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Review

Structural and functional models related to the nickel hydrogenases

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Abstract

In this review a historic overview is given of the biomimetic models synthesised since the presence of nickel in hydrogenases was first reported in 1981. The crystal structure of the [NiFe] hydrogenase isolated from *Desulvofibrio gigas* unexpectedly revealed a heterodinuclear active site, including a nickel ion and an iron centre. This report in 1995 gave an impetus to the development of new structural models for these enzymes. This review is focussed on the synthesis, spectroscopic features, and reactivity of the complexes that have been designed and synthesised as model systems for [NiFe] hydrogenases, with special attention for the heterodimetallic complexes that have been reported in the past decade. The complexes are classified according to the various ligand types, including sulfur, oxygen, nitrogen, and phosphorus donor atoms.

Keywords: [NiFe] hydrogenase; Model systems; Nickel; Iron; Structures; Biomimetic

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Abbreviations: dapa, 2,6-bis[(1-phenylimino)ethyl]pyridine; dppe, 1,2-bis(diphenylphosphanyl)ethane; terpy, 2,2′,6′,2″-terpyridine; triphos, bis(1-diphenylphosphanyl-2-ethyl)phenylphosphane; XAS, X-ray absorption spectroscopy; H_2atp, 2-aminothiophenol; H_2baopy, 2,6-bis(acetyloxime)pyridine; H_2bmes, bis(2-mercaptoethyl)sulfide; H_2btcpy, pyridine-2,6-bis(monothiocarboxylic acid); H_2mben, *N*,*N*′-bis(2-mercaptobenzyl)-1,2-diaminoethane; H_3mbtacn, 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane; Hmep, 2-(2,2-diphenyl-2-mercaptoethyl)pyridine; H_2mp, 2-mercaptophenol; Hmpm, 2-mercaptopyrimidine; H_2sitp, *N*-(2-hydroxybenzylidene)-2-aminothiophenol; H_2tpttd, 1,1,10,10-tetraphenyl-4,7-dithia-1,2dimercaptodecane; H_2tsalen, *N*,*N*′-bis(2-mercaptobenzylidene)-1,2-diaminoethane; H_2tsalphen, *N*,*N*′-bis(2-mercaptobenzylidene)-1,2-diaminobenzene; H_2ttn, 3,7-dithia-1,9-dimercaptononane

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1. Introduction

1.1. Nickel hydrogenases; a brief historical overview

It was only in 1981 that Thauer reported the presence of nickel in specific hydrogenases [1]. A search in the Web of Science with the keywords (nickel and hydrogenas∗) yields 665 hits (period 1945–2004); when, however, the search is limited to the decade after the first report of Thauer (i.e. to 1990) only 80 hits are found, most of which are related to reports of spectroscopic and biochemical research concerning the enzymes.

The rapid growth of the literature after 1990 and especially since 1995 no doubt is related to the X-ray structure of the [NiFe] hydrogenase in that year [3]. Since 1981 it had been assumed that the active site of the [NiFe] enzymes consisted of a mononuclear nickel site. Only the elucidation of the crystal structure of the [NiFe] hydrogenase isolated from *Desulvofibrio gigas* revealed a heterodinuclear active site, with cysteine thiolates bridging a nickel ion with an iron centre, as shown schematically in Fig. 1. The field of heterodinuclear complexes modelling [NiFe] hydrogenase has been reviewed recently [4], a later review focuses on both [NiFe] and [Fe-only] hydrogenases [5]. In the present review a historic overview is given of the biomimetic models for [NiFe] hydrogenases that have been synthesised since the presence of nickel was reported.

1.2. Biomimetic chemistry; the essence of synthetic model systems

One of the main directions of study, among many others, of the bioinorganic chemist is to prepare synthetic, low-molecular weight metal analogues of the active site in metal-containing enzymes. This study can lead to a better understanding of the properties of the active site and can shed light on the catalytic reaction that takes place in the enzyme. The advantage of such models is that they are low-molecular weight compounds and therefore are often more easily isolated and examined spectroscopically than the enzyme itself. Another interesting possibility is that steric and electronic modifications can be generated in the ligand environment of the model compounds that can provide additional information about the active site and its structural and catalytic properties. So, synthetic model systems are designed with several motives and approaches, as outlined below.

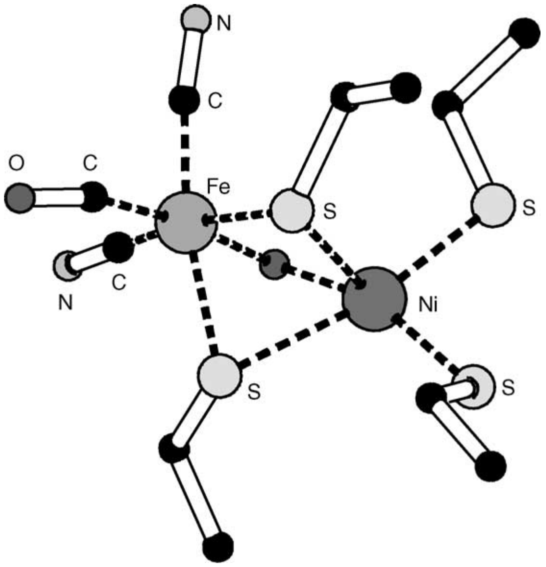

Fig. 1. Schematic drawing of the active site of [NiFe] hydrogenase in the oxidised form [2].

- Model systems may be of use to help estimate the structure of the active site of a protein, when it is not yet known. These structural model systems have generally been known as “speculative models”. The speculative models are designed based on knowledge derived from spectroscopic data such as EXAFS, and can then be used, for instance, with EXAFS spectroscopy as a standard measure to compare the results.
- The “corroborative models” are designed to yield more insight in the correlation between structure and activity of the proteins. When the structure of a protein is known in sufficient detail, and therefore the structure of the active site, low-molecular weight model compounds may give important information about the effect of ligand constraints on the spectroscopic and catalytic properties of the metal ion.
- The knowledge of the structures and properties of the active sites in metalloproteins may be used to design compounds for the application in, for instance, catalysis or as a medicine. These low-molecular weight compounds usually are called “functional models”. In certain cases of such models the structural resemblance may be minimal. For the [NiFe] hydrogenases for example, functional models containing ruthenium have been reported.

The synthesis of chelating ligands and their coordination compounds not only provides routes to a large variety of bioinorganic model systems, but ultimately offers the opportunity to incorporate these ligands in polymers, which may, for instance, lead to immobilized catalysts.

1.3. Structural and functional model complexes for [NiFe] hydrogenases

As early as 1985, the first biomimetic study concerning nickel-containing hydrogenases was reported [6]. Since then, a variety of complexes have been synthesised to structurally model the active site of hydrogenases. Despite the fact of the notation [NiFe] hydrogenases the active site was believed to contain a mononuclear nickel centre; at that time the iron ions were believed to be present solely in the [4Fe–4S] clusters necessary for electron transport. In the years preceding the X-ray structure determination a debate was ongoing concerning the environment of the nickel ion in [NiFe] hydrogenases, and the (formal) oxidation states of the nickel ion in the various redox states of the enzymes [7]. Several nickel complexes will be discussed, including some complexes from before the crystal structure in 1995, which now may seem less relevant. However, for a better understanding of nickel–thiolate chemistry also complexes from the latter category need to be covered in this literature study.

This review gives a historical overview of general trends and lines of research, primarily but not exclusively covering the period after 1995, the year in which the X-ray structure of hydrogenase was reported. As the number of structurally characterised nickel complexes containing at least one sulfur-donor atom exceeds 650 (CSD search June 2004), this review cannot be exhaustive. For more detailed summaries, especially for the period before 1995 the reader is referred to the review of Halcrow and Christou [7].

The electrochemistry data cited in this review all have been converted to values relative to the normal hydrogen electrode NHE.

2. Nickel complexes

2.1. Complexes with sulfur ligands only

Soon after it became apparent that some of the hydrogenases contained nickel in the active site, the first corroborative models were reported. The synthesis, X-ray structure, reactivity and electrochemistry of the homoleptic nickel thiolate complex, $[Ni(SR)_4]^{2-}$ was reported, and the $Ni^{2+} \rightarrow Ni^{3+}$ oxidation potential was compared with those of the hydrogenases [6]. A series of substituted arene thiolates have been used, among which are p-$MeC_6H_4S^-$, m-$MeC_6H_4S^-$, p-$ClC_6H_4S^-$, p-$NO_2C_6H_4S^-$ and Bu^tS^- [8]. The four-coordinate homoleptic complexes readily undergo ligand dissociation. The tetrahedral four-coordinated complex is high spin and paramagnetic, whereas the three-coordinated complex is low spin and diamagnetic. Because of this equilibrium the electrochemistry of the complexes is rather complicated. The $Ni^{II/III}$ oxidation potential shifts from the positive to more negative potentials as the electron-donating strength of the thiolate ligands increases, both for the tetrahedral complexes and for the three-coordinated series. The $Ni^{II/III}$ oxidation potential of the hydrogenases is found in the region of the four-coordinated species. Therefore, these authors suggested that if no anionic ligands other than cysteinates are present, the number of sulfur atoms coordinated to nickel must be four, and the first proposals for the active site of nickel-containing hydrogenases were given [8].

