reacts with labile metal centres to afford thiolate-bridged dimetallic complexes, normally retaining its square planar geometry. However, with [$PtCl_2$(bpy)] it reacts to give [$(H_2O)_2Ni(aet)_2Pt(bpy)$], which is pseudo-octahedral at Ni(II) with the amine ligands mutually *trans* and the thiolate sulfurs bridging to Pt(II) [143]. Reaction with bpy gives [(bpy)$Ni(aet)_2$Pt(bpy)]. With [$CoCl_2(en)_2$]$^+$ in water, [$Ni(aet)_2$] reacts to give an S-bridged complex $[Ni\{Co(aet)_2(en)\}_2]^{4+}$, indicating that aet$^-$ has transferred from Ni(II) to Co(III) [144]. Treatment of this with H_2O_2 resulted in cleavage of the Ni–S bonds and formation of a Co(III)-sulfinato complex. Transfer of aet$^-$ also occurs on treatment with $[CoCl(NH_3)_5]^{2+}$, but in this case only Co(III)-aet complexes were isolated [145]. Nickel(II) complexes of the dianion of bis(2-mercaptophenyl)methylamine have been described [146]. With $[Ni(acac)_2]$, the free ligand (H_2L) reacts to give polymeric $[Ni(L)]_n$. With 4-tertiarybutylpyridine (bupy), the latter reacts to give a soluble, stable five-coordinate complex $[Ni(L)(bupy)_2]$, characterised crystallographically. It is trigonal bipyramidal, with one pyridyl ligand *trans* to the nitrogen donor of L^{2-} (Ni–N(pyridyl) 2.018(5), 2.104(5) Å; Ni–N(amine) 2.221(5) Å; Ni–S 2.272(2), 2.320(3) Å).



A: R_1 = Ph; R_2 = H   C: R_1 = Me, R_2 = H

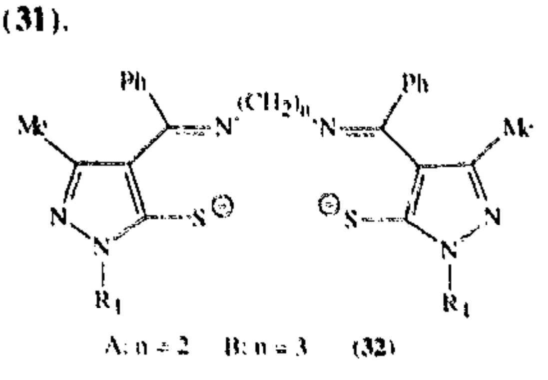
B: R_1, R_2 = Me   D: R_1 = Ph, R_2 = Me

(30)

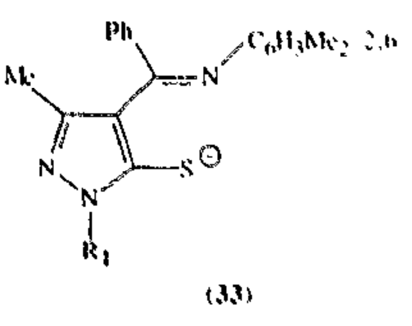


(31)

The complexes [Ni(L)] (H_2L = (30), (31)) have been prepared from H_2L and nickel acetate [147]. X-Ray crystallography reveals that when H_2L = (30)(B) the geometry is best described as distorted tetrahedral, while when H_2L = (30)(A) or (31) it is close to square planar. The magnetic susceptibilities when H_2L = (30)(B), (30)(C) could be fitted by a simple axial spin Hamiltonian ($S = 1$; $D = 34$, 53 cm^{-1}, respectively). The other complexes were diamagnetic with small temperature-independent paramagnetic susceptibilities as solids, but in solution all complexes showed planar-tetrahedral equilibria ($K_{eq} = 0.456$–0.088) except where H_2L = (31).



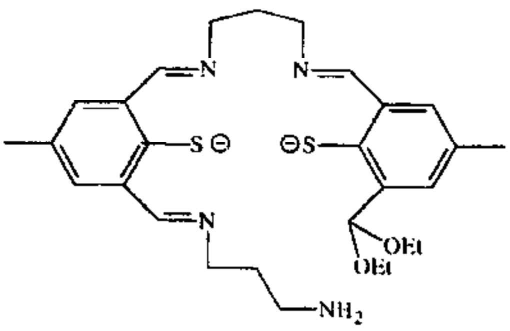
A: n = 2   B: n = 3   (32)



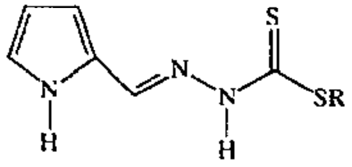
(33)

Similar complexes have been studied where H_2L = (32) [148]; these also exhibit spin equilibria in solution. With the didentate analogues (33) (HL), complexes

$[Ni(L)_2]$ have been isolated [149]. When R = Ph, the complex is tetrahedral in solution; it has a temperature-independent magnetic moment of 2.75 B.M. When R = Me, the complex exhibits square planar-tetrahedral equilibrium in solution. Both are, however, diamagnetic in the solid state.



(34)



(35)

R = Me or $PhCH_2$

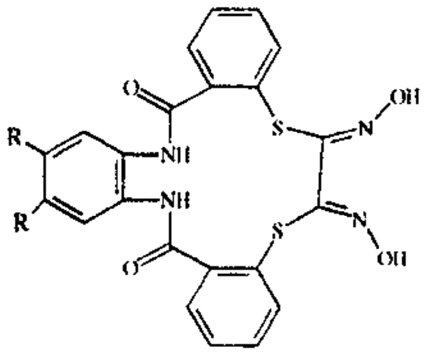
Treatment of nickel(II) perchlorate with deprotonated 2-sulfanyl-5-methylisophthaldehyde and 1,3-diaminopropane in ethanol gave the complex $[Ni_2L_2Ni](ClO_4)_2 \cdot H_2O$ (H_2L = (34)) in low yield [150]. Crystallography revealed that two of the nickel ions are in planar environments, coordinated to two diimine bridge nitrogens and two thiolate sulfurs. The central nickel ion is pseudo-octahedral, and coordinated to four nitrogens from the amine–imine pendant groups, and two bridging thiolate sulfurs, one of which is shared with each of the other nickel sites in a *cis* arrangement. The complexes $[Ni(H_2L)Cl_2]$ and $[Ni(L)]$ (H_2L = cyclohexane-1,2-dionebis(thiosemicarbazone)) have been briefly described [151]. The ligands (35) (H_2L) coordinate to Ni(II) as NS didentates in square planar $[Ni(HL)_2]$, made by treating nickel(II) chloride with the ligand in hot ethanol, and as tridentate NNS chelates in the complex formulated $\{[Ni(L)]\}_2$, made from nickel(II) nitrate and the ligand in the presence of base [152]. The syntheses of dark green, diamagnetic complexes [Ni(L)]X (L = monoanion of pentane-2,4-dionebis(thiosemicarbazone); X = NCS, NO_3) have been described, and the crystal structure of the thiocyanate salt (Ni–N = 1.863(4), 1.856(4) Å; Ni–S 2.153(2), 2.163(1) Å) determined [153].

Finally, some complexes with sulfur-containing amino acids and peptides have been described. Stability constants for ternary complexes $[NiABH_2]$, [NiABH] and [NiAB] with L-cysteine and L-cysteic acid (A), and DL-2,3-diaminopropionic acid, DL-2,4-diaminobutyric acid or DL-ornithine (B) have been determined by titration methods [154]. A study of the interaction of Ni(II) with histones, of interest in research into possible modes of nickel carcinogenesis, has been reported [155]. The peptide CH_3CO-cys-ala-isoleucine-his-NH_2 (L) with Ni(II) yielded unusual macrochelate complexes of stoichiometry NiL and NiL_2 in which the metal was bound to cys and his side chains in a square planar arrangement.

6.3. *Complexes of neutral nitrogen–sulfur ligands*

The complexes $[NiL_3]X_2 \cdot 2H_2O$ ($X = ClO_4^-$, BF_4^-), $[NiX_2L_2] \cdot EtOAc$ ($X = Br^-$, I^-), $[NiX_2L_2] \cdot H_2O \cdot EtOH$ ($X = I^-$, NO_3^-) and $NiCl_2L \cdot 3H_2O$ (L =

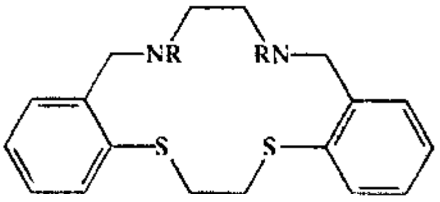
1-phenyl-4,6-dimethylpyrimidine-2-thione) have been described [156]. Coordination, as deduced from infrared spectral data, is through the unsubstituted heterocyclic nitrogen and the thione sulfur. The complexes are solvolysed completely by donor solvents like dmf.



R = H or

$-OCH_2CH_2(OCH_2CH_2)_2OCH_2CH_2O-$

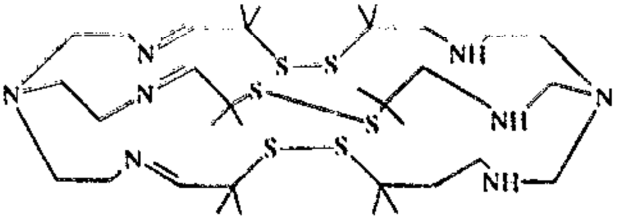
(36)



R = –2-pyridylmethyl

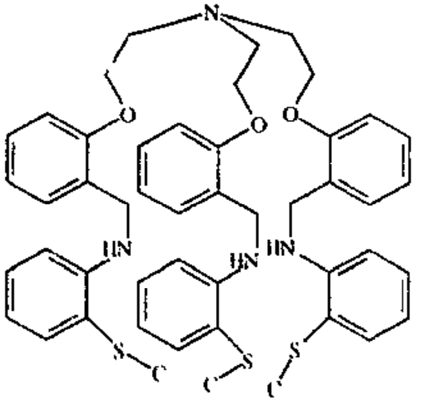
(37)

New heteroditopic macrocycles (**36**) (H_2L) have been synthesised, but attempts to coordinate Ni(II) ions to both the dioxime and the N_2S_2 macrocycle cavity failed; only the complex $[Ni(HL)_2]$, with Ni(II) coordinated to two monodeprotonated dioxime units, could be obtained [157]. The crystal structure of the complex $[Ni(L)](ClO_4)_2 \cdot H_2O$ (L = (**37**)) shows a distorted octahedral geometry with chemically identical donors mutually *cis*. The Ni–S bonds (2.513(3), 2.400(3) Å) are long, probably as a result of strain in the ligand.



(38)

The ligand tris[2-(2-aminoethyl)thio]ethane (L) has been prepared, and the complex $[Ni(L)](ClO_4)_2$ characterised crystallographically [158]. The structure consists of two independent cations, which are both disordered; the sulfur donor atoms occupy one of two sets of sites, one of which results in a net distorted trigonal prismatic geometry, the other in distorted trigonal antiprismatic geometry. The analogue tris[2-(2-aminophenyl)thio]ethane gives a similar complex, which electronic spectral data suggest is nearer trigonal antiprismatic geometry. In related work, the imine–amine cryptand (**38**), made by BH_4^- reduction of the corresponding hexaimine and characterised by ^1H NMR spectroscopy and mass spectrometry, has been synthesised [159]. The dinickel(II) complex $[Ni_2(L)](ClO_4)_4$ has been characterised; the S–S bonds are not cleaved on complex formation. The latter contains six-coordinate Ni(II), and again, the unusually large extinction coefficients of the visible absorption bands suggest trigonal prismatic distortion. The syntheses of cryptands (**39**) (L) has been described: these form distorted octahedral complexes $[Ni(L)](ClO_4)_2$, with the Ni(II) coordinated by three sulfur and three nitrogen donors only [160].

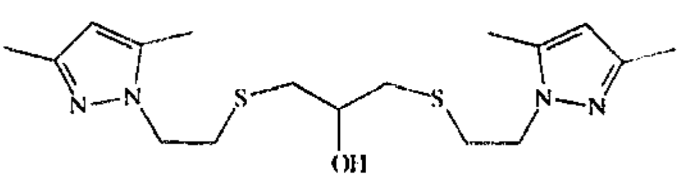


Capping group, C, =
$1,3,5\text{-}(CH_2CH_2)_3C_6H_3$,
$CH_3C(CH_2\text{-})_3$
$N(CH_2CH_2\text{-})_3$

(**39**)

7. Complexes with O,S- and N,O,S-donor ligands

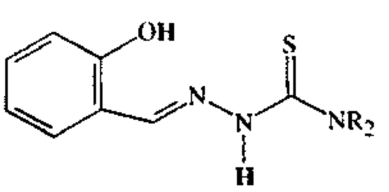
Complexes $[Ni(bpy)(dta)(H_2O)_2]\cdot H_2O$, $[Ni(phen)(atf)_2]\cdot 5H_2O$ and [Ni(phen)-$(dtc)_2]$ (dta = dithiooxamide dianion; dtc = diethyldithiocarbamate; atf = 2-aminothiophenolate) have been reported [161]. Attempts to model the active sites of various Ni-containing enzymes have stimulated interest in mixed donor ligands of these types in recent years. A full paper describing nickel(II) complexes of (**40**) (HL) has appeared; $[Ni(H_2O)_6]Cl_2$ in $EtOH/(EtO)_3CH$ gave $[Ni_3(L)Cl_5(EtOH)]\cdot 3EtOH$, and in acetonitrile $[Ni_2(L)X_3]\cdot xCH_3CN$ (X = Cl, x = 1; X = Br, x = 1.5; X = NO_3, x = 2) were formed [162]. Crystal structures of the di- and trinuclear chlorides were described in the 1993 review; the ligand bridges two (or three) metal ions and the hydroxyl group is deprotonated. When 1-(2-ı ethylsulfanyl)-2-naphthol (HL) is treated with $Ni(OAc)_2$, six-coordinate paramagnetic $[Ni(L)_2]$ [163], with deprotonated hydroxyl, thioether and aza coordination, is the product. Compared with the analogous complex with 1-(2-pyridylazo)-2-naphthol, the thioether donor stabilises the trivalent state better than the 2-pyridyl donor, as assessed by cyclic voltammetry of the complexes in dichloromethane. The ESR spectra of the electrogenerated Ni(III) species iare consistent with a metal-centred $(d_z^2)^1$ ground state.



(**40**)

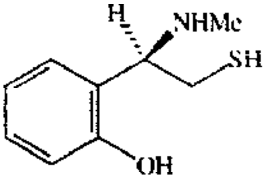
The ligand (**41**) (H_2L: H's in bold lost on complexation) also forms dinuclear complexes when treated with $Ni(OAc)_2$ in EtOH, but these are square planar

$[Ni_2(L)_2]$ with two bridging phenoxy oxygens; the complex (R = Me) was characterised crystallographically [164].



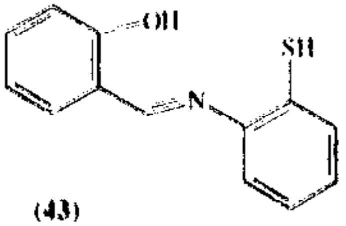
R_2 = HMe, HEt, H^nPr, Me_2, Et_2,

$(CH_2)_5$, $(CH_2)_6$ **(41)**

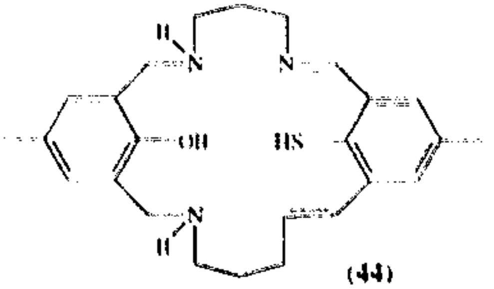


(42)

Treatment of the ligand **(42)** (HL) with nickel(II) acetate gives an unusual cluster, *rac*-$[Ni_3(\mu^3-S)(\mu^2\text{-}L)_3]OAc$, which is triangular, with each Ni(II) chelated by one L^- via deprotonated thiol and secondary amine, and the thiols additionally bridging to the neighbouring Ni(II) [165]. The Ni(II) ions and RS^- donors lie in a plane, the secondary amine donors are below the plane and the triangle of Ni(II) ions is capped by the S^{2-} ion, giving net square planar coordination at Ni(II); the complex is diamagnetic. Treatment of $[Ni(acac)_2]$ with the ligand **(43)** (H_2L), followed by 4-Bu^t-pyridine (L′) gave square planar [Ni(L)(L′)], characterised crystallographically (Ni–O 1.852(2) Å, Ni–N (L) 1.883(2) Å, Ni–S 2.1457(7) Å) [166]. There is evidence for dimerisation in solution, possible with loss of the pyridine ligands; the strongest peak in a CI MS experiment corresponded to $[Ni_2(L)_2]$.



(43)



(44)

Reaction of the appropriate two-arm diamine–phenol precursor with $[Ni(H_2O)_6](ClO_4)_2$ and 2-sulfanyl-5-methyl-isophthaldehyde in acetonitrile gave, as expected, a dinickel(II) complex of the symmetrical dinucleating macrocycle **(44)** (H_3L) [167]. However, although the two donor sites are identical, the complex, $[Ni_2(L)(CH_3CN)_2](ClO_4)_2$, crystallised from acetonitrile with one nickel ion in a square planar environment and the other octahedral, the coordination sphere being completed by acetonitrile donors.

8. Complexes with non-macrocyclic nitrogen donor ligands

8.1. Complexes of mono- and didentate amine and related ligands

The specific heat of $[Ni(NH_3)_6](NO_3)_2$ and the perdeutero analogue has been studied; the specific heat change on deuteration compared with the shift in frequency of the NH/ND bands fits the Debye–Einstein model [168]. The Hofmann clathrates $[Ni(NH_3)_2Ni(CN)_4]\cdot 2G$ and $[Ni(en)Ni(CN)_4]\cdot 2G$ (G = pyrrole, aniline) have been the subject of an extended Hückel tight binding band structure modelling study [169]. The main interactions between host and guest appear to be electron density donation from the guest π system to the host σ* N–H and from the π(C–N) orbitals of the host to the guest σ*(C–H), with no participation by metal-based orbitals. Polymeric $[\{NH_3)_4Ni\}\{(NC)_2C{=}CS_2\}Ni\{S_2C{=}C(CN)_2\}]$ has been characterised by X-ray crystallography [170]. The structure consists of zig-zag chains of alternating *trans*-$[Ni(NH_3)_4(NCR)_2]$ units and square planar $[Ni\{(NC)_2C{=}CS_2\}_2]$ units. Reaction of $TiCl_4$ with lysine in EtOH gave a complex analysing as $[(H_2N(CH_2)_4CH(NH_2)COO)Ti(OEt)_3]$, which by comparison with the glycine analogue, for which a crystal structure was determined, is probably dimeric with two bridging OEt groups [171]. The 'dangling' amine can be coordinated to $Ni(OAc)_2$ in EtOH to give $\{Ni[NH_2R]_4\}^{2+}$ (where R represents the Ti(IV) centre).

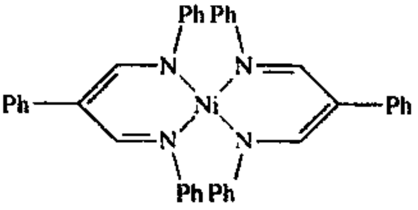
The association between acrylonitrile and Ni(II) in water has been studied by Raman spectroscopy [172]. A new and unusual complex, $[Ni_6(NC\mathit{C}HCH_2CH_2\mathit{C}HCN)_6]$, was the product when $[Ni(COD)_2]$, 2,2′-dipyridylamine and acrylonitrile were mixed in thf at room temperature and left for prolonged times under room light [173]. In the cluster, each square planar Ni(II) is chelated by the two carbon atoms of one ligand (italic in the above formula). Each ligand additionally coordinates two neighbouring Ni(II) centres through the CN nitrogen atoms.