Nearly at the same time, Rosenfield et al. have reported the synthesis and properties of the mononuclear $(R_4N)_2[Ni(SAr)_4]$ complex with $Ar = C_6H_5$, p-C_6H_4Cl, p-$C_6H_4CH_3$ and m-C_6H_4Cl [9]. From the complex $(Et_4N)_2[Ni(S$-p-$C_6H_4Cl)_4]$ a crystal structure has been reported. The arrangement of the four sulfur atoms around nickel(II) is distorted tetrahedral as shown in Fig. 2. The distortion from tetrahedral symmetry is such that two S–Ni–S angles are close to 90° and the other angles are close to 120° with the average Ni–S distance being 2.281 Å. Unfavourable steric interactions between the *ortho*-H atoms and Ni or S atoms do not allow an ideal tetrahedral geometry. In retrospect, these first reports, in fact, appear to contain already the most resembling models for the distorted geometry of the nickel site in hydrogenases. In fact, a nickel ion coordinated to four sulfur ligands has a strong tendency adopt a low-spin square-planar geometry.

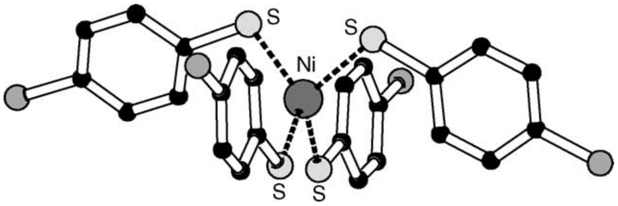

Fig. 2. Structure of $[Ni(S$-p-$C_6H_4Cl)_4]^{2-}$ [9].

After the first reports of homoleptic complexes of nickel with monodentate thiolate ligands, the focus shifted to the use of chelating didentate thiolate ligands such as ethane-1,2-dithiol (H_2L1) [10–13], butane-2,3-dithiol (H_2L2) [11], and benzene-1,2-dithiol (H_2L3) [14–16] (Fig. 3).

The complexes $(Ph_4P)_2[Ni(L1)_2]\cdot 4H_2O$ and $K_2[Ni(L2)_2]\cdot C_2H_5OH$ were obtained in high yields in the reactions of $NiCl_2\cdot 6H_2O$ and excess of the dithiolates [11]. Crystals of these complexes are stable in a dinitrogen atmosphere. However, when the complexes are dissolved in protic or wet aprotic solvents, rapid conversion to dinuclear species is observed. The half-wave potentials of $Ni^{II/III}$ in the complex $[Ni(L1)_2]^{2-}$ are in the range of −0.60 to −0.46 V versus NHE. The oxidised species can undergo degradation or other chemical reactions near the electrode surface. The complex $[Ni(L2)_2]^{2-}$ undergoes more readily reversible oxidation. With a half-wave potential of −0.51 V versus NHE it is clear that the electron-donating methyl groups of the ligand have a large effect on the stability of the complexes. The Ni^{III} complex $[Ni(L2)_2]^-$ obtained by chemical oxidation with $IrCl_4$ exhibits an axial EPR spectrum with $g_{||} = 2.187$ and $g_\perp = 2.042$ [11]. The nickel ion in the complex must have a square-planar geometry, since low-spin Ni(III) centres in square-planar geometry give rise to EPR spectra with $g_{||} > g_\perp$ [11].

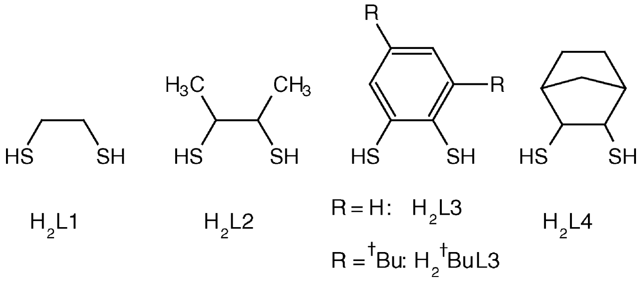

Fig. 3. Chelating didentate thiol ligands.

In a reaction of $NiCl_2(PPh)_3$ with H_2L3 in a ratio 1:2 in the presence of sodium methoxide the mononuclear complex $[Ni^{III}(L3)_2]^-$ is formed [16]. The intermediate nickel(II) complex $[Ni(L3)_2]^{2-}$ oxidises spontaneously with a half-wave potential of −0.23 V versus NHE to Ni(III) [17]. Investigations on the related *t*-butyl-substituted benzene-1,2-dithiolate ligand have shown that the complex anion $[Ni(^tBu–L3)_2]^{2-}$ can be oxidised to $[Ni(^tBu–L3)_2]^-$ and $[Ni(^tBu–L3)_2]^0$. Sellmann et al. have claimed that these oxidations are mainly "$[NiS_4]$" centred, based on an X-ray structure and spectroscopic investigations [18]. The complex $[Ni(^tBu–L3)_2]^-$ at 120 K shows a rhombic EPR signal (g = 2.18, 2.04, 2.01); a ^{61}Ni enriched sample shows the expected additional strong hyperfine coupling of the unpaired electron with the ^{61}Ni nucleus (I = 3/2) [18].

Other dithiolate ligands comprise *trans*-1,2-dimercaptocyclohexane [19] and biphenyl-2,2′-dithiol [20], both resulting in square-planar nickel complexes of general formula $[Ni(L)_2]^{2-}$. Fox et al. have used the chelating didentate ligand norbornane dithiol H_2L4 [21]. The nickel(II) ion in the complex $[Ni(L4)_2]^{2-}$ is square planar. The complex has an increased stability with respect to oligomerisation reactions compared to complexes described previously. The explanation for this is the rigid conformation of the S–C–C–S chelating unit in the norbornane backbone. The half-wave $Ni^{II/III}$ oxidation potential of this complex is −0.52 V versus NHE in DMF. This was the lowest oxidation potential reported for non-biological nickel complexes till that time. Cyclic voltammetric studies of this complex in MeOH show a cathodic positive shift to −0.22 V. When a DMF solution of $[Ni^{II}(L4)_2]^{2-}$ is exposed to air, the nickel ion is oxidised immediately and an axial EPR signal with $g_{||} = 2.14$ and $g_{\perp} = 2.05$ is obtained, consistent with a Ni(III) complex with an $S = 1/2$ ground state.

As thiolate groups have a strong tendency to form bridges between two or three metals, a reaction of a nickel(II) salt with simple alkyl thiols readily results in the formation of oligonuclear or polynuclear complexes. With the chelating didentate ligands also oligonuclear complexes are readily formed, apart from the mononuclear complexes described above [10,13]. Even for aromatic thiolates oligonuclear complexes may be formed [22], although the tendency of aromatic thiolates to form bridges is markedly less than for alkyl thiolates. With the aromatic ligand H_2L3 the neutral trinuclear nickel(II) cluster $[Ni_3((\mu)_2–L3)((\mu, \mu')–L3)_2(PPh_3)_2]$ has been obtained [16]. The average Ni···Ni distance in this unusual trinuclear cluster, shown in Fig. 4, is only 2.52 Å, which is relatively short compared to other trinuclear Ni-thiolate complexes. This cluster is asymmetric, two of the nickel centres are in a five-coordinated distorted square–pyramidal geometry and one nickel centre is four-coordinated square planar. The cluster is soluble in many solvents, including DMF, toluene and THF. The electronic spectral properties of this complex are quite different in polar solvents compared to apolar solvents. In polar coordinating solvents, the spectrum of this complex shows two charge-transfer bands at 517 and 670 nm, while in non-coordinating solvents, the bands are visible at 435 and 585 nm. The explanation for this is that in non-coordinating solvents the trinuclear complex remains intact, while in coordinating solvents it fragments into the charged species $[Ni(L3)_2]^{2-}$ and $[Ni_2(\mu-L3)(PPh_3)_2(solvent)_2]^{2+}$. Apart from the discrete mononuclear complexes described above, a large number of oligonuclear homoleptic nickel thiolate complexes have been reported that are not of relevance for the hydrogenase active site.

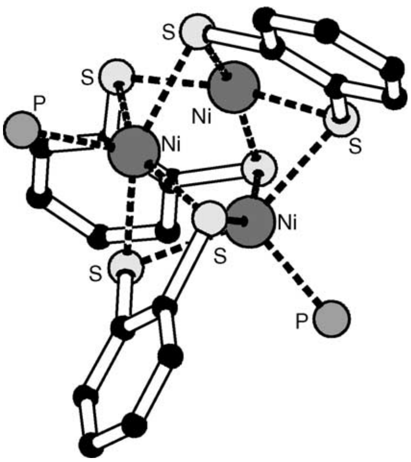

Fig. 4. Structure of $[Ni_3((\mu)_2–L3)((\mu, \mu')–L3)_2(PPh_3)_2]$, the phenyl rings of PPh_3 have been omitted for clarity [16].

To avoid the formation of undesired oligomeric complexes and as a means to gain control over the geometry of the nickel complexes, chelating ligands containing both thiolates and thioether sulfur-donors have been designed and synthesised. Yamamura et al. have used the linear aliphatic ligand 3,7-dithia-1,9-dimercaptononane (H_2ttn) and the sterically encumbered, phenyl substituted ligand 1,1,10,10-tetraphenyl-4,7-dithia-1,2dimercaptodecane (H_2tpttd) and reported the structure and spectroscopic study of the mononuclear complexes [Ni(ttn)] and [Ni(tpttd)] [23,24]. The nickel ion in both complexes is in a slightly distorted square-planar arrangement. Electrochemistry showed only irreversible waves for [Ni(ttn)]; in contrast the complex [Ni(tpttd)] shows a reversible reduction at −1.15 V versus NHE [24]. Recently the complex [Ni(ttn)] has been reinvestigated in its reactivity to other metal centres in relation with heterometallic active sites in metalloenzymes, resulting in pentanuclear Ni_3Cu_2 clusters [25].

Sellmann et al. have reported a very large number of important papers relevant to the nickel hydrogenases in the series "transition metal complexes with sulfur ligands". Nickel complexes have been synthesised with a variety of thiolato-thioether ligands, some of them including nitrogen and oxygen donors in S_6, S_5, OS_4, NS_4, S_4, and S_3 donor sets [18,26–30]. A selection of these ligands is shown in Fig. 5.

The nickel(II) ion in the complex [Ni(L7)] is square planar and diamagnetic, the two central thioether sulfur atoms do not coordinate to the nickel centre. The ligands L6O and

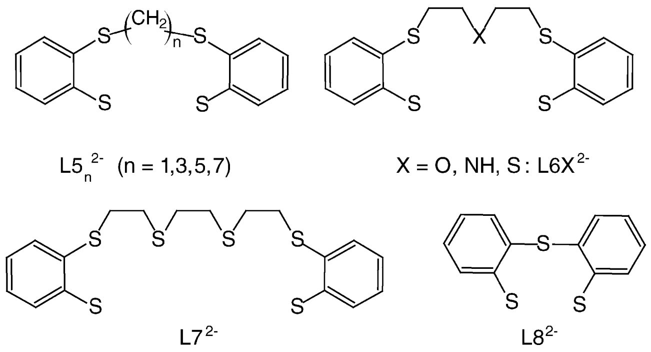

Fig. 5. A selection of the ligands used by Sellmann et al.

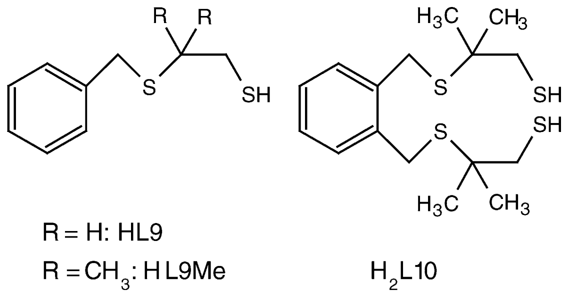

Fig. 6. Ligands used by Verhagen et al.

$L5_5$ form dinuclear nickel complexes in which the oxygen atom of the former ligand is not involved in the coordination of the nickel ion. Two sulfur atoms of one phenyl ring are coordinated to the first nickel centre and the other two sulfur-donor atoms are coordinated to the next nickel centre. In this fashion two ligands are coordinated to two nickel centres. The compounds [Ni(L6NH)] and [Ni(L6S)] are mononuclear five-coordinate complexes, in which the NH-group and the central sulfur atom are also involved in coordination. The coordination of the secondary amine to nickel has been confirmed by the result that no H/D exchange at the nitrogen takes place with this complex (see Section 5.2). In H/D exchange, both the deuteron and the hydron[1] have to bind simultaneously to the nitrogen atom, but this cannot happen while the nitrogen is coordinated to the nickel centre. The [Ni(L6S)] complex was the first example of a nickel complex with five sulfur-donor atoms. The average $Ni–S_{thiolate}$ distance is 2.19 Å, which is slightly longer than the average four-coordinated square planar nickel–thiolate complexes, but is shorter than the average nickel–thiolate distances in five-coordinated and six-coordinated nickel thiolate complexes and is also shorter than found in the hydrogenases. The average $Ni–S_{thioether}$ distance of 2.21 Å is shorter than those typically found for nickel–thioether complexes. The central thioether donor is only weakly coordinated at the apex at a distance of 2.74 Å. The ligand $L6S^{2-}$ shown in Fig. 5 and variations on this ligand have also been used by Cha et al. [15,17]. They reported that this complex remains five-coordinated in most coordinating solvents, except in pyridine, in which a paramagnetic octahedral species is formed. Electrochemical reduction of [Ni(L6S)] at −0.92 V versus NHE results in a reactive Ni(I) species that ultimately converts to the stable product $[Ni(L3)_2]^{2-}$, showing that the ligand has decomposed [17].

The reactivity of nickel with the $^{R}L8$ ligands has been studied extensively [18,31–33]. Despite the aromatic nature of the thiolates a cyclic trinuclear nickel complex with bridging aromatic thiolates is readily formed. This trinuclear complex reacts with several nucleophiles, resulting in the isolation and characterisation of a large number of mononuclear nickel(II) complexes in square-planar S_3X geometry [28,33]. The molecular structures of these mononuclear complexes show substantial tetrahedral distortion of the nickel ion geometry, with *trans* coordination angles of 160° [28,32]. The reactivity of these complexes in the activation of dihydrogen and the D/H exchange has been studied (see Section 5.2).

Verhagen et al. recently described three new ligands containing thioether and thiolate donor atoms, shown in Fig. 6 [34,35]. It was intended to synthesise ligands with two methyl groups on the carbon α to the thiolate groups in order to prevent oligomerisation of the nickel complexes. During the synthesis of those ligands, however, an unprecedented spontaneous rearrangement occurs, which is very fast and selective for the formation of only one product [35]. The square-planar complexes $[Ni(L9Me)_2]$ and [Ni(L10)] were synthesized by reactions of $[Ni(acac)_2]$ with the thiouroneum precursor salts of the ligands in ethanol in the presence of the base tetramethylammonium hydroxide, thereby circumventing the need to isolate the oxidation-sensitive thiol ligands [35]. In the square-planar complex $[Ni(L9Me)_2]$ the didentate ligands are coordinated with the thiolate groups in *trans* positions, seemingly unfavourable for bridging to a second metal ion. The mononuclear complexes, however, are reactive to other metals and for the didentate ligands comprise a rearrangement from *trans* to *cis*. Only irreversible and quasi-reversible redox couples are observed in cyclic voltammetry, which implies that the Ni(III) and Ni(I) states of the complexes are unstable [35].

Riordan and co-workers have synthesised several thioether-containing ligands based on borates (Fig. 7) [36–39]. A square-planar nickel complex with four thioether donors from two chelating ligands, $[Ni(L11)_2]$, has been obtained [38]. The Ni–S distances in this complex are 2.20 and 2.24 Å and are consistent with other Ni(II)–S(thioether) square-planar complexes. In cyclic voltammetry a quasi-reversible wave at −0.421 V versus NHE is observed, which is assigned to the $Ni^{II/I}$ couple. Frozen solution EPR of the reduced complex shows a rhombic spectrum (g = 2.27, 2.11, 2.03) consistent with metal-centred reduction. Thioethers stabilise low oxidation states of nickel, whereas thiolates tend

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[1] The word *hydron* is used as a general name for the H^+ ion, where it is not desired to distinguish between the isotopes. If one wishes to discriminate between the isotopes, the words *proton*, *deuteron* and *triton* are used for $^1H^+$, $^2H^+$ and $^3H^+$, respectively. ‘Hydronation’ then refers to what is more commonly termed ‘protonation’ but without specifying which isotope is intended.

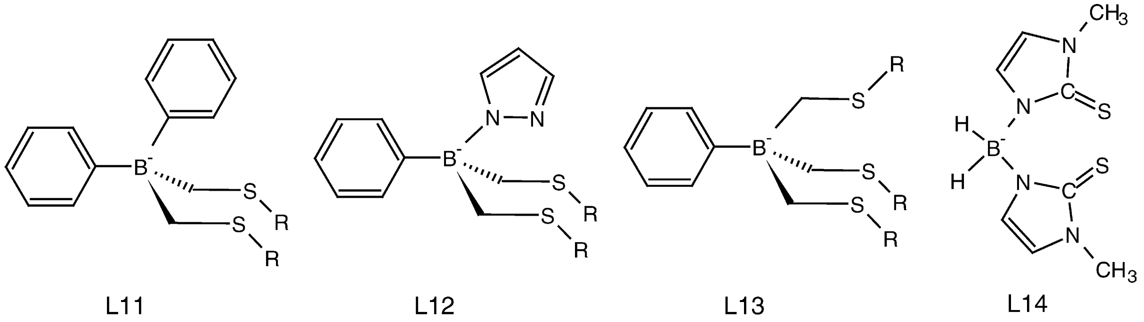


Fig. 7. Borate-based, didentate and tripodal ligands.

to stabilise the higher oxidation states. Riordan et al. claim that thioethers are competent ligands for the modelling of the $Ni^{II/I}$ redox potential for enzyme active sites that contain thiolates in the primary coordination sphere. They explain their statement with the fact that cysteines can be involved in hydrogen bonding, which will change their donor capacity and thereby the redox potential, and therefore in aprotic solvents thioethers are supposedly more accurate as ligands compared to thiolates. With the tripodal ligands L12 and L13 octahedral mononuclear nickel complexes containing two ligands can be synthesised [36,39]; the sterically encumbered tripodal ligand L13 with *t*-butyl thioether groups forms tetrahedral complexes with an additional chloride ion coordinated to the nickel ion [39]. The thioether ligands stabilise the nickel(I) oxidation state and a remarkable reactivity of these nickel complexes towards dioxygen is reported [40].

The ligand bis(2-mercapto-1-methylimidazolyl)borate L14 has been used in coordination with nickel ions by Alvarez et al. [41]. In the complex [Ni(L14)$_2$], shown in Fig. 8, the paramagnetic nickel(II) ion is in an octahedral S_4H_2 chromophore, surprisingly showing interactions with two hydrogen atoms of the borate centres in *cis* positions. The nickel to thione–S distances are rather long, being 2.36 Å, the nickel to H distances are 1.86 Å. The electrochemistry of this complex shows irreversible reductions and oxidations and is complicated by chemical reactions occurring in solution [41].