Turning to didentate ligands, a novel halogen-bridged one-dimensional Ni(III) X Ni(III) complex, $\{[Ni(en)_2Cl]Cl_2\}_n$, has been synthesised by anodic electrocrystallisation from a solution of $[Ni_2(\mu\text{-}Cl)_2(en)_4]Cl_2$ (prepared in situ in MeOH, in the presence of excess LiCl) [174]. The complex was characterised by X-ray diffraction. This completes a unique series of isomers with this formula which previously included $\{[Ni^{II}(en)_2][Ni^{IV}Cl_2(en)_2]Cl_4\}_n$ and $[Ni^{III}Cl_2(en)_2]Cl$ [175]; it would be interesting to see if $\{[Ni(en)_2Cl]Cl_2\}_n$ is identical with the latter.

Ethylenediamine as an additive has found application in the preparation of small (*ca.* 20 Å) dispersed Ni particles on silica [176]. Studies continue into thermal isomerism of Ni(II)-didentate amine complexes. With *N*-1-isopropyl-2-methyl-1,2-propanediamine (L), the complexes $[Ni(L)_2X_2]\cdot nH_2O$ ($X = 0.5SO_4^{2-}$, $n = 0$; $X = I^-$, $n = 2$; $X = CF_3CO_2^-$, $n = 0$ or 2; $X = SeO_4^{2-}$, $n = 0$ or 3) have been isolated, and studied thermogravimetrically [177]. The hydrated complexes are yellow in colour and lose water on heating, turning light blue in the process except for the iodide which remains yellow. The yellow complexes are square planar and it is suggested that the blue complexes are five-coordinate. The iodide does undergo an exothermic, irreversible phase transition, but to a darker orange form, and the trifluoroacetate undergoes a reversible change without changing colour; these changes are thought to be due to chelate ring conformational differences. Similarly, complexes $[Ni(L)_2X_2]\cdot nH_2O$ (X = Cl, NCS or Br, n = 0; X = Br, n = 3) have been studied, and the crystal structures of $[Ni(L)_2]Br_2\cdot 3H_2O$, $[Ni(L)_2Br]Br$ and $[Ni(L)_2(NCS)_2]$ determined [178]. The yellow $[Ni(L)_2]Br_2\cdot 3H_2O$ is square planar, whereas dehydrated, green $[Ni(L)_2Br]Br$ has a distorted trigonal bipyramidal geometry; the two primary amine nitrogens and one bromide ion occupy the basal sites and the secondary amines are axial. With 2,2-dimethyl-1,3-propanediamine (L), the complex $[Ni(L)_2(H_2O)_2](NO_3)_2$ has been isolated, and characterised by X-ray crystallography [179]. It has two *trans* water ligands, and the chelate rings are in the *trans* chair–chair conformation. Upon dehydration, dynamic broad-line ^1H NMR spectroscopic results are interpreted in terms of dynamic disorder of the chelate rings at the transition temperature; on loss of water, the *trans* geometry is retained, and the nitrate ions coordinate as monodentates. This ligand has also been employed in the synthesis of an azido-bridged polymeric complex, $[Ni(L)_2(\mu\text{-}N_3)]_n\{ClO_4\}_n$ [180]. The thermochromic complexes $[Ni(Et_2NCH_2CH_2NH_2)_2]X_2$ have been studied using X-ray diffraction ($X=ClO_4^-$), and ^2H NMR spectroscopy as a function of temperature ($X=ClO_4^-$, BF_4^-, I^-) [181]. Below room temperature, an almost rigid structure for the $-ND_2$ group was deduced. For ClO_4^- and BF_4^-, data support the ring-puckering model as an explanation for the thermochromism. However, the iodide, which exhibits no thermochromism, also showed continuous changes in the quadrupole coupling constants and asymmetry parameters as a function of temperature; this was attributed to a whole-complex reorientation. The thermochemical changes of $[Ni(RHNCH_2CH_2NH_2)_2(H_2O)_2]X_2$ (R = Me, Et, ^{i}Pr, Ph; X = Cl, Br) and $[Ni(Bu_2NCH_2CH_2NH_2)_2(H_2O)_2]X_2$ have been investigated by thermogravimetry and electronic spectroscopy [182]. The complexes were all *trans*. The monoalkyl-substituted complexes all underwent deaquation-anation with retention of stereochemistry. Only the dichloride with the dialkyl ligand underwent a change to *cis* geometry on anation.

Creatinine complexes $[Ni(en)(L)_2](BPh_4)_2$, as well as $[Ni(L)_2(H_2O)_4]Cl_2$ (L = creatinine) have been described [183]; different coordination modes of the creatinine ligands are observed depending upon the co-ligands. With en, the creatinines are O-bound, and with water, they are N-bound. The complexes $[Ni(RHNCH_2CH_2NH_2)_2(SO_3Cl)_2]$ (R = H, Me, Et) and $[Ni(Bu_2NCH_2CH_2NH_2)_2(H_2O)_2](SO_3Cl)_2$ (R = Me, Et) have been characterised; evidence for chlorosulfate coordination was obtained from infra red spectroscopy and conductance measurements [184]. A polymeric 2D-network structure is found for the black complex $[Ni(R,S\text{-pn})_2]_2[Fe(CN)_6]ClO_4 \cdot 2H_2O$, the product of combining $K_3[Fe(CN)_6]$ and $[Ni(R,S\text{-pn})_2](ClO_4)_2$ in aqueous solution [185]. Each $[Fe(CN)_6]^{3-}$ ion bridges to four Ni(II) ions through equatorial CN^- ions, and each Ni(II) is coordinated to two *trans* CN^- nitrogens, giving an overall square structure. There is ferromagnetic ordering of $FeNi_2$ units, but at temperatures below 10 K, antiferromagnetic coupling between sheets of squares reduces the magnetic moment. New azido-bridged Ni(II)-diamine complexes continue to attract interest. The crystal structures of $[Ni(L)_2(\mu\text{-}N_3)]_n(X)_n$ (L = pn; $X=ClO_4^-$, PF_6^-) have been described [186]. The structures are similar, with the Ni(II) ions connected by azide ligands occupying *cis* sites, giving a pseudohelical structure. The ClO_4^- salt has more compact chains. The complexes are antiferromagnetically coupled, but the hexafluorophosphate in particular shows only weak coupling ($J = -3.2$ cm^{-1}). Combination of $[Ni(H_2O)_6](ClO_4)_2$ with $Me_2NCH_2CH_2NH_2$ (dmen) or 2-aminoethylpyridine (aep), and NaN_3, afforded $[Ni(dmen)(\mu\text{-}N_3)_2]_n$ and $[Ni(aep)(\mu\text{-}N_3)_2]_n$, which have unusual structures in which each Ni(II) is coordinated to two *cis* end-to-end bridging azide ions, two *cis* bridging end-on azide ions and a chelating diamine [187]. Consistent with this, the temperature dependence of the magnetic moment is consistent with two *J* values, one for the end-to-end magnetic coupling (which is antiferromagnetic) and one for the end-on coupling (ferromagnetic).

Reaction of $[Ni(en)_3](ClO_4)_2$ with LiTCNQ gave $[Ni(en)_3](TCNQ)_2$, but attempts to react the perchlorate with neutral TCNQ gave products due to reaction of the diamine with TCNQ [188]. With tn, the complex $[Ni(tn)_2(TCNQ)_2]$ was obtained, with $TCNQ^{\cdot -}$ coordinated to Ni(II) *via* a –CN nitrogen. With the triamine dien, $[Ni(dien)_2](TCNQ)_2$ and $[Ni(dien)_2](TCNQ)_3$ were formed; the latter is not a Ni(III) complex but contains the trimer $[(TCNQ)_3]^{2-}$.



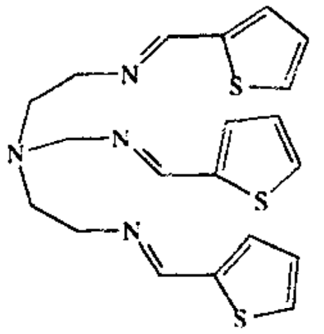
(45)

The redox chemistry of the complex [Ni(1,3,5-triphenylformazanate)$_2$] (**45**) has been investigated [189]. Depending upon conditions, it appears that both ligand-based reduction to the radical anion and metal-based reduction to Ni(I) occur. Remarkably, the ESR spectra change depending upon the alkali metal employed when these metals are used to reduce the complex, and it is suggested that there is interaction between the alkali metal cation and the SOMO of the complex anion. On oxidation, again both ligand- and metal-based oxidations occur.

8.2. *Complexes of multidentate amine and related ligands*

Complexes of the type $[Ni(dpt)_2]X_2$ nH_2O, $Ni(dpt)X_2 \cdot nH_2O$ (dpt = *N*-(3-aminopropyl)-1,3-propanediamine; X = various mono- or dianions), $[Ni(L')_2]I_2$ and $[Ni(L')I_2]$ (L′ = *N*-(2-aminoethyl)-1,3-propanediamine) and $[Ni(dien)_2]I_2$ and $[Ni(dien)I_2]$ have been studied using thermogravimetric techniques [190]. The $[Ni(dpt)_2]X_2$ (X = Br, NO_3) undergo endothermic, reversible phase transitions at around 200°C, and $[Ni(dpt)I_2]$ undergoes an irreversible, exothermic transition at the same temperature. The crystal structure of $[Ni(SO_4)(dpt)(H_2O)_2] \cdot H_2O$ has been reported [191]. The triamine coordinates meridionally. One water completes the equatorial coordination, and the other water and a monodentate sulfate occupy the axial sites. The complex $[Ni(L)](ClO_4)_2$ (L = 5,5-dimethyl-1,4,7,10-tetraazatetradecane) crystallises in yellow and orange forms, and the structures of both have been determined [192]. Both forms are square planar and the structures are identical apart from small differences in packing effects, orientation of the perchlorate anions and hydrogen bonding.

Reaction of $[Ni(H_2O)_6](OAc)_2$ with the ligand (**46**) (L), followed by recrystallisation from $CH_3CN/MeOH$ gave the complex $[Ni(L')(H_2O)(CH_3CN)](ClO_4)_2$ (L′ = (**47**)), the X-ray crystal structure of which showed the acetonitrile to be *trans* to the



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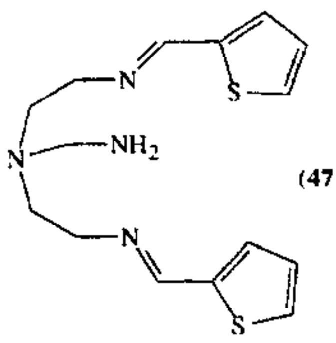


(47)

tertiary amine donor, and the two imino nitrogens to be mutually *trans* [193]. The tripodal ligand tris-(*N*-butylcarbamoylmethyl)aminato(3-) (L^{3-}) is designed to promote trigonal monopyramidal geometry at a metal centre by blocking access to the fifth coordination site. The complex [Et_4N][Ni(L)] has been isolated, and its crystal structure determined [194]. The Ni(II) ion lies 0.14 Å above the trigonal plane of the amidate donors. The mean Ni–N(amidate) bond length is 1.972(5) Å. The complex is orange, high spin (μ_{eff} = 3.49 BM at room temperature), and shows no tendency to coordinate a fifth ligand. It exhibits a quasi-reversible one-electron redox process at +0.56 V. However, the oxidised, violet species is unstable.

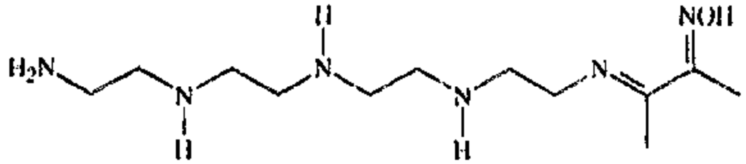
Turning now to studies of magnetic behaviour, the $S=1$ alternating chain [{$Ni_2(dpt)_2(\mu\text{-}N_3)(\mu'\text{-}N_3)_2$}$_n$]$(ClO_4)_n$ has been studied [195]. This has alternating single and double end-to-end bridging azides, and its magnetic behaviour as a function of temperature can be modelled, in an extended Hückel approach, by two different values of J ($-84.6\ cm^{-1}$ through the single azide bridge and $-41.4\ cm^{-1}$ through the double bridge). The complexes [{$Ni_2(Medpt)_2(N_3)_2$}$(\mu\text{-}1,1\text{-}N_3)_2$], [{$Ni_2(dpt)_2(N_3)_2$}$(\mu\text{-}1,1\text{-}N_3)_2$] and [{$Ni_2(Medpt)_2(N_3)_2$}$(\mu\text{-}1,3\text{-}N_3)_2$] (Medpt = *N*,*N*-bis-(3-aminopropyl)methylamine) have been characterised, the first by X-ray crystallography at two temperatures (293 K, and 190.5 K after first cooling to 118 K) because it showed a magnetic transition between 150–120 K [196]. Each Ni(II) ion is coordinated by a meridionally-arranged tridentate amine, a terminal azide ligand and two end-on bridging azide ions. The most significant difference between the structures is in the $Ni_2(\mu\text{-}N_3)_2$ unit, which is more asymmetric at low temperature. The phase transition is assigned as due to a second-order dynamic Jahn–Teller effect. The first two complexes were strongly ferromagnetic and the third one antiferromagnetic. The complexes [$(\mu\text{-ox})${Ni(L)}$_2$]$(ClO_4)_2 \cdot nH_2O$ (L = *N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine, n = 0; L = *N*,*N'*-bis(3-aminopropyl)-1,2-ethanediamine, n = 2; L = *N*,*N'*-bis(3-aminopropyl)-1,3-propanediamine, n = 3) have been prepared [197]. The crystal structure, where L = *N*,*N'*-bis(3-aminopropyl)-1,2-ethanediamine, has been determined; the bridging oxalate anion forms five-membered chelate rings with the two Ni(II) ions and the tetradentate amine is coordinated with the primary amine donors mutually *trans*. All three complexes are antiferromagnetically coupled ($J = -32.1$, -28.9, $-20.6\ cm^{-1}$, respectively).

On leaving a solution containing $K_3[Cr(CN)_6]$ and $[Ni(L)(H_2O)](ClO_4)_2$ (L = 1,4,7,10,13-pentaazatridecane) to evaporate, crystals of the heptanuclear

$[Cr(CN)_6\{Ni(L)\}_6](ClO_4)_9$ were obtained, where the single water ligand on each Ni(II) has been displaced by a bridging cyanide nitrogen [198]. The $\chi_M T$ reaches a maximum value, corresponding to a low-lying $S=\frac{15}{2}$ spin state at 6 K, and there is ferromagnetic interaction between Ni(II) and Cr(III) (fitted to $J=+16.8\ cm^{-1}$).

8.3. *Aliphatic imines, oximes and related ligands*

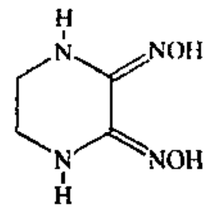
The kinetics of the reduction of $[Ni^{III}(L)]^{2+}$ (HL = (**48**)) by S(IV) and Se(IV) as a function of pH have been examined [199]. The oxidation of $SO_2 \cdot H_2O$ and HSO_3^- are proposed to proceed *via* an H-bonded adduct. Reaction with SO_3^{2-}, on the other hand, seems to be outer-sphere. Oxidation of $HSeO_3^-$ is 10^3 times slower than that of H_2SeO_3, and oxidation of S(IV) is more favourable than that of Se(IV). The reductions of the Ni(IV) complex $[Ni(L)_2]$ (H_2L = 2,6-diacetylpyridine dioxime) by aqueous solutions of Fe(II), Sn(II), I^- and U(IV) proceed cleanly to Ni(II), but are unobservably slow with the two-electron reductants H_3PO_2 and H_3AsO_3 [200]. There is no evidence for the accumulation of significant concentrations of the intermediate Ni(III) state under any conditions. Partial protonation of the oxidant is suggested by the observed dependence on pH. The overall picture suggested is of sequential 1-e^- reductions, even for the (relatively slow) reduction by Sn(II), which is thought to involve a Sn(III) intermediate, significantly stabilised by Cl^- ligation. The oxidation of ascorbic acid by $[Ni^{III}(L_1)]^{2+}$ (HL_1 = 15-amino-3-methyl-4,7,10,13-tetraazapentadec-3-en-2-one oxime) and $[Ni(L_2)_2]^{2+}$ (HL_2 = 6-amino-3-methyl-4-azahex-3-en-2-one oxime) have been investigated [199,201]. In the reduction of the Ni(IV) complex, the data implicate the involvement of a Ni(III) intermediate, and in both cases the mechanism seems to be outer-sphere, with some evidence of association of ascorbic acid or its monoanion in the appropriate pH ranges.



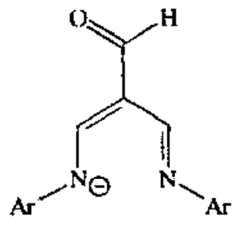
(48)

Halogen (Br_2, Cl_2) doping of $[Ni(Hdmg)_2]$ leads to enhancement of the third-order non-linear optical response [202]; this is related to the electron delocalisation in $[Ni(Hdmg)_2]$ chains. Treatment of $[Ni(Hdmg)_2]$ with BF_3 gave an adduct bis(difluoroborondimethylglyoximato)nickel(II), and doping with iodine gave a polyiodide $[Ni(L)]I_{2.92}$, which was a low-bandgap semiconductor ($1.57 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$ at room temperature; E_a 0.50 eV) [203]. The XeCl laser-induced decomposition of $[Ni(Hdmg)_2]$ thin films has been examined; the product appears to be nickel hydroxide [204].

On treatment of the octahedral complex $[Ni(H_2L)_3]Cl_2$ (H_2L = (**49**)) with LiTCNQ, a square planar complex $[Ni(HL)(H_2L)]^+TCNQ^-$ is obtained, formulated thus by comparison with its Pd analogue, which was studied by X-ray diffraction [205]. The Pd complex exhibits H-bonding between the amino protons of the stacks



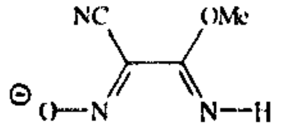
(**49**)



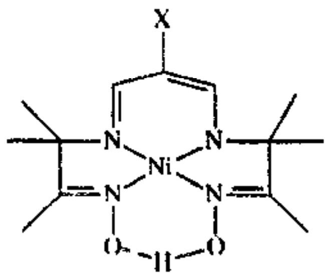
Ar = 3,5-$Me_2C_6H_3$-

(**50**)

of cations and the cyano groups of the stacks of anions. The crystal structure of the complex $[Ni(L)_2]$ (L^- = (**50**)) shows only one element of molecular symmetry, a C_2 axis, since the formyl group is coplanar with the nitrogens [206]. Thus this pseudotetrahedral complex is chiral, but the crystals are centrosymmetric and are composed of both enantiomers.



(**51**)

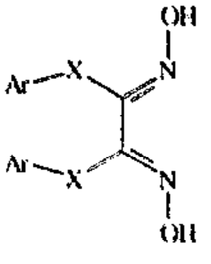


X = NO_2,

NO or NH_3^+

(**52**)

When $Ni(NO_3)_2$, $NaONC(CN)_2$ and pyrazole are combined in $MeOH/H_2O$, a colour change from light yellow green to dark red is seen; the red complex has been isolated and characterised crystallographically [207]. It is $[Ni(pz)_2(L)_2]$ (L^- = (**51**)), in which MeOH has undergone nucleophilic addition to nitrosodicyanomethanide. All equivalent donors are mutually *cis*. A careful study of the reduction of the complex ((**52**); X = $-NO_2$) by Zn/HCl or Pd/H_2 has appeared [208]. Unless carefully-controlled conditions (acid medium; exclusion of O_2) are employed, the product is an intensely purple material characterised as a conjugated dimer with two Ni units multiply bonded to a single (exocyclic) nitrogen at X, but the amine salt ((**52**); X = $-NH_3^+$) can be isolated).