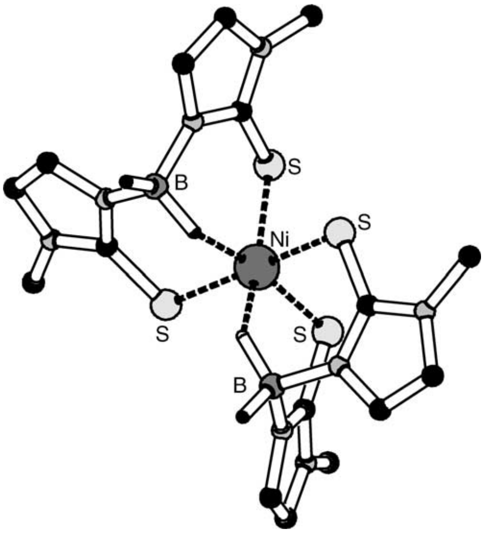


Fig. 8. Structure of [Ni(L14)$_2$] [41].

Nivorozhkin et al. have synthesised a cyclic peptide containing four cysteines and studied the coordination of this peptide with cobalt, nickel and iron [42]. Dinuclear as well as mononuclear complexes were obtained, and based on spectroscopic results and EXAFS analysis it is postulated that the nickel ion in the mononuclear complex comprises a square-planar NiS_4 chromophore.

A large number of cyclic thioether ligands, such as shown in Fig. 9, have been used in modelling the active site of nickel-containing hydrogenases [43–46]. Electrochemistry of these complexes show stabilisation of the nickel(I) oxidation state, the metal-centred reductions being confirmed with EPR studies, in agreement with the observations of Riordan and co-workers [38]. As there are no thiolate groups available that allow bridging to an iron centre, the nickel complexes that have been described with this type of ligands are not further discussed in this review.

2.2. Complexes of ligands containing phosphorus donor atoms

Despite the fact that phosphanes are not naturally occurring ligands, phosphane groups have been successfully used in chelating ligands to stabilise various oxidation states of nickel. Chelating didentate P, S-ligands, such as shown in Fig. 10, have been used in the synthesis of mononuclear nickel complexes, and a comparison has been made for the influence of the phosphorus donor atom on the oxidation potential of the nickel ion [47,48]. Chemical reduction of $[Ni(L15Me)_2]^{2+}$ with Na/Hg results in the tetrahedral Ni(0) complex [Ni(L15Me)$_2$]. This complex is photochemically unstable and dealkylates to form the

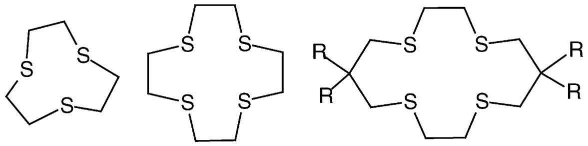


Fig. 9. Some examples of cyclic thioether ligands.

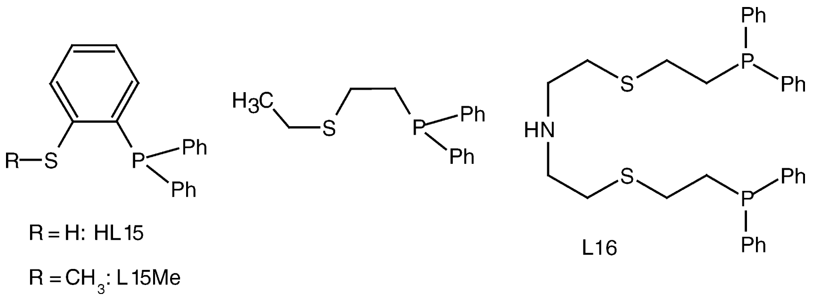


Fig. 10. Examples of chelating P, S ligands.

square-planar nickel(II) complex [Ni(L15)$_2$], in which the thiolate donor atoms coordinate in *trans* positions [48]. The redox behaviour of the nickel complexes is strongly dependent on the presence of the methyl groups. While the methylated complex [Ni(L15Me)$_2$]$^{2+}$ shows two subsequent reductions to Ni(I) and Ni(0), the thiolate-containing complex [Ni(L15)$_2$] reveals only a reversible oxidation to Ni(III). The nickel(I) species [Ni(L15Me)$_2$]$^{+}$ was characterised by an axial EPR spectrum (g values of 2.10 and 1.96) showing a coupling of the unpaired electron with two equivalent ^{31}P nuclei.

The pentadentate ligand L16 forms the five-coordinate low-spin nickel(II) complex [Ni(L16)]$^{2+}$, in which geometry is severely distorted and is actually mid-way between both square–pyramidal and trigonal–bipyramidal extremes. This complex can be chemically reduced with NaBH$_4$ to form the stable nickel(I) complex [Ni(L16)]$^{+}$ in which the geometry of the metal ion has become more regular trigonal bipyramidal with the thioether sulfurs in the apical positions (see Fig. 11) [49]. The electrochemical reduction of nickel(II) to nickel(I) is quasi-reversible and occurs at a half-wave potential of −0.03 V versus NHE. The reaction of the nickel(I) complex with acids results in near-quantitative yields of dihydrogen and a complete kinetic analysis of this reaction has been carried out [49].

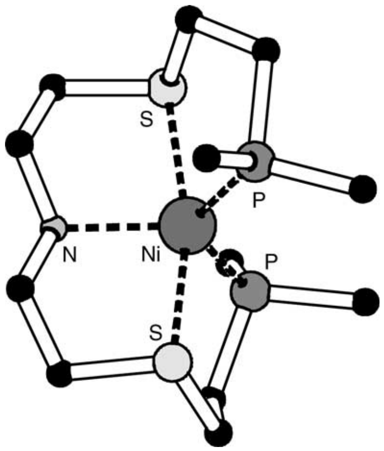


Fig. 11. Structure of [Ni(L16)]$^{+}$, phenyl rings have been omitted for clarity [49].

Phosphorus is also an excellent building block that can be used to form tripodal ligands favouring non-planar coordination geometries. Millar and co-workers have synthesised such tripodal ligands as shown in Fig. 12 [50,51]. The ligand H$_3$L17 forms a centrosymmetric dinuclear nickel(II) complex [Ni(L17)]$_2$$^{2-}$ in which the ligands are shared by the two nickel ions, but without bridging of the thiolate groups. The ligands bind in a tridentate fashion to the nickel(II) ions, which are in a square-planar PS$_2$S′ chromophore with the latter thiolate donor derived from the symmetry related ligand [50]. This dinuclear Ni(II) complex can be oxidised by two consecutive, reversible processes to give the stable Ni(II)Ni(III) and Ni(III)Ni(III) species. Chemical oxidation of the dinickel(II) complex results in the isolation of the mixed-valence complex [Ni(L17)]$_2$$^{-}$, of which the X-ray structure showed a structural rearrangement of the ligands resulting in trigonal bipyramidal nickel geometries with bridging thiolate groups that were shared in the Ni(II)Ni(II) complex, as is shown in Fig. 13. The electronic spectrum of the Ni(II)Ni(III) compound suggests a delocalised mixed-valence state; the complex gives a rhombic EPR spectrum at 100 K (g = 2.12, 2.09, 2.03) [50]. With the ligand H$_3$L17Ph the mononuclear nickel(II) complex [Ni(L17Ph)CO]$^{-}$, as well as the analogous iron complex [Fe(L17Ph)CO]$^{-}$ have been reported by Millar and co-workers [51]. The trigonal–bipyramidal Ni(II) ion appeared to be diamagnetic and showed a CO stretch at 2029 cm^{-1}. Attempts to oxidise the nickel complex results in CO loss;

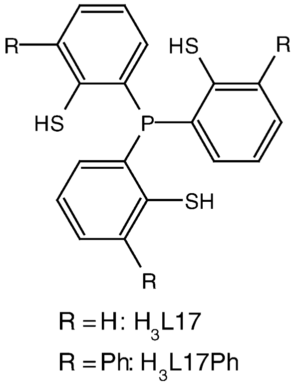


Fig. 12. Tripodal PS$_3$ ligands used by Millar et al.

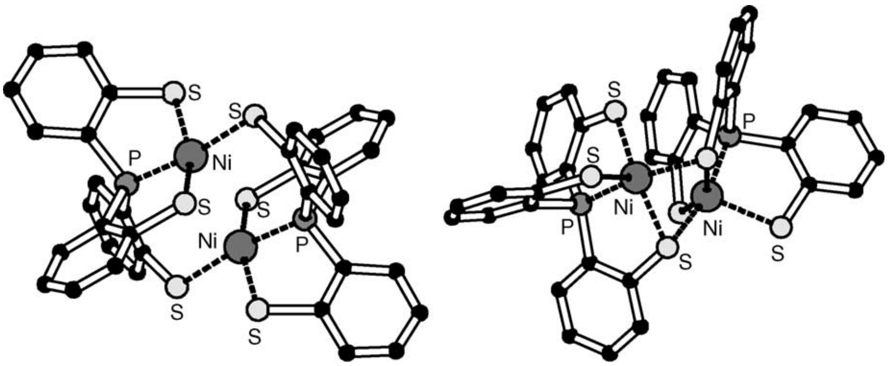


Fig. 13. Molecular structures of $[Ni(L17)]_2^{2-}$ (left) and the mixed valence $[Ni(L17)]_2^{-}$ (right) [50].

electrochemical studies revealed irreversible oxidation and reduction waves [51].