X = -S- or -NH-,

Ar = 2-$(MeO_2C)C_6H_4$

(**53**)

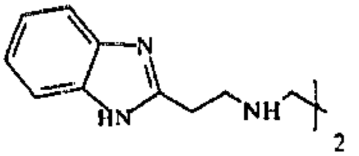
Finally, the square planar complexes $[Ni(HL)_2]$ (H_2L = (**53**)) have been prepared, and treated with BF_3 to give the corresponding complexes of the macrocyclic L^{2-}-BF_2 adducts [209].

8.4. Aromatic imine and related donor ligands

8.4.1. Pyrazoles, imidazoles and related ligands

The interactions of Ni(II) with two dipeptides, glycylhistamine (gly-hist) and sarcosylhistamine (sar-hist) have been studied by pH-metric and ^{1}H NMR spectroscopic techniques [210]. In the pH range 3–9 various complexes NiLH, NiL, $NiLH_{-1}$, $MLH_{-1}(OH)$, ML_2, ML_2H_{-1} were found, depending upon pH and Ni/L ratio. At pH > 9, the interaction between Ni(II) and L was characterised by the formation of polynuclear, imidazole-bridged species $\{Ni(LH_{-2}\}_n$ with square planar NiN_4 coordination. In the case of gly-hist, ^{1}H NMR spectroscopic evidence was found for one predominant species, n = 4, while with sar-hist a series of oligomers was found. A similar study of tetrapeptides containing histidine has shown that the imidazole nitrogen acts as the major nickel(II) binding site [211].

Approaches to the design of molecular magnets based upon metal complexes of 3-imidazoline nitroxides have been discussed, and some aspects of quantum-chemical treatment of exchange interactions considered [212]. Nickel(II) complexes of the tripodal *N,N′,N″*-tris(benzimidazolyl)methane have been synthesised; these were six-coordinate [213]. The ligand *N*-hydroxyethyl-*N,N′,N′*-tris(benzimidazolylmethyl)-ethylenediamine forms complexes of formula $NiCl_2L \cdot 2H_2O$, $Ni(SCN)_2L \cdot H_2O$ and $Ni(ClO_4)_2L$; the thiocyanate was characterised crystallographically [214]. The Ni(II) is coordinated to all three benzimidazolyl groups in a *mer* arrangement, and both amines; the pseudo-octahedral coordination is completed by a nitrogen-bound thiocyanate ion. The ligand exerts a weak field ($\Delta = 10600$–$10900\ cm^{-1}$). A study of the thermodynamics and kinetics of the interaction of 2-(2-aminoethyl)benzimidazole (HL) and Ni(II) has been published [215]. The crystal structure of $[Ni(L)(NO_3)]NO_3$ (L = (**54**)) shows that the ligand donor atoms are coplanar except for one of the benzimidazole units; the coordination is completed by a didentate nitrate ion [216].



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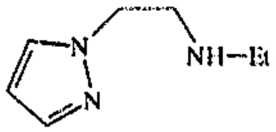
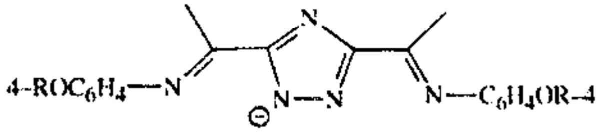


(55)

Turning to pyrazole and related systems, the amine–pyrazole ligand (**55**) (L) reacts with $NiCl_2$ to give red $[(L)ClNi(\mu\text{-}Cl)_2NiCl(L)]$, the X-ray crystal structure of which shows five-coordinate Ni(II) with a geometry intermediate between square-based pyramidal and trigonal bipyramidal [217]. The complex is weakly ferromagnetic. Ligand such as 1,2,4-triazoles frequently bridge metal ions through the two adjacent nitrogen atoms. Ligands 3-methyl-4-ethyl-1,2,4-triazole and 3-methyl-4-phenyl-1,2,4-triazole react with hydrated Ni(II) salts in EtOH to give complexes $[Ni_3(L)_6(H_2O)_6](anion)_6 \cdot xH_2O$. These probably have a linear trinuclear structure where a central Ni(II) is coordinated to six triazole nitrogens, and two groups of three ligands each bridge to the two outer Ni(II) ions, whose coordination shell is completed by three *fac* water ligands [218]. When a mixture of Ni(II) and an excess of Mn(II) salts were used, an analogous heterotrinuclear MnNiMn complex could be obtained. The complexes all show weak antiferromagnetism ($J = -1.88$ to $-4.57\ \text{cm}^{-1}$). A study of unsubstituted 1,2,4-triazole complexes has been reported; this ligand forms polymeric complexes of stoichiometry NiX_2L or NiX_2L_2 (X = Cl, Br) [219]. Electronic spectra suggest that these have halide and triazole bridges, or triazole bridges only, respectively. The NiX_2L complexes are net ferromagnetic. Schiff base-functionalised triazoles (HL) (**56**) have been isolated as their dinuclear Ni(II) complexes $[Ni_2(L)_2X_2]$ in a template reaction between 3,5-diacetyl-1,2,4-triazole and two equivalents of $4\text{-ROC}_6H_4NH_2$ in the presence of NiX_2 [220]. These complexes are of uncertain coordination geometry; they are paramagnetic and antiferromagnetic, with $J = -33\ \text{cm}^{-1}$ (X = Cl), so presumably they are not square planar.



R = Me, Et

(**56**)

The anion dihydrobis(1,2,4-triazolyl)borate (L^-) reacts with $NiCl_2$ in water to give polymeric $\{[Ni(H_2O)_2(\mu\text{-}L)_2]\}_n \cdot xH_2O$, which re-dissolves in aqueous ammonia, presumably as bridges are broken by ammine coordination [221]. However, hydrotris(1,2,4-triazolyl)borate reacts to give $[Ni(L)_2] \cdot 6H_2O$, the crystal structure of which has been determined at two temperatures (293 K, 160 K) to shed light on the arrangement of the water molecules in this layer-type clathrate system. The low temperature structure allowed H-atom positions to be refined.

8.4.2. *Pyridines and related ligands*

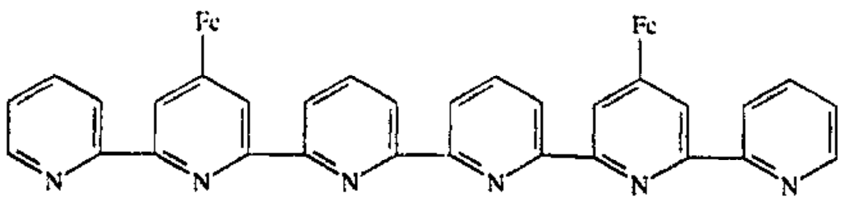
This section commences with work done on cooperative magnetic properties. A comparison of the magnetic properties of the polymeric diazine-bridged complexes $[Ni(L)_2X_2]$ (L = pyrazole; X = Cl, NO_3), $Ni(L)(4\text{-CH}_3C_6H_4SO_3)_2$, $Ni(L')(NO_3)_2$ (L′ = 2-methylpyrazole) and $Ni(L)_3(CH_3SO_3)_2 \cdot CH_3OH$ with the complexes $Ni(py)_4X_2$ (X = Cl, $4\text{-CH}_3C_6H_4SO_3$, CH_3SO_3) provided evidence for weak antiferromagnetic interactions mediated by the diazine bridges in the pyrazole complexes [222]. Both $Ni(L)Cl_2$ and $Ni(py)Cl_2$ show metamagnetic behaviour determined by intrachain ferromagnetic interactions mediated by intrachain chloride bridges, and interchain antiferromagnetism. New nitronyl nitroxide and imino–nitroxide biradical-substituted bpy (5,5′- and 6,6′-isomers), phen, 1,8-naphthyridine and 3,6-di-(2-pyridyl)pyridazine ligands have been synthesised [223]. The 6,6′-substituted bpy, and phen, ligands form mononuclear Ni(II) complexes which display strong antiferromagnetic interactions. The ligands *N,N*′-bis(2-pyridylmethyl)-1,3-propanediamine and *N,N*′-bis(2-pyridylmethyl)-*N,N*′-dimethylethylenediamine have been employed in the construction of oxalato-bridged dimers $[(L)M(\mu\text{-}C_2O_4)M(L)]^{2+}$ (M = Mn, Fe, Co, Ni, Cu, Zn) [224]. All are ferromagnetic, with *J* values that increase from Mn(II) to Ni(II) since the ferromagnetism results from interaction between the $d_{x^2-y^2}$ orbitals. Purple crystals of $[Ni(ox)(bpy)_2] \cdot 4H_2O$ have been obtained; the crystal structure shows that this is mononuclear, with an extensive network of H... O–H and C–H...O hydrogen bonds [225]. Oxamido ligands have been used to construct magnetic arrays. The dinuclear $[Ni(oxae)Ni(phen)_2](ClO_4)_2 \cdot H_2O$ (oxae = *N,N'*-bis(2-aminoethyl)oxamido dianion) has been synthesised from planar monomeric [Ni(oxae)], nickel perchlorate and phen [226]. The crystal structure shows that the Ni(oxae) unit retains its square planar geometry, and coordinates the six-coordinate $Ni(phen)_2$ *via* the carbonyl oxygens. The crystal structure of $[Ni(N_3)(MeO)(MeOH)(L)]$ (L = 2,6-bis(2-benzimidazolyl)pyridine) has been reported; the ligand occupies *mer* positions and the two methanol molecules (one deprotonated) are mutually *trans* [227].

Turning now to studies of simple pyridine-type ligands, complexes of empirical formula $[Ni(L)_2Br_2(H_2O)_2]L_2 \cdot 2H_2O$, $[Ni(L)_2(H_2O)_4]L_2(NO_3)_2$ and $[Ni(L)_2(H_2O)_4]L_2(ClO_4)_2 \cdot 2H_2O$ (L = 2,4'-bipyridine) have been described [228]. Electronic spectral data are adduced to support the octahedral coordination, and the presence of uncoordinated 2,4'-bipyridine. In solution in 4-methylpyridine, EXAFS evidence suggests that Ni(II) is six-coordinate [229]. The structures of two clathrate complexes, *trans*-$[Ni(py)_4(NO_3)_2] \cdot 2py$ and *trans*-$[Ni(py)_4(NCS)_2] \cdot 2py$, have been determined [230,231]. Crystal structures have also been reported of $[Ni(phen)_3](ClO_4)_2 \cdot 0.5H_2O$ [232], of $[Ni(terpy)_2](ClO_4)_2 \cdot H_2O$ [233] and of *cis*-$[Ni(N_3)_2(bpy)_2] \cdot H_2O$; the latter has a dimeric structure composed of two Ni units connected by H-bonding between the azide terminal nitrogens and two water molecules [234]. A Ni(II) complex of the asymmetric tridentate 1,3-bis(pyridin-2-yl)pyrazole has been described briefly [235].

Turning to electrochemical studies, the behaviour of $[Ni(bpy)_3]^{2+}$ adsorbed on silver electrodes has been studied spectroelectrochemically using surface-enhanced Raman spectroscopy [236]. The changes in the ligand modes on the first reduction are consistent with a ligand-based process, as expected. A 4-vinylterpyridine complex of Ni(II), $[Ni(L)_2](PF_6)_2$, can be electropolymerised to give a polymer film on glassy carbon electrodes, by repetitive cyclic voltammetry into the ligand-based reduction region [237]. The films undergo reductions at −1.14 and −1.45 V, and electrocatalyse the reduction of CO_2 to H_2CO commencing at −1.12 V in aqueous media. The complex $[Ni(qtpy)(MeCN)_2](ClO_4)_2$ has a reversible redox couple at −0.79 V, a quasi-reversible process at −1.15 V and another at −1.98 V, all of which are probably ligand-based [238]. The complex is a poor electrocatalyst for the reduction of CO_2 to CO, but interestingly, this reaction commences at −1.7 V, that is, before the onset of the third reduction process. The catalytic efficiency of $[Ni(qtpy)(MeCN)_2](ClO_4)_2$ is much less than that of the complex $[Co(qtpy)(H_2O)_2](ClO_4)_2$. The complex $[Ni(bpy)_3](BF_4)_2$ has been used as catalyst in the electrochemical reductive removal of allyl ether protecting groups from alcohols and phenols [239]. An *in situ* FTIR spectroscopic study of CO_2 electroreduction employing $[Ni(4,4'\text{-}Me_2bpy)_3](ClO_4)_2$ or $[Ni(phen)_3](ClO_4)_2$ as catalyst precursors shows that on reduction under CO_2, $[Ni(L\text{-}L)_2]$ form, which react slowly to give $[Ni(L\text{-}L)(CO)_2]$ [240]. These are further reduced to $[Ni(L\text{-}\dot{L}^{-})(CO)_2]$ at potentials where electrocatalysis commences, inferring that the latter are the catalytic species.

Under the conditions of the experiment, electrogenerated CO then attacks the catalyst giving, ultimately, nickel carbonyl cluster anions.

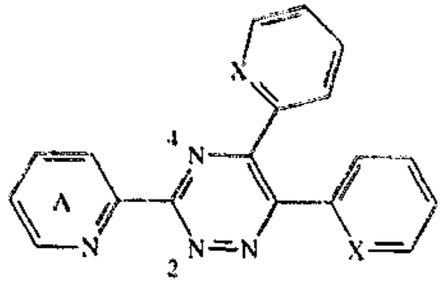
There is much current interest in polypyridines and poly(1,10-phenanthroline)s as conjugated materials and as ligands. Poly(1,10-phenanthroline-3,8-diyl) has been synthesised by dehalogenation polycondensation from the corresponding dibromide, using stoichiometric quantities of a [Ni(cod)$_2$]/bpy mixture, apparently without problems from coordination of the Ni(II) thus formed by the product [241]. Poly(2,5-pyridine) films have been deposited on gold electrodes using a Ni-catalysed cathodic route; in this case, electrochemical quartz crystal microbalance measurements, and the redox chemistry of the films, suggest the presence of nickel coordinated to bpy units [242].



(57)

The coordination chemistry of oligopyridines continues to attract attention. The compound 6-bromo-4′-ferrocenyl-2,2′:6′,2″-terpyridine reacts with nickel acetate to give (after metathesis) [Ni(L)$_2$](PF$_6$)$_2$, which shows a reversible redox process at +0.25 V (*vs* ferrocene/ferrocinium) due to the pendant ferrocenyl groups, but no accessible Ni(II)/Ni(III) process at higher potentials [243]. There is little interaction between the ferrocenyl groups in the complex. Attempts to synthesise (**57**) cleanly by Ni(0)-catalysed reductive coupling failed, but (**57**) was made using classical methods; it reacts with nickel acetate to give (after metathesis) the double helical complex [Ni$_2$(L)$_2$](PF$_6$)$_4$. The potentially dinucleating ligand (**58**) and its analogue (**59**) (L) react with [Mo(CO)$_4$(piperidine)$_2$] to give [Mo(L)(CO)$_4$], the proton NMR spectra of which show that coordination is *via* the pyridyl ring A and N2 or N4 of the triazole [244]. Reaction of [Mo(L)(CO)$_4$] (L=(**58**)) with [Ni(hfacac)$_2$] gave the bridged complex [(OC)$_4$Mo(L)Ni(hfacac)$_2$], which is stable in non-coordinating solvents, but undergoes dissociation in polar solvents. It is proposed that the Ni(II) is coordinated to the two additional pyridyl nitrogens of (**58**); the complex [Mo(L)(CO)$_4$] (L=(**59**)) undergoes no reaction with [Ni(hfacac)$_2$].

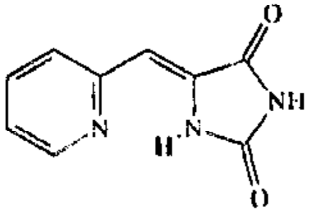
Reaction of pyridine-2-carbonitrile with metal salts, including Ni(II), in MeOH



X = N (58)

X = CH (59)

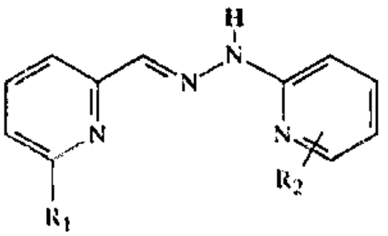
led to the formation of complexes of *O*-methylpyridine-2-carboximidate, including pink $[Ni(L)_3]Br_2$, blue five-coordinate $[Ni(L)_2(OClO_3)]ClO_4$, and $[Ni(L)_3](ClO_4)_2$ [245]. The crystal structure of the bromide salt showed the ligands coordinated *via* pyridine nitrogens and imido nitrogens, with the pyridine groups mutually *fac*. The ligand 6,6′-bis(aminomethyl)-2,2′-bipyridine (L), as its trihydrobromide (LH_3Br_3), reacted with $NiCl_2$ in water to give $[Ni(L)Br(H_2O)]Br$, the crystal structure of which showed the ligand chelating in the equatorial plane, with axial water and Br^- ligands (Ni–Br 2.6748(12) Å, Ni–N(bpy) 2.001(4), 2.008(5) Å, Ni–N(amine) 2.086(5), 2.119(5) Å) [246]. The unusually low stability constants found for complexes of this ligand are rationalised as due to its low basicity and unfavourable spacing of its donor atoms. A new synthesis of 5-(2-pyridylmethylene)-hydantoin (**60**) (Hpyhy) has been reported, along with that of the complex $[Ni(pyhy)(H_2O)_4]ClO_4 \cdot H_2O$ [247]; the latter has intramolecular H-bonding involving the coordinated water and a hydantoin carbonyl oxygen, and intermolecular H-bonds involving the aqua ligands, carbonyl oxygens and NH groups, perchlorate anion and free water molecules. Electroreduction of the ligand (**61**) (HL) in the presence of a sacrificial Ni anode gave the complex $[Ni(L)_2]$ as a red–green dichroic solid [248]. This is paramagnetic and presumably six-coordinate with the ligand coordinated *via* both pyridine nitrogens and the anionic hydrazone.



H in bold lost

on complexation

(**60**)



R_1 = H, Me, salicylidene

R_2 = H, 6′-Me, 6′-Cl, 2′-quinolyl

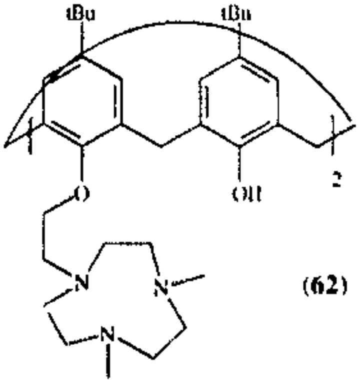
(**61**)

When 2-aminopyridine (L) was treated with nickel(II) sulfate, crystals of $\{[Ni(L)_2(H_2O)_2(\mu\text{-}SO_4)]\}_n \cdot nL$ were obtained [249]. The Ni(II) is coordinated by two pyridine nitrogens (*cis*); the sulfates are *trans* and give a chain structure, and there are uncoordinated L molecules forming columns between the nickel complex chains. On further standing, crystals of a second complex $[Ni(L)(H_2O)_5]SO_4$ were obtained, again with L coordinated through the pyridine ring nitrogen.

9. Complexes with macrocyclic amine donor ligands

9.1. *Complexes with triazamacrocycles*

Molecular mechanics calculations have been performed on complexes $[M(tacn)_2]^{3+/2+}$ redox couples (M = Fe, Ni, Co) to try and resolve the discrepency between experimental inner-shell activation enthalpies, and values predicted using the harmonic oscillator model [250]. It is found that most of the inner-shell barrier derives from M–N bond stretching. The calixarene–macrocycle ligand (**62**) reacts with nickel perchlorate in the presence of sodium azide to give a complex $[Ni_2(\mu\text{-}N_3)_3(H_2L)]ClO_4$, and with nickel acetate in acetonitrile-MeOH to give the solvate $[Ni_2(\mu\text{-}N_3)_3(HL)]\cdot 1.5MeCN\cdot 1.5MeOH\cdot 2H_2O$, in which one of the two phenol groups is deprotonated [251]. The crystal structure of the latter shows two Ni(II) ions octahedrally coordinated by one *fac*-triamine, and sharing three end-on azide bridges, the first time this mode of azide bridging has been encountered. The complex shows ferromagnetic coupling ($J = +17.2\ cm^{-1}$).