Phosphane-containing ligands not only have been used in the design of chelating ligands, but have also been added as auxiliary ligands for stabilisation of the desired complexes to prevent oligomerisation by bridging thiolates. A recent publication of Wang et al. shows that the prevention of bridging thiolates cannot always be achieved; the didentate phosphane ligands merely function as capping ligands to the oligonuclear structures [52]. Successful use of chelating diphosphane ligands in the synthesis of [NiFe] complexes will be described in Section 4.

2.3. Complexes of oxygen-donor containing ligands

Also in the years following the report of the X-ray structure of [NiFe] hydrogenase in 1995, nickel complexes containing donor atoms other than sulfur have been reported. This is of course partly due to a lag time; the work had been submitted or carried out before the actual structure of the enzyme was known. Nevertheless, especially for obtaining active functional models of hydrogenases, nitrogen and/or oxygen donor atoms seem indispensable (see Section 5). Again, this review is not exhaustive, and only some typical examples will be discussed. Common feature of the oxygen-containing ligands is that in most cases the oxygen donor atom is of the phenol type, and originates from Schiff-base condensations of salicylaldehyde with a variety of amines.

Kang et al. have used 2-mercaptophenol (H_2mp) as a ligand for vanadium, cobalt and nickel [53]. The nickel ions in the dinuclear complex $[Ni_2(mp)_2(Hmp)_2]^{2-}$ are bridged by the thiolate group of two non-chelating monoanionic ligands and each is capped by a chelating dianionic ligand [53]. The commercially available dipeptide *N*-(2-mercaptopropionyl)glycine forms a trianionic S, N, O donor ligand in the formation of a trinuclear complex $[Ni_3(CysGly)_3]^{3-}$ in which the thiolate group bridges the nickel(II) ions [54]. The trinuclear cluster can be disrupted with additional ligands such as CN^-, imidazole or pyridine, thereby forming square-planar mononuclear complexes. Electrochemistry showed irreversible oxidations to unstable Ni(III) species [54].

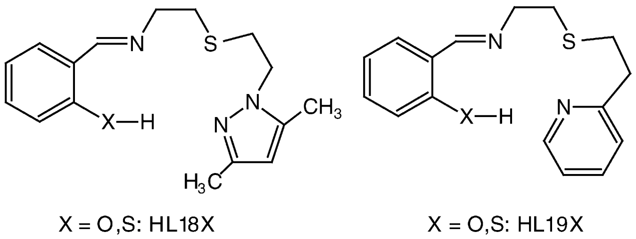
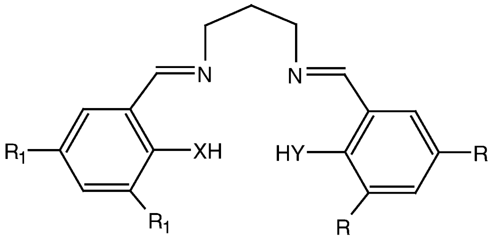


Fig. 14. Asymmetric tetradentate ligands used by Kaasjager et al. [55].

Four new nickel(II) complexes with dissymmetric tetradentate ligands, containing a mixed-ligand donor set of NSNS and NSNO (Fig. 14) have been synthesized by facile template reactions, resulting in square-planar monocationic nickel complexes [55]. In methanol solution the thiophenolate-containing complexes remain square planar, but the phenolate-containing complexes become octahedral, by adduct formation with methanol. Titration of the thiophenolate-containing complexes with the stronger ligand 1-methylimidazole results in diamagnetic five-coordinated complexes. The cyclic voltammograms show a slightly more easy accessible Ni(I) state for the thiophenolate complexes $[Ni(L18S)]BF_4$ and $[Ni(L19S)]BF_4$, than for $[Ni(L18O)]BF_4$ and $[Ni(L19O)]BF_4$. The differences, however, are small, not allowing strong conclusions [55].

Similarly, de Castro and co-workers have synthesised an array of symmetric salen-type tetradentate Schiff-base ligands with phenol or thiophenol, as well as asymmetric N_2SO ligands (Fig. 15) [56]. The crystal structure of the asymmetric



R = Cl, R_1 = H, X = S, Y = O: H_2L20

Fig. 15. Salen-type ligands used by the group of de Castro [56].

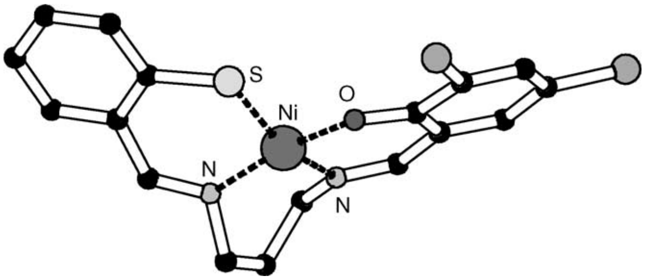
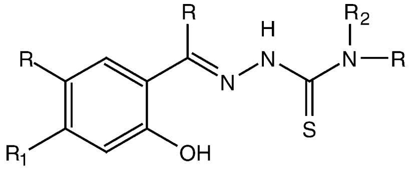


Fig. 16. Structure of [Ni(L20)] [56].



$R,R_1,R_2 = H$: H_2L21
$R,R_1 = CH_3$; $R_2 = H$: H_2L22
$R,R_2 = CH_3$; $R_1 = H$: H_2L23

Fig. 17. NOS ligands used by the group of Crabtree.

complex [Ni(L20)] shows the nickel ion to be in a distorted square-planar geometry with a dihedral twist angle of 24° (Fig. 16). The reduction potentials of the nickel(II) complexes of the N_2O_2, N_2OS and N_2S_2 ligands were found to be mainly related to the tetrahedral distortion [56]. The EPR studies of the Ni(I) complexes obtained by electrolysis show that the *g* values are very sensitive both to the donor atoms in the coordination sphere and to the electronic nature of the substituents on the ligands. Earlier work of the group of de Castro comprised a series of ligands with methyl dithiocarboxylate groups as the sulfur-donor atoms [57,58]. Again, the ligand field d-d transitions of the nickel(II) complexes, as well as the reduction potentials and EPR data showed a linear dependence on the twist angle of the square-planar nickel(II) complexes. The complexes can be oxidised, but it appeared that the ligands are non-innocent in nature and the oxidised solutions did not show any evidence of Ni(III) species [57,58].

Complicated chiral asymmetric tridentate and pentadentate ligands derived from salicylaldehyde have been synthesised by Berkessel et al. [59–61]. The chiral salen-type ligand with a thioether pendant arm did not result in the expected five-coordinate nickel complex; the crystal structure revealed that the thioether pendant arm was dealkylated and the resulting thiolate group is coordinating the nickel ion. One of the phenol groups is coordinating to the nickel ion, the other is non-coordinating, but involved in hydrogen bonding [60]. Electrochemistry showed only irreversible oxidation processes. The tridentate “half salen-type” chiral ligands with a pendant thioether group showed versatile coordination behaviour: didentate NO and NS, as well as tridentate NOS binding is reported [61]. Depending on the choice of solvent or anion, diamagnetic square-planar nickel complexes or paramagnetic octahedral complexes are obtained. The use of an enantiomerically pure tridentate ligand resulted in a racemic nickel complex, the racemisation apparently being metal induced [61].

Zimmer et al. have reported a series of tridentate NOS ligands shown in Fig. 17, obtained by the condensation of (substituted) salicylaldehyde with thiosemicarbazones [62,63]. An X-ray structure of the cation $[Ni(H_2L21)_2]^{2+}$ shows the nickel(II) complex to be in an octahedral geometry of two ligands binding meridionally in the phenol rather than in the phenolato mode [63]. In solution the complex is diamagnetic, probably because of dissociation of the phenol oxygens. Electrochemical reduction of the complex results in a rather stable Ni(I) complex with a rhombic EPR spectrum ($g = 2.25$, 2.12, 2.06). The nickel(II) complex is active in D_2/H^+ exchange (see Section 5.2) [63]. The crystal structure of the dinuclear product $[Ni(L23)]_2$ surprisingly showed bridging to occur via the phenolate oxygen rather than via the iminothiolate group [62].

The template reaction of salicylaldehyde and 2-aminoethanethiol in the presence of nickel acetate results in a trinuclear nickel(II) compound, in which the three nickel ions are connected to each other by the thiolate donor atom from each ligand, resulting in a six-membered ring consisting of alternating thiolate and nickel atoms [64]. The ligand H_2sitp obtained from the condensation of salicylaldehyde with 2-aminothiophenol has resulted in a mononuclear nickel(II) complex with the use of an additional monodentate thiophenol or phenol [65]. The mononuclear nickel(II) complex [Ni(sitp)(SPh)] is irreversibly oxidised at 0.49 V versus NHE to yield the dinuclear complex $[Ni(sitp)]_2$ and the disulfide of thiophenol [65]. Condensation of 2,4-pentanedione with 2-aminoethanethiol [64] or 2-aminothiophenol [66] also gives rise to tridentate NOS ligands. The nickel(II) complexes of these ligands are dinuclear with bridging thiolates in a butterfly shape [64,66]; a mononuclear nickel(II) complex containing an additional thiocyanate ligand is also reported [66]. The reported complexes are not redox-active within the usual potential window.