(**62**)

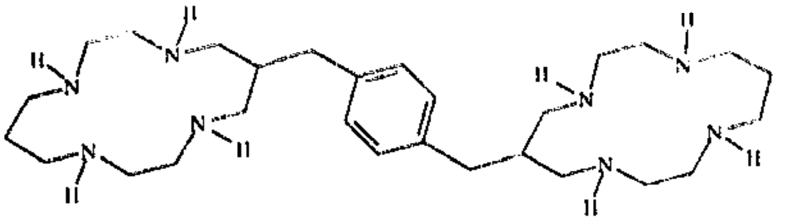
The pendant arm ligands 1-(2-pyridylmethyl)-1,5,9-triazacyclododecane (L_1) and 1-(2-pyridyl-2′-ethyl)-1,5,9-triazacyclododecane (L_2) have been prepared and their coordination behaviour with nickel nitrate investigated [252]. In solution and as solids, the coordination geometry of the complexes was octahedral, and the crystal structure of $[Ni(L_1)(O_2NO)]NO_3$ was determined. The ligand 1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane forms a very inert complex $[Ni(L)(H_2O)]^{2+}$, the aquation of which (60°C, $I = 2.0$ M) in chloride-containing media has been examined [253]. The potentially hexadentate 1,4,7-tris(*o*-aminobenzyl)-1,4,7-triazacyclononane reacts with nickel perchlorate to give $[Ni(L)](ClO_4)_2\cdot H_2O$; the crystal structure of $[Ni(L)](ClO_4)(BPh_4)(C_3H_6O_2)\cdot H_2O$ indeed shows a distorted octahedral structure with C_3 symmetry (mean Ni-tertiary amine 2.116(6) Å; Ni–NH_2 2.214 Å) [254]. For completeness it is worth mentioning here a study of the oxidation of [Ni(L)] (L^3 = 1,4,7-triazacyclononane-*N*,*N*′,*N*″-triacetate). This complex undergoes a reversible one-electron oxidation in aqueous solution at +0.94 V at pH < 4; in more basic media, an irreversible reaction of the Ni(III) species occurs, apparently with fragmentation and decomplexation of the ligand [255].

9.2. *Complexes of tetraamine macrocyclic ligands*

9.2.1. *Cyclam and other 14-membered tetraazamacrocycles*

In aqueous solution, yellow planar $[Ni(cyclam)]^{2+}$ is in equilibrium with violet, octahedral $[Ni(cyclam)(H_2O)_2]^{2+}$; the latter has been isolated in crystalline form for the first time as $[Ni(cyclam)(H_2O)_2]Cl_2 \cdot 4H_2O$ (mean Ni-N 2.069(7) Å; Ni–O 2.176(2) Å) and the electronic spectrum of a single crystal measured [256]. The mechanism of oxidation of $[Ni(cyclam)](ClO_4)_2$ by peroxynitrate has been examined [257]. The thermodynamics and kinetics of CO_2 and H^+ binding to $[Ni(cyclam)]^+$ in aqueous solution have been explored [258]. Reduction of $[Ni(cyclam)]^{2+}$ by hydrogen atoms proceeds by an inner-sphere mechanism ($k = 5 \pm 2 \times 10^9\ M^{-1}\ s^{-1}$) to give $[Ni(H)(cyclam)]^{2+}$, which decomposes to $[Ni(cyclam)]^+$ and H^+ ($k = 5.3 \pm 0.7 \times 10^5\ s^{-1}$). Reduction by $CO_2^{\cdot -}$ is also inner-sphere ($k = 6.7 \pm 0.2 \times 10^9\ M^{-1}\ s^{-1}$); the intermediate $[Ni(CO_2)(cyclam)]^+$ decomposes to $[Ni(cyclam)]^+$ and CO_2 ($k = 2.0 \pm 0.2 \times 10^6\ s^{-1}$). The equilibrium constant for CO_2 dissociation is 0.062 M; this compares with a pK_a of 1.8 for the hydride complex, and suggests why $[Ni(cyclam)]^{2+}$ is selective as a catalyst for CO_2 electroreduction even in aqueous solution at pH 4. The reductive incorporation of CO_2 into epoxides in aqueous dmf to give cyclic carbonates is catalysed by $[Ni(cycam)]Br_2$, using a sacrificial Mg anode and a stainless steel cathode [259].

Cyclam (and also the linear tetradentates *N,N'*-bis(2-aminoethyl)-1,3-propanediamine, *N,N'*-bis(3-aminopropyl)-1,2-ethanediamine, *N,N'*-bis(2-aminethyl)-1,2-ethanediamine and 1,4,7,10,13-pentaazatridecane) has been intercalated into nickel-loaded zeolite Y; the nickel becomes coordinated to the ligand and this process has been monitored using infrared and electronic absorption spectroscopies [260]. The cyclam complex, though inside the zeolite pores, can still coordinate axial ligands; the complex turns from yellow (square planar) to purple (six-coordinate) on exposure of the zeolite to water. The ligand (**63**) has been reported [261]. With nickel(II) perchlorate it forms square planar $[Ni_2(L)](ClO_4)_4 \cdot 4H_2O$, the crystal structure of which has been determined; the two metal complex sites adopt an *anti*-conformation in the solid state with respect to the benzene ring plane.



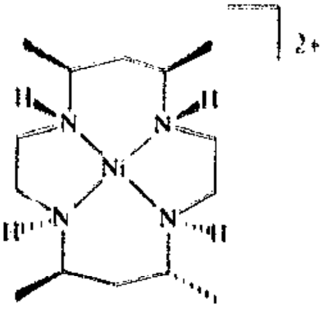
(63)

Turning now to complexes of tmc (tmc = 1,4,8,11-tetramethylcyclam), nickel complexes of this ligand are often used in modelling the F430 prosthetic group of methyl coenzyme M reductase. Both *R,S,R,S* and *R,R,S,S* isomers of $[Ni(tmc)](OTf)_2$ (*i.e.* those with, respectively, the boat and chair conformation of the macrocyclic ring) react with NaSPh to give the corresponding isomers of the high-spin, 5-coordinate [Ni(tmc)(SPh)]OTf [262]. The crystal structures of both isomers are reported. Moreover, the disulfides RSSR (R = Ph, Et) undergo oxidative addition with [Ni(tmc)]OTf to give [Ni(tmc)(SR)]OTf. The thiolate [Ni(tmc)(SPh)]OTf reacts with RI or $PhCH_2Cl$ to give [Ni(tmc)X]OTf (X = I, Cl) and PhSR. Methyl group transfer from $[MeCo(dmgBF_2)_2(py)]$ to [Ni(tmc)]OTf has been shown to occur, yielding the Co(I) complex $[Co(dmgBF_2)_2]^-$ and stoichiometric amounts of

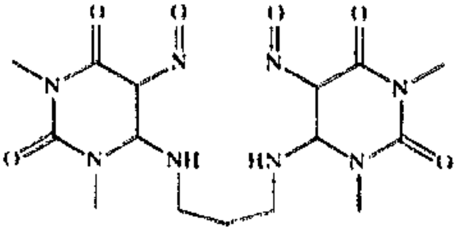
$[Ni(tmc)]^{2+}$ and $[MeNi(tmc)]^{+}$ [263]. The coordination of water and chloride ions to square planar $[Ni(tmc)]^{2+}$ in aqueous solution to give the corresponding five-coordinate high spin complex has been investigated as a function of ionic strength [264]. In aqueous solution, 63% of the complex is $[Ni(tmc)(H_2O)]^{2+}$. In concentrated $NaClO_4$ electrolyte, the equilibrium is shifted entirely in favour of the square planar complex. Chloride-containing electrolytes exhibit a behaviour which depends significantly upon the cation. Thus, the concentration of $[Ni(tmc)Cl]^{+}$ increases almost linearly with $[Me_4NCl]$, but with increasing [NaCl] or $[CaCl_2]$, the concentration levels off, then falls.

The effects of *N*-methylation on the Ni(II)/Ni(I) couples and on the properties of the Ni(I) complex in solution have been studied for a series of tetraazamacrocyclic cyclam analogues [265]. The positive shift in redox potential always observed on methylation is largely a consequence of the decrease in solvation energy of the Ni(II) complex. The Ni(I) complexes may exist in different isomeric forms, and the form obtained may depend upon whether pulse radiolysis of electroreduction are employed to synthesise them.

Two papers this year describe complexes of isocyclam (1,4,7,11-tetraazacyclotetradecane). The $[Ni(isocyclam)][ClO_4]_2$ undergoes a square planar-octahedral equilibrium in aqueous solution ($\Delta H^{\circ} = -22.6 \pm 1$ kJ mol^{-1}; $\Delta S^{\circ} = -74.9 \pm 2$ J K^{-1} mol^{-1}) [266]. Reaction with en leads to folding of the macrocycle and formation of blue $[Ni(isocyclam)(en)](ClO_4)_2$. The isocyclam complex catalyses the electroreduction of CO_2, but is not as efficient as $[Ni(cyclam)]^{2+}$. The crystal structure of $[Ni(isocyclam)(en)](ClO_4)_2$ has also been reported [267].



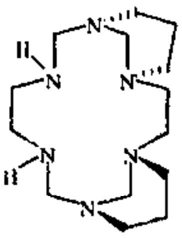
(64)



(65)

The crystal structure of the Ni(II) complex, diastereoisomer (**64**), as a diperchlorate salt, has been determined [268]. Three papers report Ni(II) complexes where a cyclam analogue is largely a 'spectator' ligand. The copper complex $[Cu(\mu\text{-}HL)Cu(H_2O)_2(EtOH)](ClO_4)_3$ (H_2L = (**65**)) reacts with $[Ni(L')](ClO_4)_2$ to give a dinuclear complex in which the Ni(II) site coordinates to one nitrosyl oxygen and the adjacent carbonyl oxygen, and the macrocycle adopts a folded, *cis* co-ordination, $[(O_3ClO)Cu(\mu\text{-}L)Ni(L')](ClO_4)_2$ (L′ = *d,l*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) [269]. There is strong antiferromagnetic exchange between Cu(II) and Ni(II) sites ($J = 136.4$ cm^{-1}). The crystal structure and magnetic behaviour of the uniform $S = 1$ chain complex $[\{Ni(L)(\mu\text{-}N_3)\}_n](ClO_4)_n$ (L =

2,3-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,3-diene), in which the azide ligands are 1,3-bridging and mutually *trans*, have been reported [270]. This complex has the largest antiferromagnetic J parameter ($-97.8\,\mathrm{cm}^{-1}$) found to date for this kind of chain. The crystal structure of a TCNQ salt [Ni(*C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane)]$(TCNQ)_2$ has appeared; the Ni(II) coordination is square planar and the stacks of $(TCNQ^{\cdot -})_2$ dimers do not significantly interact with the cations [271].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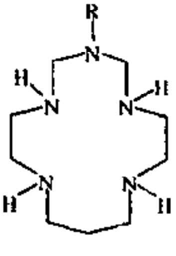
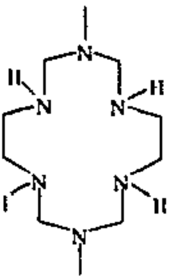

R = H (67)

R = Me (68)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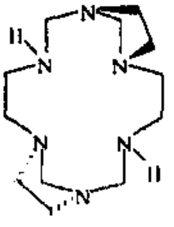
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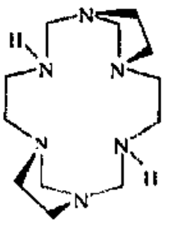
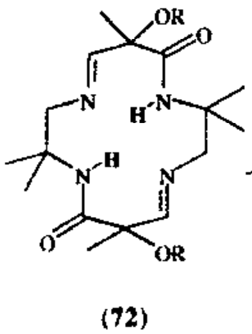
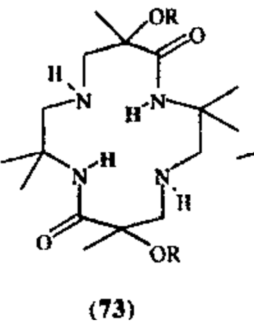

(71)

Turning now to complexes of cyclam analogues with non-coordinated nitrogen atoms in the ligand framework, the Ni(I) complex $[Ni(L)](ClO_4)$ (L = (**66**)) has been prepared by sodium amalgam reduction of $[Ni(L)](ClO_4)_2$ and characterised crystallographically (three Ni–N distances averaging 1.978(3) Å, one at 1.878(4) Å) as well as by electronic and ESR spectroscopies [272]. The Ni(I) has a tetrahedrally-distorted planar environment and the macrocyclic cavity is not significantly expanded compared with that of the Ni(II) complex. A study of the binding of additional ligands by complexes $[Ni(L)]^{2+}$ (L = cyclam, (**67**)–(**71**)) shows that, firstly, the tendency of these complexes to become six-coordinate in neutral aqueous or polar solvents is lowest for (**70**) and (**71**) [273]. In acidic aqueous media, complexes of ligands with additional distal nitrogen atoms show a tendency to six-coordination that increases with decreasing pH, independent of the acid used, indicating that H-bond formation between protonated distal N and coordinated water may drive coordination of the latter. With sulfuric acid, data indicate coordination of HSO_4^- ions, driven by the same type of interaction, and this was strongest for L = (**70**). Interestingly, the same behaviour was not seen at higher pH's for the $H_2PO_4^-$ ion; the latter is negligibly bound even by $[Ni(\mathbf{70})]^{2+}$.

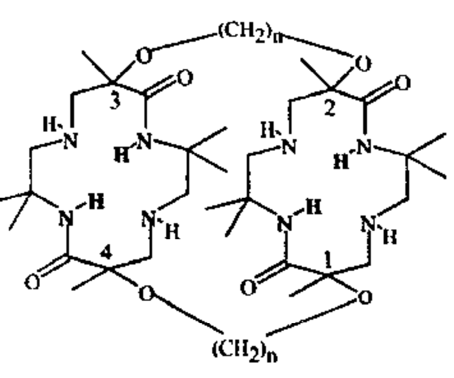


(72)



(73)

(1:1 mixtures of diastereoisomers employed)



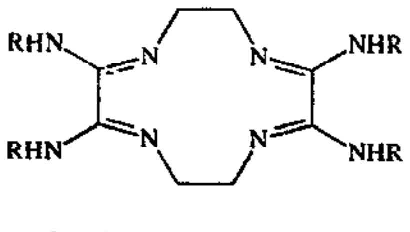
(74)

Finally, series of unusual 5,12-dioxocyclams (**72**), (**73**) and (**74**) have been synthesised using chromium carbene chemistry, and some of their Ni(II) complexes have been described [274]. The crystal structures of square planar, neutral [Ni(L)] (H_2L=(**72**); R=CH_2Ph, (**73**); R=CH_2Ph, (**74**); n=3; stereochemistry at 1,2,3,4=*R,R,R,R*;), [Ni_2(L)] (H_2L=(**74**); n=3; stereochemistry at 1,2,3,4=*R,R,R,R*) and [Ni_2(L)] (H_2L=(**74**); n=3; stereochemistry at 1,2,3,4=*R,R,S,S*) were determined, as were those of the corresponding free dinucleating ligand (**74**). There is considerable difference in structure between the dimetallic complexes of the ligands (**74**) with different stereochemistries. The *meso* ligand (stereochemistry at 1,2,3,4=*R,R,S,S*) gives a dinuclear complex with the two coordination sites virtually parallel, and eclipsed. The *d,l* ligand (stereochemistry at 1,2,3,4=*R,R,R,R*) gives a dinuclear complex with the two coordination sites at an angle of 65.1° to each other.

9.2.2. Tetraazamacrocycles with other ring sizes

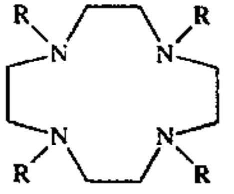
New ligands (**75**) have been synthesised [275]; with $NiCl_2$ complexes [Ni(L)Cl_2] are formed in which changes in $\nu_{(N-Cl)}$ suggest coordination to the ring nitrogens. These complexes are non-electrolytes in dmso. Ligands (**76**) give complexes with NiX_2 which, in the solid state, are five-coordinate, high spin [Ni(L)X]X·nH_2O (X=NO_3, Cl) [276]. In aqueous solution, there is an equilibrium between high spin $[Ni(L)(H_2O)]^{2+}$ and low spin $[Ni(L)]^{2+}$, which in the presence of Cl^- or SCN^- is complicated by the additional presence of $[Ni(L)X]^+$ (X=Cl, NCS). When R=benzyl, solution equilibria favour the planar form more than when R=Me, and the former complex is also more difficult to oxidise and easier to reduce electrochemically.

The ligand (**77**) forms pseudo-octahedral [Ni(L)Cl(H_2O)]Cl·H_2O, the crystal structure of which shows the ligand in a *cis*-folded conformation, with the two pyridine nitrogens (mean Ni–N 2.021(3) Å) *trans* to the chloride and water ligands, and the two *trans* tertiary amines (mean Ni–N 2.199(3) Å) considerably bent (angle N–Ni–N 154.1(1)°) [277]. Interestingly, this complex has a quasi-reversible Ni(II)/Ni(III) redox couple (+0.91 V), and the Ni(III) complex has been characterised by ESR spectroscopy.



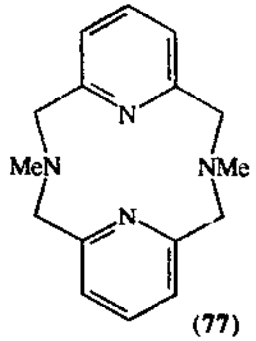
R = CH_2CO_2H, Ph, 2–C_5H_5N

(75)



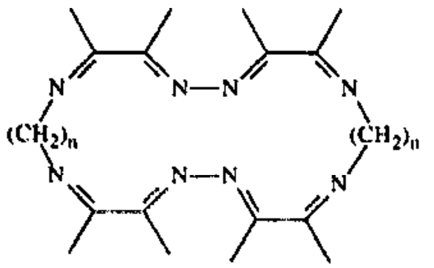
R = H, Me, CH_2Ph

(76)



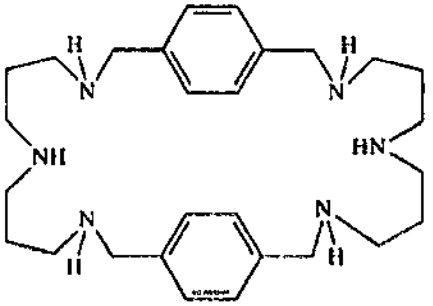
(77)

A detailed 2D ^1H NMR spectroscopic study of $[Ni(L)](ClO_4)_2$ (L = 1,4,7,10-tetraazacyclotridecane) in D_2O reveals that the 90% of the complex present in solution in the low-spin, planar form has the 1*R*,4*S*,7*R*,10*S* conformation [278]. The crystal structure of $[Ni(L)][ZnCl_4]$ confirms that this isomer is present in the solid state for this salt also. The same paper reports that significant concentration of the diamagnetic *trans-I* (*R,S,R,S*) isomer is present in aqueous solutions of $[Ni(cyclam)]^{2+}$.



n = 2, 3

(78)

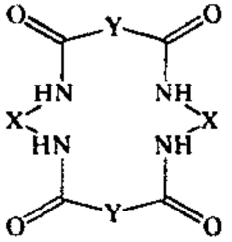


(79)

Turning now to larger ring macrocycles, condensation of aliphatic primary diamines with 3,6-dimethyl-4,5-diazaocta-3,5-diene-2,7-dione in MeOH in the presence of metal ions, including Ni(II), afforded complexes of the dinucleating macrocycles (**78**) [279]. Complexes $[Ni_2(L)X_4]$ (L = (**78**); X = Cl, NO_3) have been isolated, which on the basis of spectral data are assigned *trans* six-coordinate geometry. Another type of dinucleating macrocycle described this year is (**79**), which forms green complexes $[Ni_2(L)Cl_4] \cdot H_2O$ and $[Ni_2(L)(ClO_4)_4]$. The latter are water-soluble, giving 4:1 electrolyte solutions suggesting $[Ni_2(L)(H_2O)_4]^{4+}$ formation, and also react reversibly with pyridine. An unusual series of complexes is claimed of the ligands (**80**), namely $[Ni(L)]Cl_2$; these are all apparently yellow, diamagnetic and square planar [280].

9.2.3. *Tetraazamacrocycles bearing pendant groups*

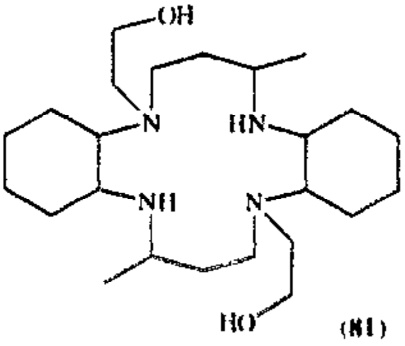
The crystal structure of $[Ni(L)](ClO_4)_2$ (L = (**81**)) shows that the complex ion is centrosymmetric, and the pendant arms are coordinated axially to give a



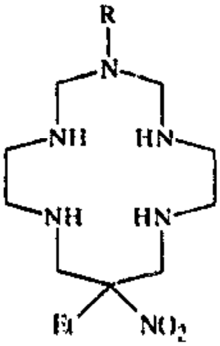
X = $(CH_2)_2$, Y = $(CH_2)_n$ (n = 1–4)
X = $(CH_2)_3$, Y = $(CH_2)_n$ (n = 1–4)
X = $(CH_2)_n$ (n = 2,3), Y = o-C_6H_4

(80)

pseudo-octahedral complex [281]. In contrast, the presence of pendant hydroxyl groups in complexes $[Ni(L)](ClO_4)_2$ (L = **(82)**; R = Et, CH_2CH_2OH) restricts the attainment of octahedral coordination (formation of $[Ni(L)(CH_3CN)_2]^{2+}$) in acetonitrile, and neither hydroxyl nor nitro group coordinates to Ni(II) in aqueous media although there is an equilibrium between planar $[Ni(L)]^{2+}$ and six coordinate $[Ni(L)(H_2O)_2]^{2+}$ [282]. Other complexes of azamacrocycles with pendant alcohols are dealt with in Section 9.

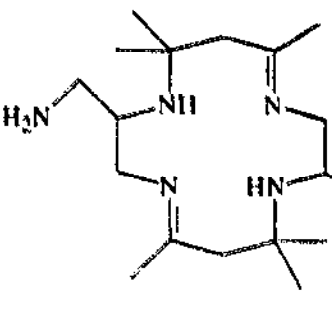


(81)



(82)

The ligand **(83)** forms either six-coordinate $[Ni(L)](ClO_4)_2$ or, with its pendant groups protonated, square planar $[Ni(LH_2)](ClO_4)_4$; both complexes have been characterised crystallographically [283]. The pendant amino groups of similar ligands have been used to prepare ditopic receptors by condensation with formylbenzo-15-crown-5, and their Ni(II) complexes have been investigated [284].



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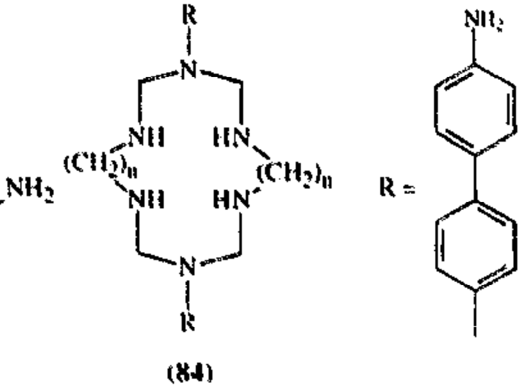
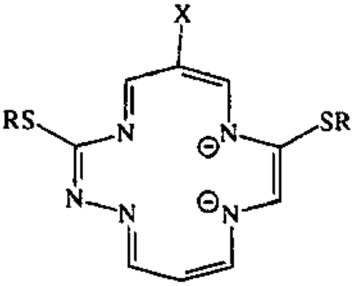


(84)

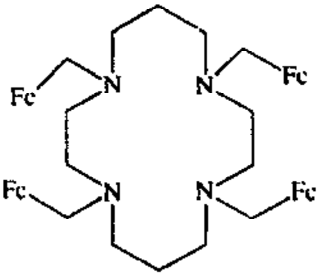
The crystal structure of [Ni(L)] (L^{2-} = 6-(4-aminobenzyl)-1,11-diaza-4,8-diazanidacyclotetradecane-5,7-dione) has been reported: this has a square planar geometry as expected, but with the unusual feature that the pendant benzene ring is aligned over, and almost parallel with, the NiN_4 plane [285]. Template condensation of en or pn with formaldehyde and benzidene in the presence of $NiCl_2$ is reported to give pseudo-octahedral $[Ni(L)Cl_2]$ (L=(**84**)). Neutral square planar complexes [Ni(L)] (L^{2-}=(**85**)) have been reported; the crystal structures of both examples show that they are square planar with the sulfur atoms playing no role in coordination [286].



R = Et; X = H

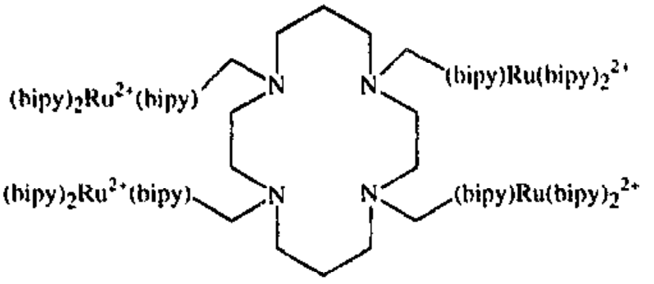
R = Pr; X = NO_2

(**85**)



(**86**)

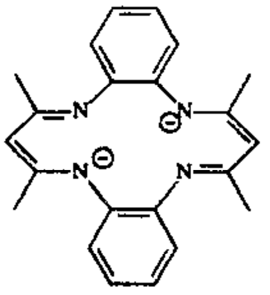
Two papers this year describe complexes of tetraazamacrocycles functionalised with pendant redox-active groups. In the five-coordinate complex $[Ni(L)(CH_3CN)](PF_6)_2$, the ligand L (L=(**86**)) adopts a conformation with all four ferrocenyl groups above the N_4 plane; the acetonitrile molecule coordinates Ni(II) on the same side of the NiN_4 plane as the ferrocenyl groups. The complex shows a ferrocene/ferrocinium redox process at +0.449 V. The ligand 1,4,8,11-tetrakis(2,2′-bipyridyl-5′-ylmethyl)-1,4,8,11-tetraazacyclotetradecane (L) reacts with four equivalents of *cis*-$[RuCl_2(bpy)_2]$ to give a highly fluorescent macrocyclic ligand (**87**). This can complex Ni(II) to form $[Ni(L^{8+})](ClO_4)_{10}$ in which the fluorescence is quenched.



(**87**)

9.3. Complexes with tetraazaannulene-type ligands

Nickel(II) complexes of tetraazaannulenes such as (**88**) have been electropolymerised to afford polymeric deposits on electrode surfaces, and these have been employed in electrocatalysis of carbohydrate oxidation in aqueous alkaline solutions [287]. It appears that on repeated cycling in aqueous base, the NiN_4 coordination is probably lost, but the electrode resembles NiOOH in its electrochemical behaviour; the Ni species remain trapped within the polymer [288]. The electropolymerisation mechanism has been investigated; the reduced form $[Ni(\mathbf{89})]^{2+}$ does not undergo electropolymerisation upon oxidation.



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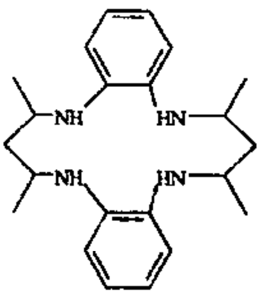
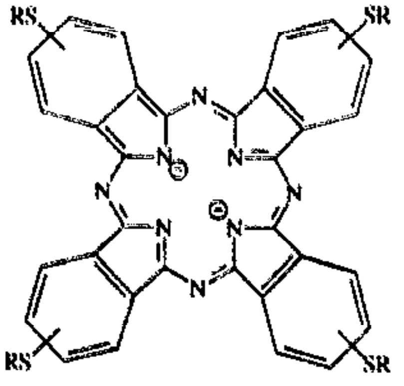


(89)

The condensation reaction between tetraaza[14]annulenenickel(II) and a series of 4-substituted benzoyl chlorides gives the corresponding 7,16-dibenzoylated products [289]. In spite of this substitution, the electronic spectra suggest barely any change in donor strength. Similar reactions with three dibenzoic acid chlorides gave the corresponding 'strapped' tetraazaannulene complexes in low-moderate yield [290]. Finally, the syntheses of dibenzotetraaza[14]annulenenickel(II) bearing four, six or eight long alkyl chains have been described [291]. Preliminary results show that some of these complexes exhibit a hexagonal columnar liquid crystal phase.

9.4. Complexes with phthalocyanines and related ligands



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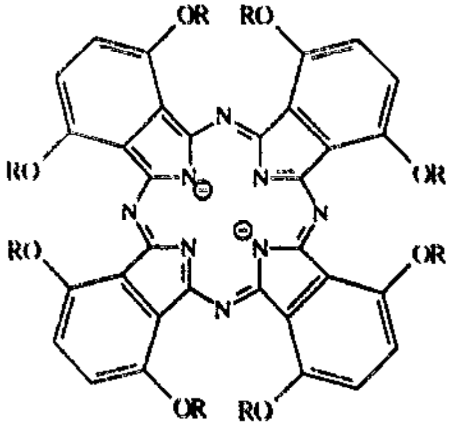
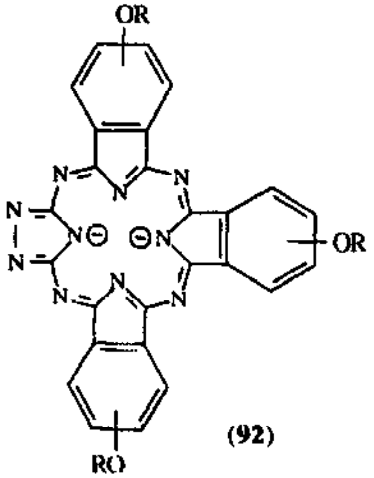


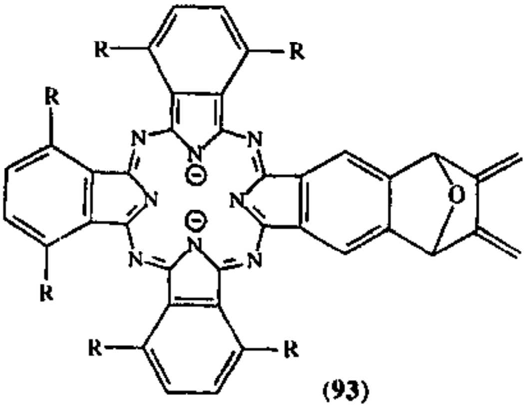
(91)

The ESR spectrum and magnetic susceptibility of solutions of [Ni(Pc)] in pyridine have been studied; in frozen (77 K) solution, high-spin $[Ni(Pc)(py)_2]$ forms [292]. The complex [Ni(L)] (L^{2-} =(**90**); R = hexyl), together with a polymeric analogue with the metal centres linked by alkanediyldisulfanyl bridges, have been made [293], and palladium(II)-thioether complexes were obtained by treatment of these with $PdCl_2$. Whereas the monomeric complex could be cast into films, the polymeric complexes were insufficiently soluble. Various applications of phthalocyanine complexes, particulary those of nickel, have been suggested, and studies continue in this area. Langmuir–Blodgett (LB) films have been made using [Ni(L)] (L^{2-} =(**91**);

R = pentyl), and their electrochromism investigated. They are pale brown at +1.2 V and blue–purple at +1.8 V, but lifetimes were short (*ca.* 100 cycles). The complex [Ni(L)] (L^{2-} = (**92**); R = octyl), with one polar 1,2,4-triazole subunit and three alkyl chains, are particularly suitable for LB film formation [294]. Moreover, ordered (in-plane oriented) films were produced when Ni(II) ions were present in the aqueous subphase to complex the 1,2,4-triazole unit.



(**92**)

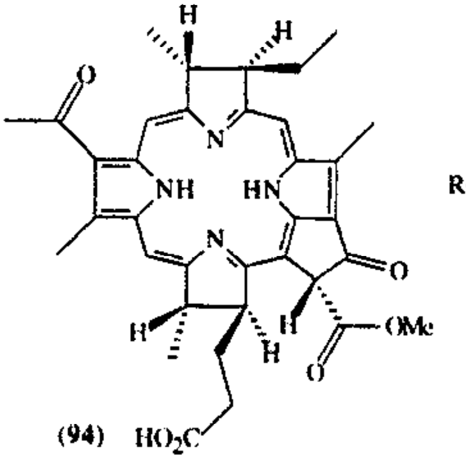


(**93**)

Current density-voltage characteristics of [Ni(Pc)] thin films have been investigated [295]. The third order nonlinear optical properties of donor- and acceptor-substituted phthalocyanine complexes (including those of Ni(II)) have been investigated [296]. The pressure dependence of the optical spectra of the mixed valence species [Ni(Pc)](AsF$_6$)$_{0.5}$ has been studied [297–299]. Finally, a Diels–Alder adduct of C$_{60}$ with the complex [Ni(L)] (L^{2-} = (**93**); R = heptyl) has been prepared [300]. Spectroelectrochemical measurements show that both the C$_{60}$ moiety and the phthalocyanine centre show multiple reductions, with changes to the optical properties of the phthalocyanine centre on C$_{60}$ reduction.

9.5. Complexes with porphyrins and related ligands

Beginning with naturally-occurring ligands, XAS studies of Ni(I), Ni(II) and Ni(III) complexes of relevance to the nickel-containing cofactor F430 have been reported [301]. A spectroelectrochemical study of transmetallated bacteriochlorophyll *a* (**94**) (including its Ni(II) complex) has been reported [302]. In thf/0.1 M Bu$_4$NPF$_6$, two reversible oxidations and two reversible reductions were seen, all ligand-centered. The decreased HOMO–LUMO gap deduced from the electrochemical measurements for the Ni(II) complex compared with the free ligand was attributed to a deformation of the macrocycle caused by the short Ni–N bonds. The FTIR spectra of the first oxidation and first reduction product have also been studied [303], and the difference spectra (monocation-neutral complex) show changes in the macrocycle skeletal modes which differ from the corresponding experiment on the free macrocycle, again consistent with a deformation of the macrocycle. The issue of non-planarity, and its role in the function of porphyrin-based metalloenzymes, has been reviewed [304]. The Q-band excited resonance Raman spectra of geologically significant nickel(II) complexes of etio-, cycloalkano- and tetrahydrobenzoporphyrins have been reported [305,306]. The frequencies of skeletal modes above 1300 cm^{-1} indicate more planar structures for nickel tetrahydrobenzoporphyrins than for nickel octaethylporphyrin. A controversy has arisen as to whether or not depolarization dispersion apparently seen in the Raman spectra of metalloporphyrins, including Ni(II) complexes, is real or a consequence of spectral crowding [307,308].



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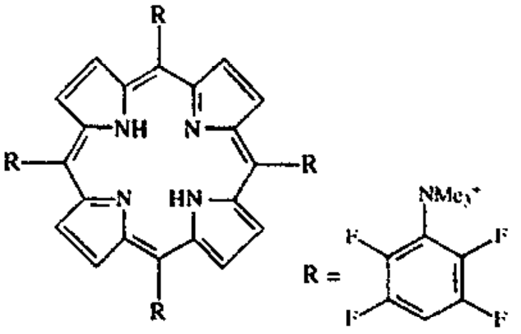
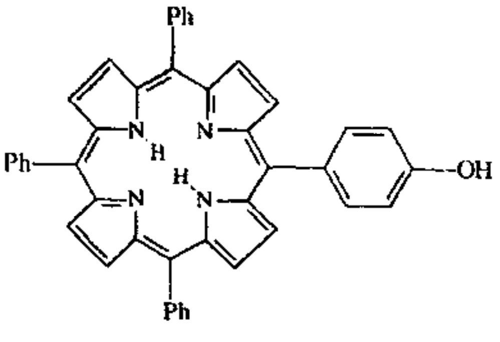


(95)

Turning now to synthetic studies, the preparation and film-forming properties of porphyrin pentamers, where tetraphenylporphyrin units are linked through α,ω-dioxy-propyl or -butyl spacers, have been reported [309], and the formation of LB films of the Ni(II) complexes explored. The X-ray crystal structure of $[Ni(L)](CF_3SO_3)_4 \cdot 2CH_3CN \cdot 2(CH_3)_2CO$ (H_2L = (**95**)) has been reported [310]. This complex binds axial ligands quite strongly, with a square planar-six coordinate equilibrium ($K = 0.63$) in aqueous solution, although the crystal structure revealed a square planar geometry in the solid state with no interaction with the solvent or anions. By heating $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}Cl_2]$ with [Ni(L)] (H_2L = (**96**)), $[Mo\{HB(3,5\text{-}Me_2C_3HN_2)_3\}(Cl)\{(OC_6H_4)(Ph)_3porphyrin)Ni]$, a dimetallic complex, has been synthesised [311]. There is little communication between metal centres as assessed by cyclic voltammetry. The rotational isomers of $[Ni(tetrakis\{N\text{-methyl-2-pyridiniumyl}\}porphyrin)]^{4+}$ have been isolated, as stable solids, using preparative thin layer chromatography [312].

Asymmetric porphyrin dimers (**97**) have been prepared *via* Vilsmeier formylation, and subsequent reactions, of the mono-nickel(II) complex of 1,2-ethanebis(octaethylporphyrin) ((**97**); R = H) [313]. Oxidation of the mono-Ni compounds gave the corresponding *trans*-ethylene-bridged dimers, but the corresponding free base porphyrins, under the same conditions, gave only 10′-formyl-1,2-ethylenebis(octaethylporphyrin).

Another method of preparing bisporphyrin complexes has been reported briefly, namely Ni(0)-induced reductive coupling of the complex (**98**), which afforded the corresponding $[Ni_2\{15,15'\text{-bis(chloroethyl)-5,5'-diphenylethanebisporphyrin}\}]$



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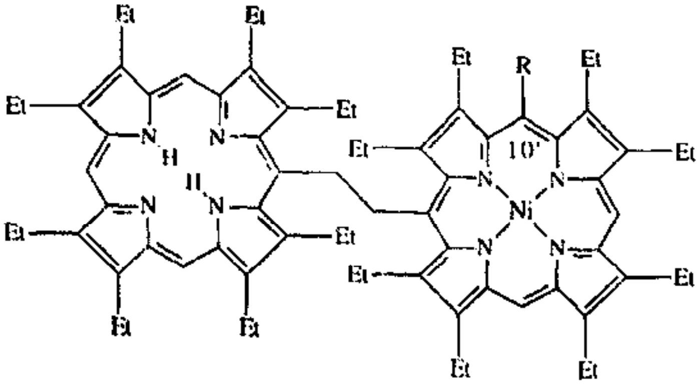
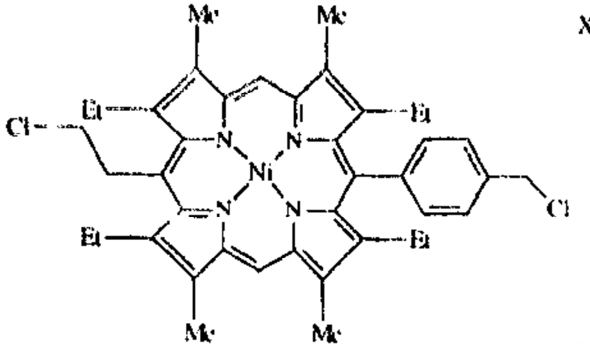


R = -(CH=NMe$_2$)$^+$PO$_2$Cl$_2^-$, -CH$_2$NMe$_2$,
CH$_2$OMe, CHO (97)

complex, together with some of the reduction product [Ni(15-chloroethyl-5-tolylporphyrin)] [314].