Brooker and Croucher have synthesised a macrocyclic ligand incorporating phenol and thiophenol head units (L^{2-}, cf. Fig. 29) [67,68]. Asymmetric dinuclear nickel complexes have been reported in which the two nickel ions are bridged by the (thio)phenol oxygen and sulfur-donors. In the complex $[Ni_2(L)(MeCN)_2]^{2+}$ one nickel ion is octahedral with two coordinated acetonitrile molecules, the other nickel ion is square planar in an N_2OS chromophore [67]. In DMF in the presence of an excess of NCS^- this complex reacts to form another asymmetric dinuclear nickel complex, $[Ni_2(L)(dmf)(NCS)_2]$, in which one thiocyanate is coordinated to each nickel centre and a DMF coordinated to only one nickel centre, resulting in square pyramidal and octahedral coordination geometries [68]. The Ni···Ni distance in these complexes is 3.10–3.17 Å. In both cases the macrocycle is bent, with the aromatic rings inclined at 100–112°.

2.4. Complexes with N,S-donor ligands

This class of ligands is extremely large, comprising Schiff base ligands, amine-containing ligands, as well as amides and macrocyclic ligands.

A separate class of model compounds was synthesised using simple nitrogen-containing ligands with additional monodentate thiolate ligands [69–71]. Reaction of [Ni(terpy)Cl_2] with different aromatic thiolates in various conditions results in the formation of dinuclear [Ni(terpy)(μ-SR)(SR)$]_2$ with octahedral nickel ions, the mononuclear trigonal bipyramidal complex [Ni(terpy)(SR$)_2$], or octahedral [Ni(terpy)(SR$)_2$(solvent)] [69]. Reduction of [Ni(terpy)(SR$)_2$] with $NaBH_4$ results in a rhombic EPR signal (g = 2.24, 2.29, 2.05) with hyperfine coupling, suggesting the formation of the hydride adduct [Ni(terpy)(SR$)_2$H$]^-$ [69]. These complexes have been used for XAS (X-ray absorption spectroscopy) measurements and comparison with the data for [NiFe] hydrogenase from *Thiocapsa roseopersicina* at that time seemed to indicate that the nickel site in the enzyme should have a mixed N/O- and S-donor environment [71]. Similar complexes were prepared with the ligand 2,6-bis[(1-phenylimino)ethyl]pyridine (dapa); the complex [Ni(dapa)(SPh$)_2$(CH_3CN)$]^{2-}$ appeared to be the first example of a model system for [NiFe] hydrogenases that could easily be oxidised and reduced [70]. The complex shows complex redox chemistry and various states have been characterised by differences in the rhombic EPR spectra [70]. The dapa complexes bind H^- more readily than the terpy analogues and can be reduced by H_2 to produce the hydride complex, [Ni^I(dapa)(EPh$)_2$(H)$]^{2-}$, with E = S or Se [72]. The latter complex was reported as a model for [NiFeSe] hydrogenases. Because of the resemblance in XAS spectra between the hydride-containing complex and hydrogenase, that work supports the presence of a Ni(I)–H^- species in the so-called form C of [NiFe] hydrogenases.

Simple, commercially available didentate NS ligands such as cysteine, D-penicillamine, 2-mercaptopyridine, and 2-mercaptopyrimidine have been widely used in the synthesis of nickel complexes. Cysteine and D-penicillamine bind to nickel as dianionic didentate ligands, thereby forming [Ni(L$)_2]^{2-}$ complexes with *trans* and *cis* square-planar chromophores, respectively [73,74]. In both cases the carboxylate groups, although dehydronated, are not coordinated to the nickel ion, but act as ligands to the potassium cation and participate in extensive hydrogen bonding. Possibly because of the rather small bite angle of the four-membered chelate rings in 2-mercaptopyridine and 2-mercaptopyrimidine, the monoanionic ligands form octahedral nickel complexes with formula [Ni(L$)_3]^-$ [75]. These mononuclear complexes were isolated in aprotic media, but insoluble polymeric species were also obtained. The bite angle of the ligands in these complexes is around 67°, resulting in rather distorted octahedral geometries. Electrochemical studies in acetonitrile showed irreversible oxidations at the potentials +0.31 and +0.56 V versus NHE for the pyridine and the pyrimidine ligand, respectively. The oxidised species rapidly decomposed near the working electrode [75]. Yamamura et al. have recently synthesised 2-(2,2-diphenyl-2-mercaptoethyl)pyridine (Hmep), a didentate NS ligand with a larger bite angle and bulky phenyl groups to prevent polymerisation [76]. The nickel ion in the complex [Ni(mep$)_2$] is square-planar with the ligands binding in *cis* positions. The Ni–N and Ni–S distances are 1.92 and 2.17 Å, respectively.

Triangular nickel clusters with a bridging μ_3 sulfide are obtained with a chiral aminoethanethiolate ligand (1*S*,2*S*)-1-mercapto-1-phenyl-2-(methylamino)propane [77]. The nickel(II) ions in this cluster are in an NS_3 square-planar geometry with the thiolate group of the ligand bridging between two nickel centres. The molecule is cone shaped with the μ_3 sulfide at the apex. The sulfide ion must be originating from partial decomposition of the ligand, explaining also the relatively low yield of the complex syntheses [77].

Tridentate NS_2 ligands have been synthesised by a number of groups. Some representative examples are shown in Fig. 18. Upon reaction with a nickel salt the ligand H_2L24 yields an amorphous product, probably of formula [Ni(L24)$]_n$. Only polar, coordinating solvents are able to take this compound in solution. Addition of *t*-butylpyridine to these solutions yield the mononuclear complex [Ni(L24)(*t*-Bupy$)_2$], in which the nickel(II) ion is five-coordinate in a distorted square–pyramidal geometry with one of the pyridine nitrogens in the apical position [78]. The other ligands shown in Fig. 18 all yield dinuclear nickel complexes [NiL$]_2$ with bridging thiolates [79–81]. These dinuclear nickel complexes readily react with nucleophiles to form mononuclear

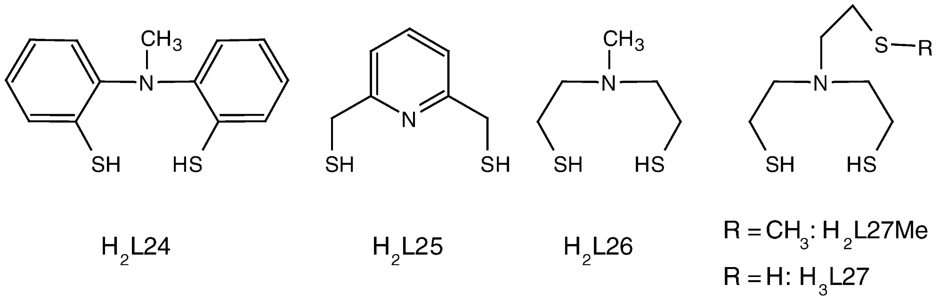
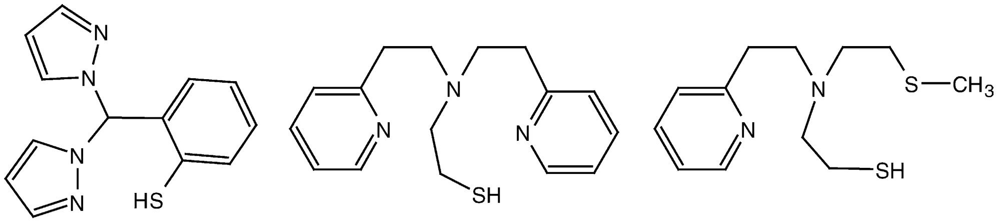


Fig. 18. Representative examples of tridentate NS_2 ligands.



HL28 HL29 HL30

Fig. 19. Scorpionate and tripodal NS ligands.

compounds [NiLX]. The electrochemistry of the complex $[Ni(L25)]_2$ shows a reversible one-electron reduction at −0.97 V versus NHE in DMF solution. The EPR spectrum of the electrochemically reduced solution shows an axial spectrum with $g_{\perp} = 2.058$ and $g_{||} = 2.196$, indicating a metal-centred reduction with the electron delocalised over the two nickel centres [79]. Reaction of $[Ni(L25)]_2$ with ethanethiol or benzenethiol results in mononuclear complexes with square-planar NS_3 chromophores; the electrochemistry of these complexes, however, is complicated, showing oxidation of the thiolates to disulfides [79]. The nickel complexes of the ligand H_2L27Me show some interesting reactivity, which will be discussed in Section 5.1. The dinuclear complex $[Ni(L27Me)]_2$ in DMF reacts with two equivalents of cyanide to form the mononuclear $[Ni(L27Me)CN]^-$ [82]. Electrochemical oxidation of the dinuclear complex $[Ni(L27Me)]_2$ results in an rhombic EPR signal with g values of 2.17, 2.11 and 2.07. Chemical oxidation of this dimer with I_2 results in the formation of the cyclic disulfide; the resulting oxidised ligand remains coordinated to nickel with its nitrogen donor, the thioether sulfur and one of the disulfide sulfur atoms. The coordination sphere of the mononuclear nickel(II) ion is completed by two iodide ions, resulting in a square–pyramidal geometry [82]. Similar reactivity has been reported for the nickel complexes of the tridentate ligand H_2L26 as well as for the analogous diselenoate ligand. It was observed that the selenoate ligand was less sensitive to oxidation. The electrochemistry of the nickel complexes of both ligands is characterised by irreversible processes [81].

Reaction of the tridentate ligand (2-sulfanylphenyl)bis(pyrazolyl)methane (HL28, Fig. 19) with nickel in acetone results in the trinuclear complex $[Ni_3(L28)_4]^{2+}$ [83]. In this linear trinuclear complex, the two peripheral nickel ions are in octahedral N_4S_2 coordination geometries formed by two ligands with the thiolate groups binding in *cis* positions. These two octahedral nickel sites are held together by the central nickel(II) ion, which is in a distorted-tetrahedral S_4 geometry with coordination angles in the range of 90–130° [83]. In acetonitrile the dinuclear complex $[Ni_2(L28)_2(MeCN)_2(H_2O)_2]^{2+}$ is obtained; all attempts to isolate a mononuclear nickel complex with this ligand have failed. The electrochemistry of the trinuclear complex in nitromethane appeared to be dominated by an oxidation near +0.69 V versus NHE, but no firm conclusion regarding the site of oxidation has been made [83].

Thiolate-bridged dinuclear nickel complexes have been obtained with the tripodal ligands HL29 and HL30 shown in Fig. 19 [84–86]. The complex $[Ni_2(L30)_2]^{2+}$ has a thiolate-

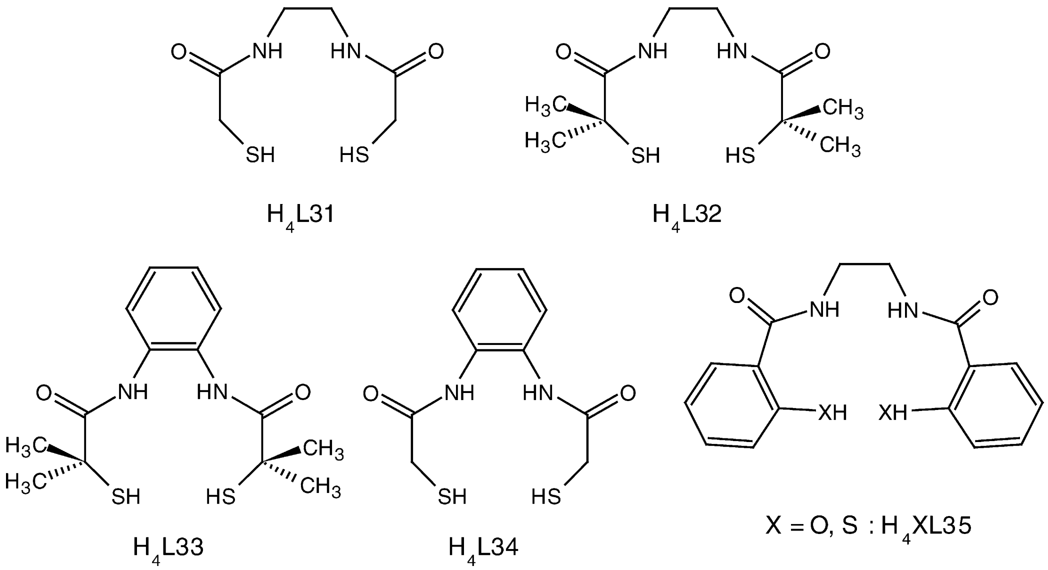


Fig. 20. Ligands used by Krüger and co-workers [87–89].

bridged dinuclear structure, in which each nickel ion is coordinated in a square-planar N_2S_2 donor set with a weak apical coordination of the pendant thioether group [86]. The $[Ni_2(L29)_2]^{2+}$ cation has a dinuclear structure in an unusual mixed-spin state containing a low-spin and a high-spin Ni(II) ion. One of the nickel ions is coordinated by a square-planar N_2S_2 donor set; the second nickel ion has a distorted square–pyramidal coordination of an N_3S_2 donor set with the pendant pyridyl nitrogen coordinating at the apex [85].

Krüger and Holm have stabilised nickel(III) species with different amide-containing N_2S_2 ligands shown in Fig. 20. The nickel(II) complexes $[Ni(OL35)]^{2-}$ and $[Ni(SL35)]^{2-}$ are square planar and diamagnetic and do not react with dioxygen for at least 24 h. However, they are readily oxidised electrochemically to the Ni(III) state with a stability sufficient to detect its presence with EPR [87]. Unexpectedly, substitution of the sulfur-donors by oxygen donors results in an increase of the oxidation potential by 0.160 V. The half-wave potentials of the Ni(II)/Ni(III) couple are at −0.035 V versus NHE for the thiolate ligand and at +0.125 V for the phenolate ligand. The oxidised species readily bind pyridine as is observed from the nitrogen hyperfine splitting in the rhombic EPR spectra. The complex $[Ni(L33)]^{2-}$ can also be electrochemically oxidised; the nickel(III) complex is extremely stable and has been characterised with an X-ray structure [89].

The structure of $[Ni(L33)]^{-}$, shown in Fig. 21, reveals that the coordination geometry of the nickel ion essentially is unaltered upon oxidation, only a small reduction in bond lengths is observed. The bond lengths within the ligand are unaltered with respect to the values for the Ni(II) complex confirming the oxidation to be metal centred. The magnetic moment of the Ni(III) complex is 1.78 μ_B, which corresponds to a low-spin complex. Nickel complexes of the other ligands shown in Fig. 20 essentially show the same behaviour [88]. Interestingly, the complexes $[Ni(L31)]^{2-}$ and $[Ni(L34)]^{2-}$ show different behaviour when the electrochemistry is carried out at low temperature (−30 °C). Whereas after oxidation at room temperature an EPR signal typical for Ni(III) can be observed, at low temperature the solutions are diamagnetic. This different behaviour is ascribed to the formation of antiferromagnetically coupled dimers by bridging thiolates, consistent with the tendency of nickel(III) species to bind axial ligands [88]. Krüger and Holm have also reported the stabilisation of trivalent nickel with the use of the tridentate ligands 2,6-bis(acetyloxime)pyridine (H_2baopy) and pyridine-2,6-bis(monothiocarboxylic acid) (H_2btcpy). These ligands form octahedral complexes $[Ni(baopy)_2]^{2-}$ and $[Ni(btcpy)_2]^{2-}$, in which the ligands are bound meridionally [90]. The average Ni–S distance of 2.418 Å in $[Ni(btcpy)_2]^{2-}$ is in the range of six-coordinated Ni(II)–S bond lengths observed with high-spin complexes of anionic sulfur ligands, and also in the range of the distances found in hydrogenases. In the nickel(III) complex $[Ni(btcpy)_2]^{-}$ the Ni–N and Ni–S distances have decreased by 0.01 and 0.14 Å, respectively. The EPR spectrum of the complex $[Ni(btcpy)_2]^{-}$ shows an axial signal with $g_{\perp} = 2.137$ and $g_{||} = 2.038$, consistent with a tetragonally distorted geometry [90].

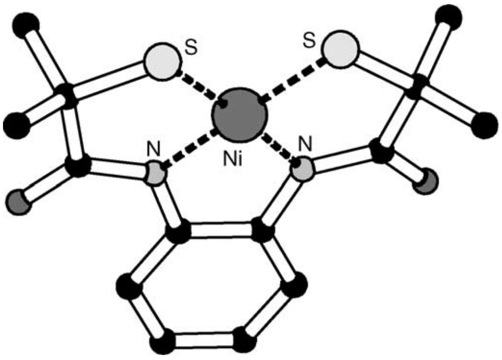


Fig. 21. Structure of the nickel(III) complex $[Ni(L33)]^{-}$ [89].

Schiff-base ligands derived of thiosalicylaldehyde have been synthesised by a number of groups [91–93]. The nickel(II) complexes of the tetradentate N_2S_2 ligands derived from 1,2-diaminoethane (H_2tsalen) or 1,2-diaminobenzene (H_2tsalphen) are essentially square planar [91,93,94]. Reduction of the imines in H_2tsalen results in the diamine ligand *N*,*N*′-bis(*o*-mercaptobenzyl)-1,2-diaminoethane (H_2mben); Ni–N distances in the structure of the corresponding complex [Ni(mben)] are significantly longer than those in [Ni(tsalen)], being 1.94 and 1.86 Å, respectively [95]. Electrochemistry of [Ni(tsalen)] shows quasi-reversible reduction to nickel(I) at the half-wave potential −1.17 V versus NHE and an irreversible oxidation at +1.19 V versus NHE, whereas the complex [Ni(mben)] shows only irreversible responses [91].

New nickel complexes of Schiff base ligands incorporating thiosalicylaldehyde have also been prepared using precursors in which the thiolate function had been protected with either a tertiairy butyl group [96,97], or by the formation of the disulfide [92]. 2-Aminothiophenol and 2-*tert*-butylthiobenzaldehyde react in ethanol to form a benzothiazolidine derivative ^{t}BuL36 (Fig. 22), which is isolated as a yellow solid [97]. The benzothiazolidine ring opens upon reaction with nickel acetate in ethanol to form the square-planar mononuclear complex $[Ni(^tBuL36)_2]$ with a *cis* N_2S_2 chromophore, in which the *t*-butylthioethers do not participate in the coordination and which shows weak agostic interactions with two *ortho* hydrogens of the ligands (Ni–H distances of 2.52 and 2.58 Å). These C–H···Ni interactions are retained in solution, as reflected in the ^{1}H NMR spectra of the complex. With other nickel salts, the same benzothiazolidine ligand reacts in ethanol to form dinuclear species $[Ni(L36)]_2$, with loss of the protecting tertiary butyl group. An analogous ligand, constructed from 2-aminoethanethiol and 2-*tert*-butylthiobenzaldehyde was synthesised in a template reaction with nickel salts in ethanol to form the dinuclear compound $[Ni(L37)]_2$. The dinuclear complexes are in a ‘butterfly’ shape, with bridging thiolates. The nickel ions in these two complexes are in a NS_3 chromophore with a square-planar geometry [97]. A new tetradentate N_3S