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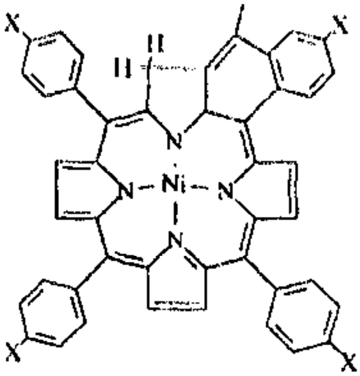
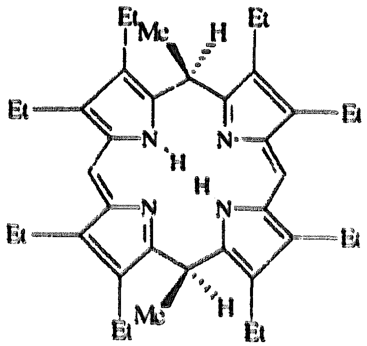


(99)

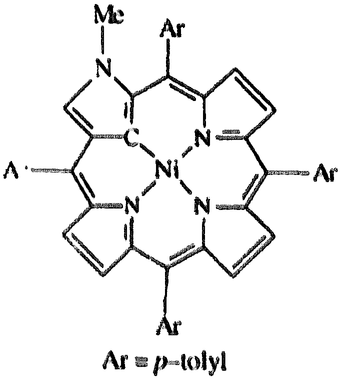
The ruffling distortion in a series of *meso* tetraalkyl-substituted porphyrin complexes of Ni(II) has been examined using molecular mechanics calculations and comparison with known X-ray crystal structures [315]. The frequencies of structure-sensitive Raman lines, and the size of the red shifts in the π-π* absorption bands, change nonlinearly with increasing ruffling angle. Based upon the fact that the B_{1u}

nonplanar distortion (ruffling) is localised in C_α–C_m bond torsion whereas the saddle-type distortion is not, a method of distinguishing these types using resonance Raman spectroscopy is suggested. The X-ray crystal structure of [Ni(*meso*-tetrakiscyclohexylporphyrin)] shows that the ligand adopts a highly ruffled conformation, as expected for a substituent of this size [316]. The complex [Ni(β-vinyl-*meso*-tetraphenylporphyrin)], on treatment with dilute sulfuric acid, did not demetallate as expected, but formed the complex (**99**), a naphthochlorin [317]. The acid-catalysed solvolyses of transition metal complexes of *N*-methyl-*meso*-tetrakis(*p*-sulfonatophenyl)porphyrin, including the Ni(II) complex, have been examined [318].

The product of one-electron electro-oxidation of [Ni(TPP)] has been re-examined in detail [319]. The initial product in solution in CH_2Cl_2 is [$Ni^{II}(TPP^{\cdot+})$], but on addition of coordinating solvents L (L=pyridine, thf, CH_3CN), intramolecular electron transfer to form $[Ni^{III}(TPP)(L)_2]^+$ occurs; contrary to previous reports these are stable under inert atmospheres for extended periods. These are low-spin d^7 complexes with the unpaired electron in the d_z2 orbital. Addition of CO or PPh_3 to solutions of [$Ni^{II}(Tpp^{\cdot+})$] results only in reduction back to [Ni^{II}(TPP)], while addition of CN^- produces the short-lived $(d_{x^2-y^2})^1$ Ni(III) species $[Ni(TPP)(CN)_2]^-$ and ultimately results in reduction.

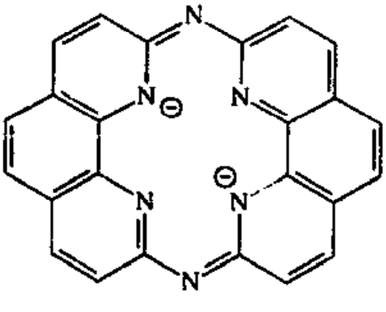


(**100**)



(**101**)

Turning now to porphyrin derivatives, in porphodimethenes the macrocycle is reduced by the addition of two hydrogen atoms (or, for stability to re-oxidation, alkyl groups) at opposite *meso* positions. The complex [Ni(L)] (H_2L=(**100**)) is electrochemically reduced to [$Ni^{II}(L^{\cdot-})$] and oxidised to [$Ni^{II}(L^{\cdot+})$] [320]. The HOMO of [Ni(L)] looks like a porphyrin a_{1u} orbital, with the two pyrromethenes coupled through the Ni(II) ion, while in the LUMO the pyrromethene units are not coupled. The redox and unpaired spin densities for the radical cation and anion are surprisingly similar to those of the corresponding [Ni(octaethylchlorin)] radical cation and anion. Treatment of 2-aza-21-carba-*meso*-tetra-*p*-tolylporphyrin with MeI resulted in methylation of the exocyclic nitrogen, to give a ligand which readily complexed Ni(II) to give (**101**) with a very stable Ni(II)–C bond [321]. A density functional theory study of metal–porphine complex second-order hyperpolarisabilities has been published [322]. The nickel complex had a similar calculated value to the free porphine, and lower than all other metal complexes investigated, a consequence of the effective atomic charge at nickel(II).



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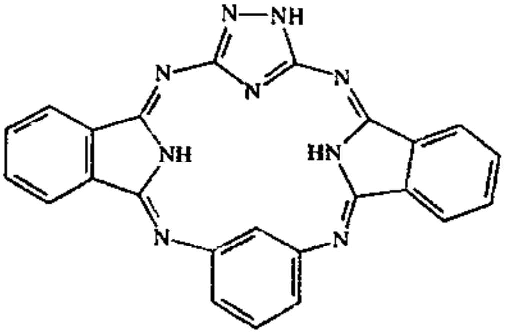
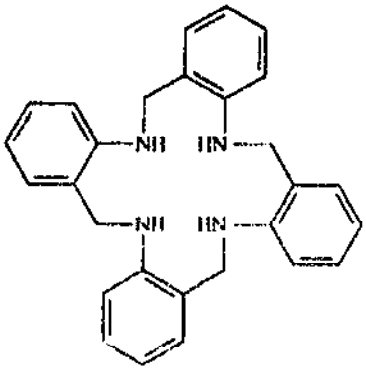


(103)

A quantum chemical study of the geometry, electronic structure and electronic spectra of hexaazacyclophane and the Ni(II) complex of its dianion (**102**) has been carried out [323]. Both the ligand and its Ni(II) compex are predicted to have singlet ground states. Although these ligands are often considered as analogous to porphyrins, the calculated spectra cannot be described in terms of Q and B (Soret) bands. The triazolehemiporphyrazines are likewise considered analogous to porphyrins and phthalocyanines. The unsymmetrical ligand (**103**) has been prepared; the Ni(II) complex of its dianion was insoluble and unstable to mineral acids and was only characterised by FAB–MS [324].

The ligand (**104**) (L) is often referred to as a porphyrin analogue. A report this year details the crystal structure of the complex $[Ni(L)(MeOH)_2](ClO_4)_2 \cdot 2MeOH$, together with that of L itself [325]. The complex has two axial methanol ligands, and the ligand L is saddle-shaped (opposite NH protons on the same side of the NiN_4 plane). A crystal structure of the complex [Ni(L)] (L = (**105**)) has very briefly been reported; although bond lengths and angles are not given, there appears, from the ORTEP diagram, to be considerable tetrahedral distortion in the complex [326].



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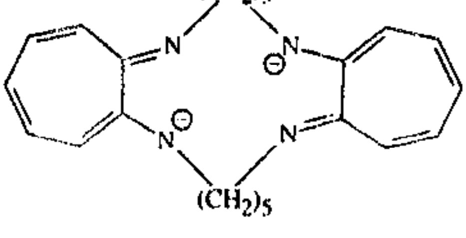
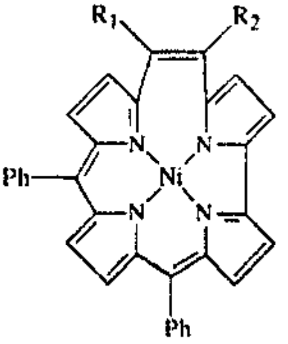


(105)

The syntheses of 'ladder'-type dimers and trimers from Ni(II)-hemiporphyrazine complexes bearing suitable fused substituents using Diels–Alder reactions have been described [327]. 'Hemiporphycene' isomers (**106**) have been isolated in small (1–6%) yield as their Ni(II) complexes by acid treatment of the corresponding homoporphyrin followed by metallation with nickel acetate, and the crystal structure of [Ni(**106A**)] has been determined [328]. The complex has square planar geometry, with one Ni–N distance (1.872(4) Å) considerably shorter than the other three (1.924(4), 1.948(4), 1.953(4) Å). The ligand is aromatic, but slightly distorted into a saddle conformation.



R_1 = Ph, R_2 = EtO_2C (**106A**)
R_1 = EtO_2C, R_2 = Ph (**106B**)

10. Complexes with mixed nitrogen-oxygen donor ligands

10.1. Metalloenzymes and related systems

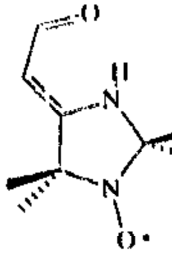
Urease contains Ni(II) ions, which EXAFS studies previously established have a mixed nitrogen and oxygen coordination. The crystal structure of the urease from *Klebsiella aerogenes* has been determined (2.2 Å resolution, $R = 8\%$) [329]. The active site has two Ni ions 3.5 Å apart. One site has three ligands (and low occupancy of a fourth), and the other has five ligands. A carbamylated lysine provides an oxygen ligand to each Ni; it is thought that this explains why CO_2 is required for the activation of the apoenzyme [330]. It is possible that the mechanism consists of urea binding to the first Ni(II) and a hydroxide ligand from the second Ni(II) attacking the carbonyl carbon.

10.2. Amine–oxygen donor ligands

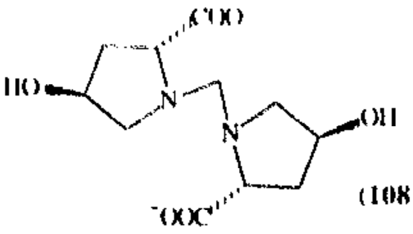
The complexation of Ni(II) by diethanolamine (L) in water as a function of ionic strength has been examined [331]. The results were consistent with the formation of $[Ni(L)]^{2+}$ and $[Ni(L)_2]^{2+}$. The crystal structure of $[Ni(L)_2]Cl_2$ (L = tris(2-hydroxyethyl)amine) has been determined [332]. The two tertiary amine donors are mutually *trans* (Ni-N 2.113(1) Å) and each ligand binds Ni(II) additionally *via* two of its three OH groups (Ni-O 2.068(1), 2.067(1) Å). The thermodynamic and kinetic properties of the Ni(II) complexes of the pendant arm macrocycles *N,N',N'',N'''*-tetrakis(2-hydroxyethyl)-1,4,7,10-tetraazacyclododecane and -1,4,8,12-tetraazacyclopentadecane have been studied [333]. Formation constants for the Ni(II)-pendant arm ligands are lower than for the corresponding complexes of the unfunctionalised macrocycles. The decomplexation rate constant for the 12-membered ring was pH-dependant, but for the 15-membered ring ligand was very slow even in 1.00 M HNO_3.

Turning to amine-carboxylate ligands, the ligands 1,3-propanediamine-*N,N'*-diacetate (pdda) and ethylenediamine-*N,N'*-dipropionate both form complexes $[Ni(L)_2(H_2O)_2]$ which have the all-*cis* geometry; the complex with pdda was the subject of a crystal structure determination (mean bond lengths Ni–N 2.075(6) Å, Ni–O 2.045(6) Å, Ni–O(water) 2.131(6) Å) [334]. This contrasts with ethylenediamine-*N,N'*-diacetate which forms $[Ni(L)_2(H_2O)_2]$ with *cis* amines and *trans* carboxyl ligands. The ligand (**107**) (HL) reacts with $Ni(OAc)_2$ to give centrosymmetric pentacoordinated $[Ni_2(L)_4]$ [335]. The isomorphous Co(II) complex has a structure in which two ligands chelate each metal ion, but the carbonyl group of one ligand additionally bridges to the second metal. The magnetic properties are consistent with weak ferromagnetism between Ni(II) and the nitroxide radicals, and strong antiferromagnetism ($J = -31.1(6)$ cm^{-1}) between Ni(II) centres.

The condensation of bis(4-hydroxy-L-prolinato)nickel(II) with formaldehyde gave $[Ni(L)(H_2O)_2]$ (L^{2-} = (**108**)); this is the first time a chelated amino acid has reacted in this fashion [336]. The crystal structures of the isomorphous all-*cis*-$[Ni(glycinate)_2(bpy)]\cdot 3H_2O$ and $[Ni(glycinate)_2(phen)]\cdot 3H_2O$, with the glycinate chelating *via* carboxyl oxygen and amine nitrogen, have been determined [337].



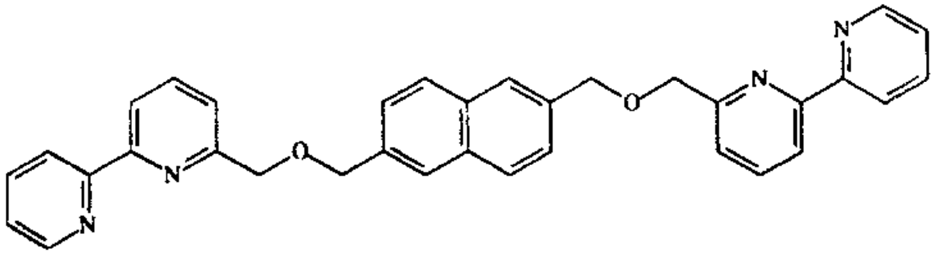
(**107**)



(**108**)

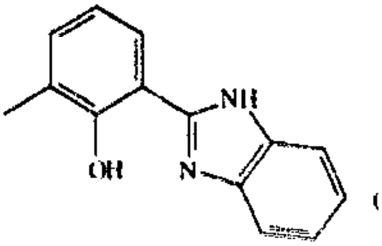
The formation of the complexes formed by Ni(II) with Asp–Asp–Asp and a series of tetrapeptides containing one or two Asp residues or a Glu residue have been studied [338]. The β-carboxylate group of the Asp residue stabilises the complexes formed significantly, particularly when it is present as the *N*-terminal amino acid, and postpones the formation of square planar Ni(II) complexes of deprotonated amide groups to higher pH values. The side chain of Glu residues had a much smaller effect. The kinetics of complex formation between $[Co(H_2nta)(NH_3)_5]^{2+}$ (H_3nta = nitrilotriacetic acid) and Ni(II) have been investigated [339]. General base catalysis indicates that deprotonation of the protonated tertiary amine is the likely rate determining step.

10.3. Imine–oxygen donor ligands



(109)

The ligand (**109**) (L) reacts with nickel(II) acetate in acetonitrile to afford, after metathesis, $[Ni_2(L)_2](PF_6)_4$. The crystal structure of this complex reveals that the dimeric cation has a non-helical structure, with each Ni(II) coordinated to four bipyridyl nitrogens and two ether oxygens in a grossly distorted octahedral geometry. The two naphthalene rings are parallel and offset by 4.11 Å. With nickel(II) acetate in the presence of KOH, the ligand (**110**) (HL) gave a complex formulated as distorted tetrahedral $[Ni(L)_2] \cdot 2MeOH$ [340].

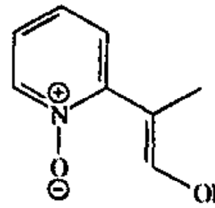


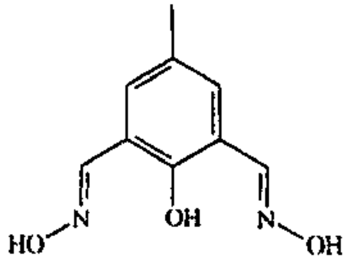
(110)

With nickel(II) acetate in dmf, the ligand 2-(2-hydroxyphenyl)pyridine (HL) gave a dinuclear complex $[Ni_2(L)_2(dmf)_6][BPh_4]_2 \cdot 2Et_2O$ after metathesis [341]. The crystal structure of the latter showed one pyridyl donor coordinated to each Ni(II), with both phenolate oxygens bridging and the remaining coordination sites occupied by O-bound dmf ligands.

The complex all-*trans*-$[Ni(L)_2(4\text{-methylpyridine})_2] \cdot H_2O$ (HL = anion of 8-hydroxyquinoline) has been characterised structurally, and by XPS [342]. The kinetics of dissociation of the complex $[Ni(L)_2]$ (HL = 2-methyl-8-hydroxyquinoline) by acid has been studied in aqueous solution and in micelles formed by a range of surfactants (neutral, anionic and cationic) [343]. The rate-determining step in all cases is dissociation of the NiL^+ complex, which in micelles occurs predominantly at the micelle–water interface. The rate is about 100 times faster in anionic than neutral or cationic micelles.

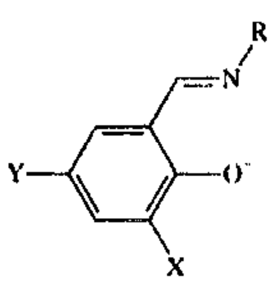
Turning to ligands bearing oxime donor groups, the reactions of substituted 2-hydroxyaryloximes with Ni(II) have been studied, and the crystal structure of square planar *trans*-[Ni(1-{2-hydroxyphenyl}oximate)$_2$] has been determined (Ni–N 1.884(3) Å, Ni–O 1.825(2) Å) [344]. The ligand (**111**) (L) normally reacts with Ni(II) salts to give octahedral $[Ni(L)_2X_2]$, but a 1:1 complex $Ni(L)Cl_2 \cdot H_2O$ has also been isolated [345]. On the basis of magnetic measurements, X-ray powder pattern and electronic spectral data, this is assigned a halide bridged polymeric structure of *N*-oxide-bridged dimeric units, with the water molecules not coordinated. The reaction of [Fe(L)Cl$_3$] with [Ni$_2$(HL')$_2$] (L = 1,4,7-trimethyl-1,4,7-triazacyclononane; H$_3$L' = (**112**)) in the presence of acetate and triethylamine produces dark brown [L$_2$Fe$_2$(μ_2-O$_2$CMe)$_2$(L')$_2$(MeOH)$_2$Ni$_2$]$^{2+}$, isolated as the tetrafluoroborate [346]. The crystal structure of this complex reveals the two Ni(II) ions at the centre of a near-linear FeNiNiFe chain, with the Ni(II) ions bridged by the two L' ligands coordinated *via* phenolate oxygens (bridging) and terminal oxime nitrogens. These also bridge to neighbouring Fe(III) ions *via* the deprotonated oxime hydroxyl groups. The coordination is completed by one acetate ion per Ni(II), also bridging to an adjacent Fe(III), and one MeOH. The complex has complicated magnetic properties, with a non-diamagnetic ground state, and weak antiferromagnetic coupling between adjacent metal ions.


(**111**)

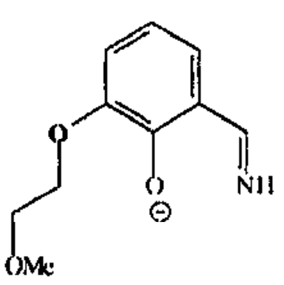

(**112**)

10.4. Schiff base and related ligands

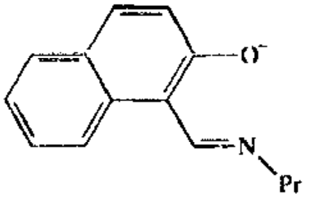
The ^{1}H, ^{13}C and ^{15}N NMR spectra of substituted Ni(II) complexes of the Schiff base of (*S*)-2-(*N*-benzylprolyl)aminobenzophenone and glycine have been recorded [347]. Schiff base polymers poly-5,5'-methylenebis(salicylaldehyde)-tetramethylethylenediimine, -*meso*-stilbenediimine, -*dl*-stilbenediimine and -2,6-diiminopyridiene, and their Ni(II) complexes, have been prepared, and characterised spectroscopically [348]. Dodecylsalicylaldoxime is commonly used in recovery of copper from its ores, and a study of the study of the extraction of Ni(II) by this ligand into hexane from aqueous solution has appeared [349].


(**113**)

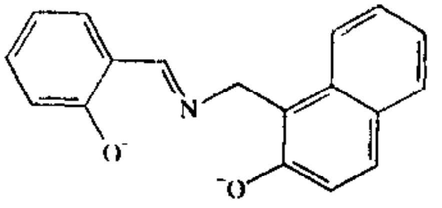
X	Y	R
Bu^t	Me	H, Me, Et, ^{n}Pr, ^{i}Pr, ^{n}Bu, ^{i}Bu, ^{t}Bu, *neo*Pe
^{i}Pr	H	Et, ^{i}Pr
^{t}Bu	H	Et, ^{i}Pr
NO$_2$	Me	Et, ^{i}Pr
Br	Me	Et, ^{i}Pr


(**114**)

A series of bis(*N*-alkylsalicylaldiminato)nickel(II) complexes [Ni(L)$_2$] (HL = (**113**)) has been prepared, and the crystal structure of one example (R = Et, X = ^{t}Bu, Y = Me) obtained; the latter is *trans* square planar [350]. The fast square planar-tetrahedral equilibrium of these complexes in solution has been studied using variable temperature ^{1}H NMR spectroscopy; the planar structure is favoured over tetrahedral except with the bulkiest substituents (R and X = ^{t}Bu). The coordination of pyridine to $[Ni(L)_2]$ occurs to a lesser extent with bulky substituents, and the displacement of the didentate L^- ligands by salen^{2-} and related tetradentates is slower. The complex $[Ni(L)_2]$ (L^- = (**114**)) reacts with $NaClO_4$ in apolar solvents to afford $[Ni(L)_2] \cdot NaClO_4$, the crystal structure of which shows a square planar Ni(II) environment, with the two *cis*-arranged phenolate donors bridging to a sodium ion, which is further coordinated to the oxygens shown in bold, and to two *trans*, bridging perchlorato oxygens [351].

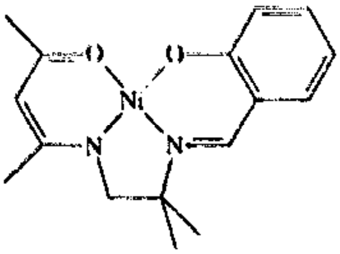


(**115**)



(**116**)

The crystal structures have been determined of HL and square planar $[Ni(L)_2]$ (L^- = (**115**)) [352] (mean Ni–N 1.912(2) Å, Ni–O 1.826(2) Å), and square planar [Ni(L′)(piperidine)] (L'^{2-} = (**116**)) (Ni–N(L′) 1.859(4) Å, Ni–O 1.829(4), 1.857(4) Å, Ni–N(pip) 1.943(4) Å) [353]. Electrooxidation of a nickel anode in acetonitrile solutions of tridentate Schiff bases H_2L, synthesised from salicylaldehydes and 2-aminophenols, afforded complexes of empirical formula [Ni(L)], which are probably polymeric [354]. In the presence of bpy or phen, the corresponding [Ni(L)(bpy)] or [Ni(L)(phen)] were obtained, which electronic spectra suggest are octahedral, therefore also presumably polymeric.

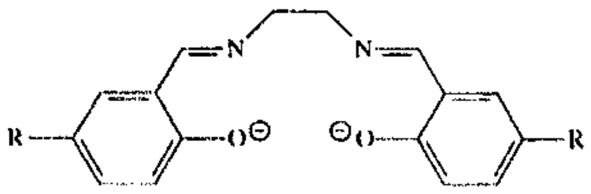


(**117**)

A general procedure for obtaining 1:1 condensation products from aldehydes or ketones, and 1,2-diamino-2-methylpropane, has been described, and this has been employed to make unsymmetrical tetradentate Schiff bases and their Ni(II) complexes (e.g. (**117**)) [355]. By using imidazole-2-carboxaldehyde, tetradentate Schiff bases with an additional potential bridging ligand function have been made, and these have been used to make dimetallic complexes with imidazole bridges. By using chiral 1,2-diaminopropane, this chemistry has also been employed to make chiral Schiff base complexes of Ni(II) with both symmetrical and unsymmetrical Schiff bases [356]. Electronic, CD and NMR spectra of these have been studied. The

Cotton effect for a given transition reflects the conformation of the five-membered chelate ring of the diamino chain, the preferred conformation of which has the methyl substituent in an axial orientation.

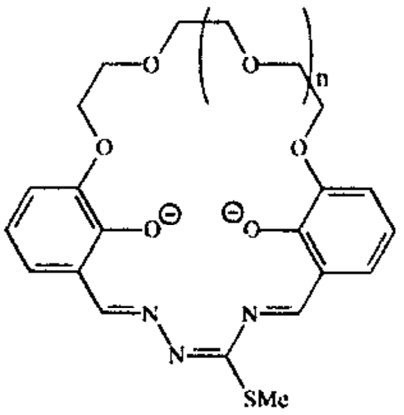
The reaction of diorgaotin(IV) nitrates with $[Ni(L)]\cdot H_2O$ (H_2L = *N,N′*-bis{3-methoxysalicylidene}propane-1,3-diamine) has been examined; the reactions usually result in transfer of nitrate from tin to nickel, and the crystal structure of the $Me_2Sn(NO_3)_2$ adduct has been determined [357]. This shows Ni(II) coordinated by the tetradentate Schiff base, an axial monodentate nitrate ion and a water molecule. The Sn(IV) is coordinated to the two Me groups, the two RO^- ligands (which therefore bridge the Ni(II) and Sn(IV)) and the two methoxy oxygens. The positive ion methane CI–MS and EI–MS spectra of [Ni(salen)] have been studied to elucidate the gas-phase chemistry of this complex [358]. The complex ionises at the metal and undergoes little EI fragmentation at 70 eV. $[Ni(salen)]^-$, generated by controlled-potential electrolysis in dmf, catalytically reduces α,ω-dihaloalkanes by a one-electron process that involves a radical intermediate [359]. Potentially tetradentate Schiff base ligands (H_2L) prepared from 2,5-dihydroxyacetophenone and either en or pn have been reported to form complexes $[Ni(H_2L)]X_2$ (X = Cl, NO_3), $[Ni(H_2L)(OAc)_2]$ and $[Ni(H_2L)](SCN)_2\cdot 4H_2O$ [360].



(118)

The complex [Ni(L)] (L^{2-} = (**118**); R = butyl) has been characterised crystallographically; it exhibits an unusual packing arrangement whereby dimers are present as a result of π π stacking [361]. There are, additionally, CH π interactions between one butyl group of one molecule, and the π system of the other molecule. This arrangement is suggested to explain the unusual liquid crystalline behaviour of complexes [Ni(L)] (L^{2-} = (**118**); R = dodecyl or hexyl) which exhibit, on heating, first a smectic E phase, then a smectic A phase; the transition is due to the breaking up of the dimeric units. Attempts to lower the melting points of complexes of this type (L^{2-} = (**118**); R = $-OC_6H_{13}$, $-OC_8H_{17}$, $-OC_{11}H_{23}$) by introducing a fluorine atom at position 5 in the aromatic ring have been described, along with the crystal structure of [Ni(L)] (L^{2-} = (**118**); R = $-C_6H_{13}$) [362]. Interestingly, the packing arrangement in this structure is quite different from that in [Ni(L)] (L^{2-} = (**118**); R = butyl). Introduction of the F atom lowers the melting point but greatly narrows the temperature range over which liquid crystalline behaviour is observed.

Template condensation (Ba^{2+}) of the appropriate dialdehyde with *S*-methyisothiosemicarbazidehydroiodide, follwed by treatment with nickel(II) acetate, afforded $[Ni(L)Ba](CF_3SO_3)_2$ (L = (**119**), n = 1) or $[Ni(L)Ba](I_3)I$ (L = (**119**), n = 2) [363]. Barium-free Ni(II) complexes could be obtained from these by treatment with guanidinium sulfate in water. The crystal structures of the barium–nickel complexes



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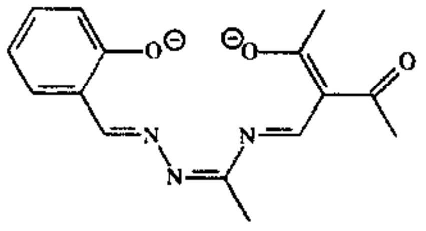
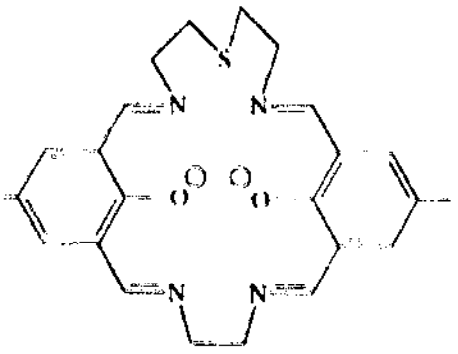


(120)

were determined; both have square planar geometry. The coordination chemistry of the barium-free complexes with alkali and alkaline earth metals have been further examined; the ligands show similar size preferences to 15-crown-5 (n = 1) and 18-crown-6 (n = 2), but differ from these prototype crowns in their formation of M:L 1:2 complexes in solution [364]. A related complex [Ni(L)] (L^{2-} = (**120**)) has been prepared by template reaction of salicylaldehyde acetamidrazone with $Ni(acac)_2$ and Hacac [365].

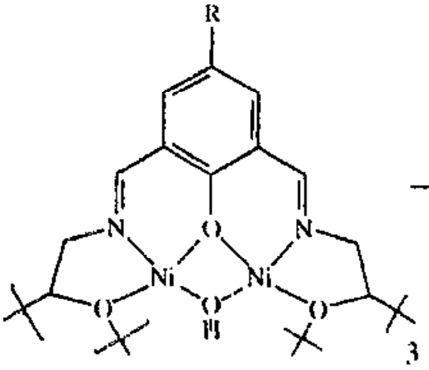


(121)

Turning now to potentially dinucleating Schiff base ligands, reaction of 2,6-diformyl-4-methylphenoldi(benzoylhydrazone) (HL) with $NiCl_2$ gave a complex formulated as $[Ni_2(L)(\mu\text{-}Cl)Cl_2(H_2O)_2]\cdot 2H_2O$ [366]. The dinucleating macrocycle H_2L (**121**) has been prepared, and its coordination chemistry with copper explored; as part of this work, a heterodimetallic complex $[Cu(L)Ni(NCS)_2]\cdot H_2O$, in which the Cu(II) is located in the site with the $-CH_2CH_2-$ lateral chain, was prepared [367]. This has pseudo-octahedral Ni(II) coordination as determined by electronic spectroscopy and magnetic measurements; the complex is antiferromagnetic ($J = -90\ cm^{-1}$). The compartmental macrocycle produced by condensation of 2,6-diformyl-4-chlorophenol with 1,5-diamino-3-oxapentane reacts with nickel(II) acetate to give green $[Ni_2(L)(CH_3COO)_2]$, which spectroscopic evidence suggests has octahedral coordination, with didentate acetate ions and no ether oxygen coordination [368]. When 1,8-diamino-3,6-dioxaoctane was employed, complexes analysing as $Ni_4(L)(X)_{6-x}(OH)_x\cdot nH_2O$ ($X = NO_3^-$, CH_3COO^-, Cl^-, ClO_4^-) were obtained.

in which presumably coordination of ether oxygens occurs, and hydroxyl ions as well as phenolate oxygens bridge the metal ions. Mononuclear complexes $[Ni(L)]\cdot nH_2O$ (H_2L = condensation product of 2,3-dihydroxybenzaldehyde or 2-hydroxy-3-methoxybenzaldehyde with 1,5-diamino-3-oxapentane) were also prepared.

Template condensation of 2,6-diformyl-4-R-phenol (R = Me, ^{t}Bu) with 1,3-diamino-2-hydroxypropane in the presence of nickel(II) perchlorate or nitrate gave novel hexanickel(II) complexes of a 30-membered macrocycle consisting of three diformylphenol and three diamine units, the general arrangement of which is shown in **(122)** (H_6L) [369]. The Ni(II) ions have octahedral geometry and the coordination is completed by water molecules and by additional OH bridging between two adjacent Ni_6 macrocycle units as found crystallographically for the Cu(II) complex, giving a formula $[Ni_6(L)(\mu\text{-}OH)_3(H_2O)_6]_2X_6\cdot nH_2O$ ($X = NO_3$, $n = 16$; $X = ClO_4$, $n = 4$).



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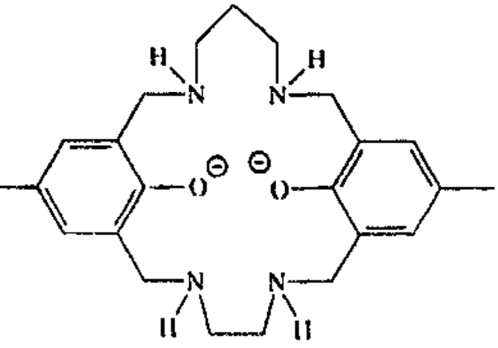
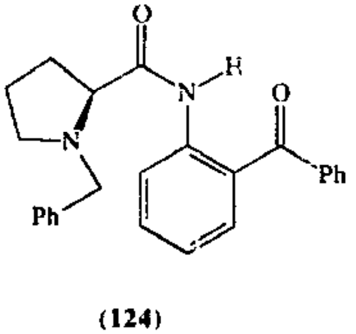


(123)

Mixed V(IV)/Ni(II) and V(V)/Ni(II) complexes of the unsymmetrical dinucleating ligand **(123)** have been reported [370]. Treatment of the ligand with $V(O)(acac)_2$ gave a mixture, which on treatment with nickel(II) perchlorate gave three complexes. The first, $[\{V^{IV}O(L)Ni(H_2O)\}\{V^{V}O_2(HL)\}](ClO_4)_2\cdot 3H_2O\cdot 2.5MeOH$, was characterised crystallographically. The six-coordinate V(IV) occupies the larger compartment of one macrocycle, and a second $V^{V}O_2$ group is coordinated by the smaller N_2O_2 compartment of a second ligand (the larger compartment is unoccupied, and one of its amine nitrogens is protonated). Both the *cis*- $V^{V}O_2$ oxygens additionally bridge, one to the V(IV) and one to the octahedral Ni(II); the Ni(II) is additionally coordinated by a water molecule. The other two complexes isolated are $[V^{IV}O(L)Ni(H_2O)_2](ClO_4)_2$ and $[Ni(L)V^{IV}O](ClO_4)_2$, where the metal ion on the left hand side of the formulae represents the ion occupying the smaller compartment of the macrocycle. A complex $[Ni(L)V^{IV}O(SO_4)]\cdot H_2O$ was also obtained using vanadyl sulfate as precursor.

The *R* and *S* isomers of **(124)**, in the presence of Ni(II), undergo Schiff base condensation with glycine to afford square planar complexes with the Ni(II) coordinated to carboxylate, imine, deprotonated amide and tertiary amine donors [371]. These can then undergo aldol condensations with aldehydes with a high degree of



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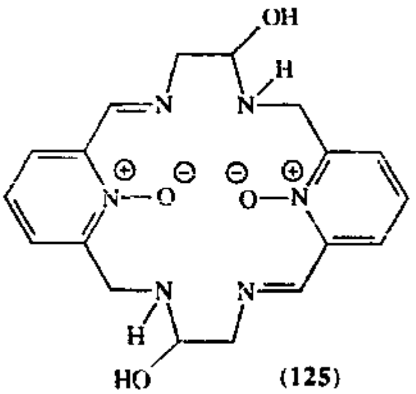


(125)

enantio- or diastereoselectivity. Subsequent hydrolysis leads to *syn*-(2*R*)- or *syn*-(2*S*)-3-substituted serines; the chiral Ni(II) complex can be recycled by condensation with more glycine.

Template condensation of 2,6-diformyl-pyridine-1-oxide, en and nickel(II) nitrate gave a complex $[Ni_2(L)(H_2O)_4](NO_3)_4 \cdot 2H_2O$ (L = (**125**)), in which partial hydrolysis of the expected Schiff base macrocycle has occurred. In this centrosymmetric complex, the macrocycle adopts a folded conformation, and the coordination shell of each Ni(II) ion is completed by two *cis* waters. There is antiferromagnetic coupling ($J = -15.5$ cm^{-1}) between Ni(II) ions.

10.5. *$R_2P(O)NR'$ ligands*

The complexes $[Ni\{^tBu_2P(O)NR\}_2]$ ($R = {}^iPr$, cy) are very unusual in being both square planar and paramagnetic, with $S = 1$ ground states. A theoretical study attributes this to the very small N–Ni–O angle (74°), which lowers the energy of the $d_{x^2-y^2}$ orbital and raises that of the d_{xy} orbital, rather than the asymmetry in the donor strengths of N and O in these ligands, which had previously been put forward as the explanation [372].

11. Complexes with phosphines and related donor ligands

11.1. *Ligands with a single phosphorus donor atom*

The cyanation of vinyl halides with alkali metal cyanides catalysed by $[Ni(PPh_3)_n]$ species has been studied; the reaction gave better selectivity over Ni-catalysed reductive coupling when a degree of solubility of MCN was achieved by using dmf as solvent [373]. Alkylation of $[NiCl_2(PMe_3)_2]$ with $Mg\{CH(SiMe_3)_2\}Cl$ yields the chloro-bridged dimer $[Ni\{CH(SiMe_3)_2\}(\mu\text{-}Cl)(PMe_3)]_2$. This readily inserts CN^tBu to afford $[Ni\{\eta^2\text{-}C(N^tBu)CH(SiMe_3)_2\}Cl(PMe_3)]$, the first structurally characterised Ni(II) complex with an η^2-alkaneimidoyl ligand [374]. The complex $[Ni(N_3)(PMe_3)_4]BF_4$ has been the subject of an X-ray crystallographic study [375]. This is trigonal bipyramidal, with the azide ion axial (Ni–N 1.929(6) Å), is the only known five-coordinate Ni(II) complex with an azide ligand, and has the largest observed Ni–N–N angle yet seen for a terminal azide ligand for Ni(II), 138.6(5)°. The crystal structure has also been reported of *trans*-$[Ni(SPh)_2(PBu_3)_2]$ (centrosymmetric, Ni–S 2.217(2) Å, Ni–P 2.245(2) Å) [376]. As part of a study of relativistic effects on M–L bond strengths in π-complexes, the bonding in $[Ni(PH_3)_2(\eta^2\text{-}L)]$ ($L = O_2$, C_2H_4, C_2H_2) has been modelled using density functional methods [377]. The ^{61}Ni NMR spectra of dicarbonylnickel and tricarbonyl nickel phosphine complexes have been studied [378]. The ^{31}P suspension NMR spectra of silica-immobilised bifunctional phosphines, and of their di- and tricarbonylnickel complexes, have been recorded and the results compared with those from conventional MAS–NMR spectroscopic methods [379]. New methods for immobilising nickel carbonyl–phosphine complexes to silicas via reactions of surface-immobilised aminosilanes have been described [380]. Reaction of hydroxyl-terminated surfaces with $SiCl_4$ followed by NEt_2H gave covalently-anchored O_3SiNEt_2 species, which were either directly reacted with $[Ni(CO)_2(PPh_3)_2]$ to give surface-localised $[Ni(CO)_2(PPh_3)(O_3SiNEt_2)]$ species, or treated with $HO(CH_2)_3PPh_2$ then $[Ni(CO)_2(PPh_3)_2]$ to give surface-anchored $[Ni(CO)_2(PPh_3)(O_3SiO\{CH_2\}_3PPh_2)]$.

Addition of KNHAr′ to the complex *trans*-$[Ni(Ar)Cl(PMe_3)_2]$ (Ar = Ph, 2,4,6-$Me_3C_6H_2$; Ar′ = Ph, 2,6-$^iPr_2C_6H_3$) gave monomeric Ni(II)-arylimido complexes $[Ni(PhNH)(Ar)(PMe_3)_2]$ [381]. In solution, these are in equilibrium with dimeric complexes formed by loss of PMe_3. The complexes $[Ni(Ar'NH)(Ar)(PMe_3)_2]$ (Ar = 2,4,6-$Me_3C_6H_2$) react with H_2O to form $[Ni(\mu\text{-}OH)(PMe_3)(Ar)]_2$, and the coordinated arylimido group can undergo insertion of small, electrophilic molecules into either the Ni–N or N–H bonds. The crystal structures have been reported of $[Ni(PhNH)(Ar)(PMe_3)_2]$ (Ar = 2,4,6-$Me_3C_6H_2$) [382], and of one of the insertion products, *trans*-$[Ni(2,4,6\text{-}Me_3C_6H_2)\{N(Ph)C(O)N(H)^tBu\}(PMe_3)_2]$ (Ni–C 1.930(7) Å, Ni–N 1.978(6) Å, Ni–P 2.212(3), 2.206(3) Å) [383]. Complexes *trans*-$[Ni(Ar)(PR_3)_2(OAr')]$ (R = Et, cy; Ar = 2-MeC_6H_4, 2-FC_6H_4; Ar′ = 4-FC_6H_4, 4-$NO_2C_6H_4$) have been synthesised by the reaction of Ar′OK with cationic Ni(II) complexes generated by treatment of $[Ni(Ar)(PR_3)_2Cl]$ with $TlBF_4$ [384]. Exchange reactions of the phenoxy ligands have also been examined.

Treatment of $[Ni(cod)_2]$ with either PEt_3 or 1,2-bis(dicyclohexylphosphino)ethane (dcpe), and 2,3-dichloropyridine, gave $[NiCl(3\text{-}ClC_5H_3N\text{-}2)(PEt_3)_2]$ or $[NiCl(3\text{-}ClC_5H_3N\text{-}2)(dcpe)]$, whereas reaction with $[NiCl_2(PPh_3)_2]$ in presence of excess Zn gave dimeric (C,N-bridged) $[Ni_2Cl_2(\mu\text{-}3\text{-}ClC_5H_3N\text{-}2)_2(PPh_3)_2]$, characterised by X-ray crystallography [385]. A similar reaction between $[NiBr_2(PPh_3)_2]$ and 3,4-dichloropyridine gave a mixture of isomers $[NiBr(3\text{-}BrC_5H_3N\text{-}4)(PPh_3)_2]$ and $[NiBr(4\text{-}BrC_5H_3N\text{-}3)(PPh_3)_2]$, which readily reacted with dcpe with displacement of PPh_3. Alkali metal reduction of these complexes gave unstable species thought to be Ni(0) complexes of 2,3- or 3,4-pyridynes.

Turning to phosphine ligands including other potential donor atoms, paramagnetic complexes $[NiX_2(L)_2]$ (X = Cl, Br; $L = PPh_{3-n}(2\text{-pyridyl})_n$) were isolated, usually as hydrates, on treatment of $NiX_2 \cdot nH_2O$ with L in glacial acetic acid or toluene [386].

An unusual complex $[NiCl_2\{P(2\text{-pyridyl})_3\}]\cdot H_2O$ was also isolated. Characterisation of these complexes was hampered by their instability in solution; tetrahedral geometry is postulated, although one example, $[NiBr_2\{P(2\text{-pyridyl})_3\}_2]\cdot 2H_2O$, is pale pink. The Ni(0) complexes $[Ni(CO)_2(Ph_2P\{2\text{-pyridyl}\})_2]$ and $[Ni(L)_4]$ ($L = Ph_2P(2\text{-pyridyl})$, $PhP(2\text{-pyridyl})_2$) are also described; the ligands bind only *via* P in these complexes, which could not be isolated free of paramagnetic impurities. Complexes of Ni(II) with the aminomethylphosphine formed on reaction of 4′-amino-15-crown-5 with Ph_2PH/H_2CO have been characterised [387]. The coordination chemistry of the enolates of $R_2PCH_2C(O)Ph$ (L^-; R = Cy, ${}^iPr$) with Ni(II) has been examined. Square planar chelate complexes $[Ni(L)(Ph)(PPh_3)]$, with the ligand bound *via* both phosphine and alkoxy oxygen, have *trans*-disposed phosphine ligands as established by ${}^{31}P$ NMR spectroscopy. Complexes *trans*-$[Ni(L)_2]$ were also characterised. The ligand bis(2-ethoxyethyl)benzylphosphine (L) forms a complex $[NiCl_2(L)_2]$ which X-ray crystallography revealed has a *trans* square planar geometry with the ligands bound only through phosphorus (Ni–Cl 2.1628(10) Å, Ni–P 2.2431(11) Å) [388]. Attempts to abstract chloride ions with silver salts, to promote ether coordination, failed, and treatment with $NiBPh_4$ resulted in formation of *trans*-$[NiCl(Ph)(L)_2]$, also characterised crystallographically.

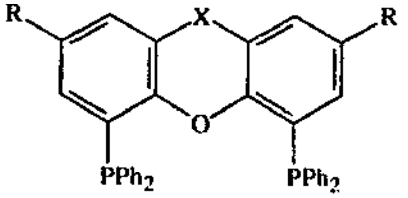
When the iminozirconiophosphorane $Me_2P(Zr\{Cp\}_2Cl){=}NAr$ ($Ar = 2,4,6\text{-}{}^tBu_3C_6H_2$) was treated with $NiCl_2$, the complex $[NiCl_2(Me_2P\text{-}N(H)Ar)_2]$ was isolated, with the ligand bound *via* phosphorus only [389].

11.2. Ligands with two phosphorus donor atoms

Beginning with dppm and its analogues, the syntheses and characterisation of complexes $[Ni(CO)_2(\eta^1\text{-dppm})_2]$, $[Ni_2(CO)_4(\mu\text{-dppm})_2]$ and $[Ni_2(CO)_2(\mu\text{-CO})(\mu\text{-dppm})_2]$ has been suggested as a suitable topic for undergraduate experiments [390]. The crystal structure of *trans,trans*-$[Ni_2(CN)_4(\mu\text{-}Me_2PCH_2PMe_2)_2]$, prepared by reaction of $NiCl_2\cdot 6H_2O$, the diphosphine and $NaBH_3CN$ in EtOH, has been determined (centrosymmetric; Ni–CN 1.869(3), 1.896(3) Å, Ni–P 2.190(1), 2.198(1) Å) [391]. Mass spectra of $[Ni_3(\mu_3\text{-}L)(\mu_3\text{-}I)(\mu\text{-dppm})_3]^{n+}$ ($L = I^-$, CO, NO^+, various CNR; n = 0, 1 or 2) have been determined by the plasma desorption and FAB techniques [392]. Strong molecular ion peaks were seen for all complexes except the nitrosyl, and similar ion fragmentation patterns occurred with both techniques. Dimers of trimer clusters, made using bridging CN–R–NC ligands, were indistinguishable from complexes of RNC by NMR spectroscopic methods, but were unambiguously identified by mass spectrometry. *In situ* FTIR experiments have shown that a Pt electrode modified with a layer of polyvinylalcohol containing $[NiCl_2(\eta^1\text{-dppm})(\eta^2\text{-dppm})]$ electrocatalyses the reduction of CO_2 to with, uniquely for a Ni-catalysed reduction, C–C bond formation to give oxalate [393].

Whereas treatment of Ni(III) (or Ni(IV)) complexes of $1,2\text{-}C_6H_4(EMe_2)_2$ (E = P, As) with I^- yielded Ni(II)-polyiodide complexes rather than Ni(II)-iodo complexes, oxidation of $[NiI_2(L\text{-}L)_2]$ ($L\text{-}L = 1,2\text{-}C_6H_4(AsMe_2)_2$, $1,2\text{-}C_6F_4(AsMe_2)_2$) suspended in 40% HBF_4 with HNO_3 gave Ni(III) complexes $[NiI_2(L\text{-}L)_2]BF_4$ [394].

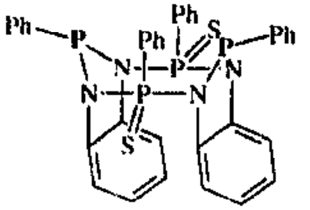
These were characterised by electronic and ESR spectroscopy, and also using Ni K-edge EXAFS (Ni–As 2.35 Å, Ni–I 2.73 Å). Interestingly, attempts to make phosphine analogues failed. The crystal structure of [Ni(dppe)(4-morpholinecarbodithioate-*S,S'*)]$ClO_4 \cdot CH_2Cl_2$ has been determined (Ni–P 2.168(1), 2.160(1) Å; Ni–S 2.1948(12), 2.2139(12) Å) [395].



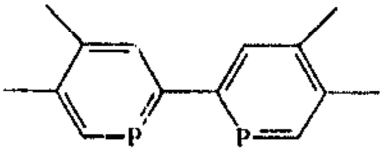
(126)

X	R	Bite angle
H,H	H	101°
$SiMe_2$	H	105°
S	Me	106°
CMe_2	H	109°
(bond)	H	131°

A series of new diphosphines, designed to have large bite angles (**126**) (bite angles calculated using molecular mechanics), has been synthesised, and their application in Ni-catalysed hydrocyanation of styrene examined [396].



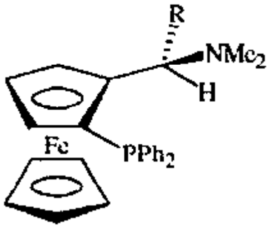
(127)



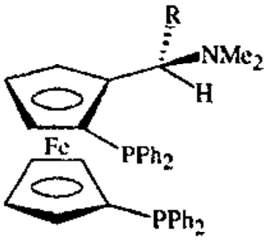
(128)

The cyclotetraphosphazene (**127**) (L–L; phosphorus donor atoms in bold) reacts with [$Ni(CO)_2(PPh_3)_2$] in refluxing CH_2Cl_2 to afford tetrahedral [$Ni(CO)_2$(L–L)], the crystal structure of which shows that relatively little distortion of the cyclotetraphosphazene ring occurs on coordination [397]. The 2,2'-biphosphinine (**128**) (L–L) reacts with [$NiCl_2$(dppe)] or [$NiCl_2(PPh_3)_2$] in presence of excess Zn powder to afford [Ni(L–L)(dppe)] or [Ni(L–L)($PPh_3)_2$], and with $NiBr_2$ under the same conditions to afford [Ni(L–L$)_2$] which was characterised crystallographically [398]. The Ni–P bonds (2.141(1)–2.149(1) Å) are significantly longer than those in [$Ni(PPh_3)_4$] (2.1274(5) Å), probably because of the small P–Ni–P angle (85°) imposed by the biphosphinine rings in [Ni(L–L$)_2$]. Cyclic voltammetry revealed two reversible monoelectronic reductions for [Ni(L–L$)_2$] at −1.64 and −1.89 V. Thus the biphosphinine complex is more readily reduced than [Ni(bpy$)_2$] (first reduction wave at −1.97 V; not reversible).

Turning to ligands containing other potential donor atoms, the ligand (2-pyridyl$)_2PCH_2CH_2P$(2-pyridyl$)_2$ (L–L) reacts with $NiBr_2$ to give brown [$NiBr_2$(L–L)], which is square planar with only the phosphorus donors coordinated. On reaction with [$Ni(CO)_2(PPh_3)_2$] the ligand gave air-stable [$Ni(CO)_2$(L–L)]$\cdot 2H_2O$, which is water-soluble, and [Ni(L–L$)_2$] could also be made from [Ni(cod$)_2$] [386]. The synthesis and crystal structure of the square planar cyclometallated complex [Ni(L)Br] (HL = 2,6-[{*cyclo*-C_6H_{12}}$_2$$PCH_2$]$_2$$C_6H_4$) have been reported [399].



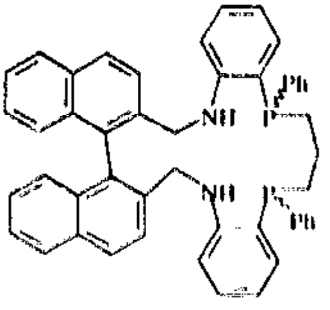
(129)



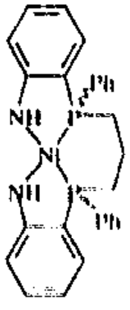
(130)

R = Et, Bu

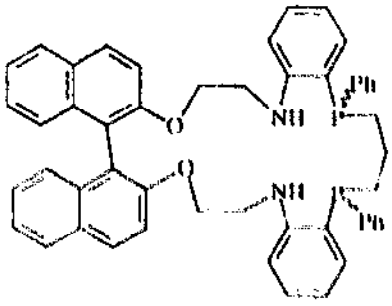
New chiral phosphines (**129**) and (**130**) have been tested in catalytic asymmetric nickel-catalysed cross-coupling reactions [400]. In a variety of reactions, they gave higher e.e.'s than the analogue with R = Me. Sulfonated aminomethylphosphines (Et_3NH)[(R_2PCH_2)$_2$N(CH_2)$_n$$SO_3$] (R = Ph, n = 1,2 or 3; R = cy, n = 1) have been prepared [401]. Reaction of Et_3NH[({C_6H_{12}}$_2$$PCH_2$)$_2$$NCH_2SO_3$] ({$Et_3NH$}L) with $NiCl_2$ in EtOH gave (Et_3NH)[$NiCl_2$(L)], which was insoluble in organic solvents or water.



(131)

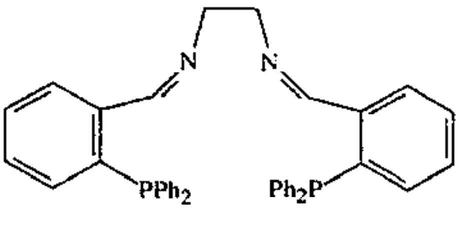


(132)



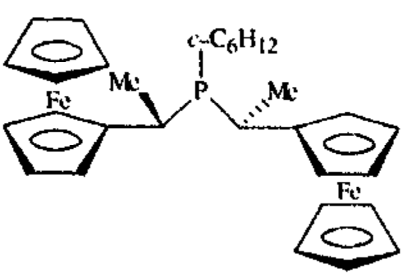
(133)

The ligands (**131**) (three diastereoisomers) have been synthesised; of these, only the C_2-symmetric isomers gave a complex [NiCl(L)]Cl, which was the subject of X-ray crystallography [402]. The Ni(II) ion is square planar and coordinated to both phosphorus atoms, one chloride ion and one of the amine nitrogens. The relative configuration is $(R)_{axial}(R,R)_P$ (and $(S)_{axial}(S,S)_P$ for the enantiomer). Treatment of the neutral Ni(II)-amide complex (**132**) with the appropriate ditosyl compound gave (**133**) as its Ni(II) complex; the free ligand was isolated by treatment of the latter with CN^-. This ligand also reacted with $NiCl_2$ to afford [NiCl(**133**)]Cl, with a structure very similar to that of [NiCl(**131**)]Cl. Finally, treatment of the ligand (**134**) (L) with NiI_2 gave [Ni(L)I]I, the X-ray crystal structure of which showed distorted square pyramidal geometry, with an axial iodide ligand weakly coordinated (Ni–I 2.807(6) Å) [403]. The room temperature magnetic moment of this complex (2.35 B.M.) is anomalous; a spin-state equilibrium is postulated to account for this. Also examined was the reaction between the product of treatment of **(134)** with iodine (of stoichiometry LI_4) and Ni powder, which gave a yellow complex of composition $NiLI_4$, which it is suggested is $[Ni(L)I]I_3$.

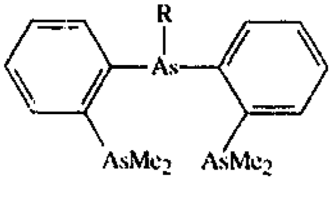


(134)

11.3. *Ligands with more than two phosphorus donor atoms*



(135)



R = Me, Ph

(136)

The new chiral ligand **(135)**, and its square planar Ni(II) complex $[Ni(L)(CH_3CN)](ClO_4)_2$, have been described [404]. Further studies have been reported of five-coordinate homoleptic Ni(II)-arsine complexes $[Ni(L)\{o\text{-}C_6H_4(AsMe_2)_2\}](ClO_4)_2$ (L=**(136)**) [405]. The crystal structure of the complex (R=Ph) has been determined. The geometry is distorted square based pyramidal, with the central and one terminal donor atom occupying basal sites and the remaining terminal donor occupying the axial site. The didentate ligand occupies the remaining basal site. As is usual in these low-spin d^8 species, the $Ni–As_{apical}$ distance (2.400(2) Å) is larger than the mean $Ni–As_{basal}$ distance (2.285(2) Å). Variable temperature ^1H NMR spectroscopic data reveal unusual fluxional processes. At low temperatures, there is rapid exchange of square pyramidal enantiomers as one of the donor atoms of the didentate oscillates between equivalent sites. At higher temperatures, both donor atoms of the didentate migrate over the three positions of a facial site on the complexes. The tridentates appear rigid during these processes.

The complexes $[Ni(L)(py)](BF_4)_2$ and $[(L)Ni(\mu\text{-}4,4'\text{-bipyridine})Ni(L)](BF_4)_4$ (L=tris-[2-diphenylphosphinoethyl]phosphine) have been described; these are low-spin, five-coordinate species, and the crystal structure of the pyridine derivative has been determined [406]. The electrochemistry of $[Ni(L)X]^+$ (L=tris[2-diphenylphosphinoethyl]phosphine; X=Cl, Br, I) has been studied in CH_3CN and CH_2Cl_2 [407]. The cations undergo reduction to the Ni(0) complexes $[Ni(L)X]^-$. For X=Br and I, this is followed by loss of X^- and formation of a L-bridged Ni(0) dimer. In CH_3CN, $[Ni(L)I]^-$ also undergoes iodide displacement by solvent. All the complexes were reversibly oxidised to Ni(III), and a further irreversible oxidation at more positive potentials was attributed to a Ni(III)/Ni(IV) couple.

Finally, photoinduced intramolecular electron transfer in the 1,2,4,5-tetrakis(diphenylphosphino)benzene (L)-bridged Os(II)/Ni(II) complex $[(bpy)_2Os(L)Ni(dppb)]$ (dppb = 1,2-bis(diphenylphosphino)benzene) has been investigated [408]. Emission quantum yields reflect substantial intramolecular interaction between the metal centres in the excited state. Slight shifts in the redox potentials compared with model complexes $[Ni(dppb)_2]^{2+}$ and $[Os(bpy)_2(dppb)]^{2+}$ indicate modest interactions in the ground state also. There is evidence for quenching of the Os(II) MLCT excited state by Ni(II).

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