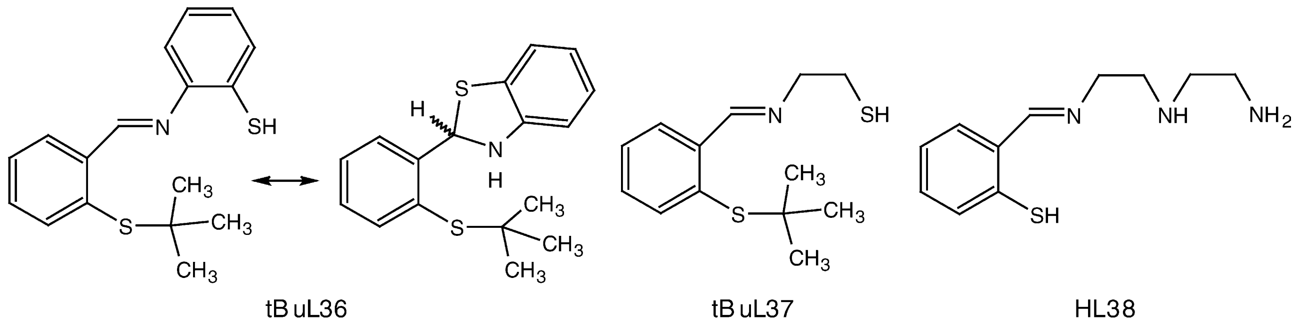


Fig. 22. Schiff base ligands synthesised with protected thiosalicylaldehyde.

ligand HL38 has been prepared via two different routes from the reaction of diethylenetriamine with protected thiosalicylaldehyde [92,96]. The nickel complex $[Ni(L38)]^+$ is in a square-planar geometry formed by a primary and a secondary amine, an imino nitrogen and a thiolate group.

The groups of Bereman and Toftlund have designed the new didentate NS and tetradentate N_2S_2 ligands shown in Figs. 23 and 24, some of which incorporate constraints that enforce non-planar geometries [98–100]. Bereman et al. have synthesised nickel and copper complexes with the tetradentate ligands H_2L39 with ethylene ($n=2$), propylene ($n=3$) and butylene ($n=4$) bridges. The nickel(II) complexes of these ligands are mononuclear and show increased distortion from the square-planar geometry with increasing chain length [100]. The dihedral angles of the NiN_2 and NiS_2 coordination planes are 3.4, 18.9 and 38.6° for $n=2$, 3, and 4, respectively. From the distances within the ligands it becomes clear that they coordinate to the nickel ion in a Schiff-base-like tautomeric form, with an imine-type nitrogen and a thiolate sulfur. Electrochemistry shows that the nickel complexes are both more readily reduced and more easily oxidised going to the complex with the largest tetrahedral distortion; the potential difference ΔE between the reductive and the oxidative wave decreases from 2.29 V for $n=2$ to 1.86 V for the complex with $n=4$ [101].

The complexes $[Ni(L40)_2]$ of the didentate NS ligands reported by Toftlund et al. (Fig. 24) are diamagnetic and square-planar in the solid state, but may convert to tetrahedral high-spin species in solution, depending on the steric bulk of the R groups [102]. Despite the influence of the 6,6′-dimethyl-biphenyl backbone, which tends to enforce a tetrahedral geometry on a metal, crystal structures of nickel

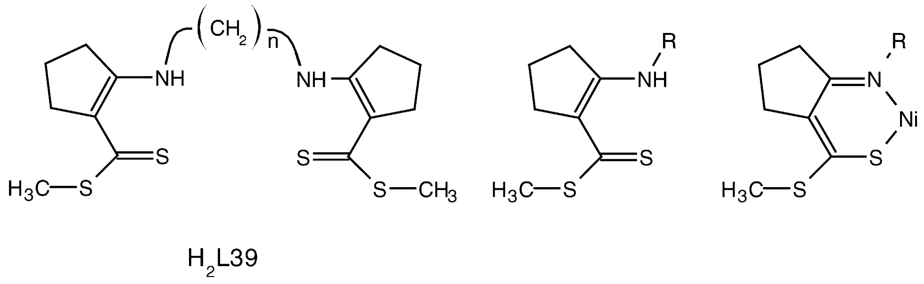


Fig. 23. Ligands synthesised by Martin and Bereman [98]. The figure on the right shows the tautomeric iminothiolate form in which the ligands bind to a metal ion.

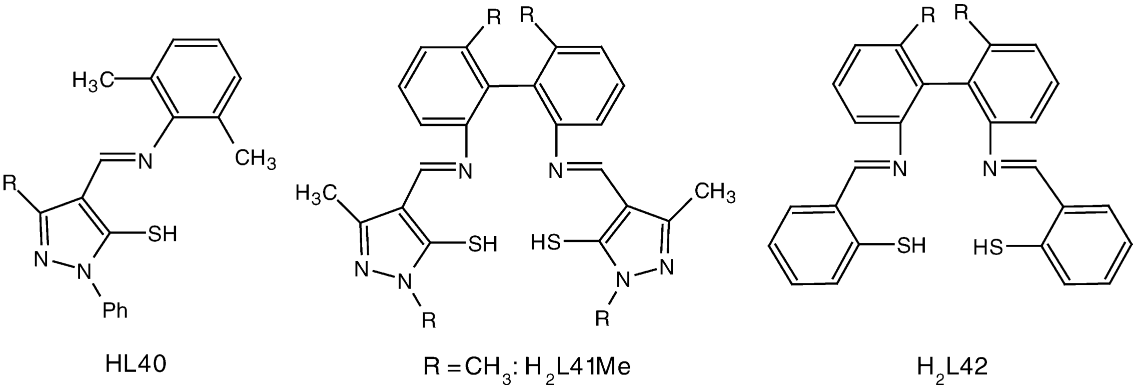


Fig. 24. Didentate and tetradentate ligands synthesised by Toftlund and co-workers [99].

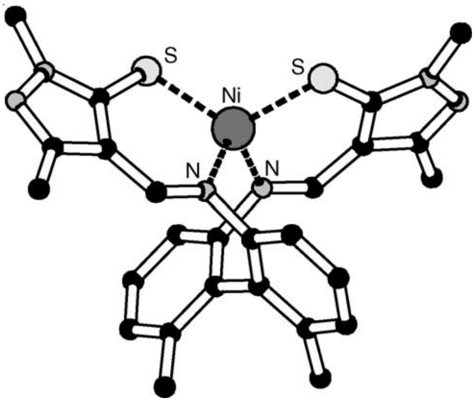


Fig. 25. Molecular structure of [Ni(L41Me)] [99].

complexes with the tetradentate ligands H_2L41 and H_2L42 in Fig. 24 show varying degrees of tetrahedral twists [99]. A nickel(II) complex of the thiophenyl-containing ligand H_2L42 is nearly square-planar, with a dihedral angle of only 14°, whereas the nickel complex of H_2L41Me, shown in Fig. 25, is nearly tetrahedral with a dihedral angle of 77° [99]. In solution these nickel complexes are in a dynamic equilibrium between low-spin and high-spin states.

Similar nickel complexes, but with remarkable differences in reactivity have been reported for the linear tetradentate N_2S_2 ligands with mercaptoethyl side arms shown in Fig. 26. In aprotic media the mononuclear complexes can be isolated, whereas in protic media the thiolate groups have a tendency to form trinuclear nickel complexes [103]. The X-ray structures of the mononuclear complexes [Ni(L44Me)] [104], [Ni(L44Et)] [105], [Ni(L45)] [106], [Ni(L45Me)] [107], and [NiL46] [108] have shown the nickel ions to be in square-planar N_2S_2 geometries. In the complexes with alkylated linear ligands, [Ni(L44Me)] and [Ni(L44Et)], the alkyl groups are both at the same side of the coordination plane [104,105]. When coordinated to a metal ion, the two six-membered rings formed by the cyclic 1,5-diazacyclooctane backbone with the metal ion can have different conformations, i.e. chair/boat, chair/chair and boat/boat. In the complex [Ni(L45Me)] this ligand is coordinated to the nickel centre in the chair/chair conformation [107], but the backbone shows disorder in the crystal structure of [Ni(L45)], with equal distribution of the chair/boat and chair/chair conformations [106]. Crystal structures of the trinuclear complexes $[Ni_3(L43)_2]^{2+}$ and $[Ni_3(L45)_2]^{2+}$ have also been reported [103,109]. In these linear trinuclear structures two mononuclear nickel complexes in a square-planar N_2S_2 geometry act as a didentate ligand to the central nickel ion, which is in a square-planar S_4 chromophore. The overall shape of the molecules can be described as a chair consisting of the three coordination planes, with the three nickel ions in a row.

Both the 1,5-diazacyclooctane and 1,4-diazacycloheptane backbones in the ligands L45 and L46, respectively, exert a considerable constraint on the flexibility of the ligand. This is reflected in the differences in reactivity of complexes of the ligands L45 and L46 in comparison with that of the more flexible ligands L43 and L44. The complexes [Ni(L45)] and [Ni(L45Me)] have been a precursor to a broad range of derivatives modified at sulfur as described in Section 5.1.

The group of Kovacs has used several pentadentate ligands shown in Fig. 27. The ligands L47 and L48 yield the octahedral nickel(II) complexes $[Ni(L47)Cl]^+$ and $[Ni(L48)(MeCN)]^{2+}$, respectively [17]. The dithiolate ligand L49 was obtained by a template reaction of 3,3′-iminobis(propylamine) with 2,5-dihydroxy-2,5-dimethyl-1,4-dithiane with nickel acetate. The rigidity of

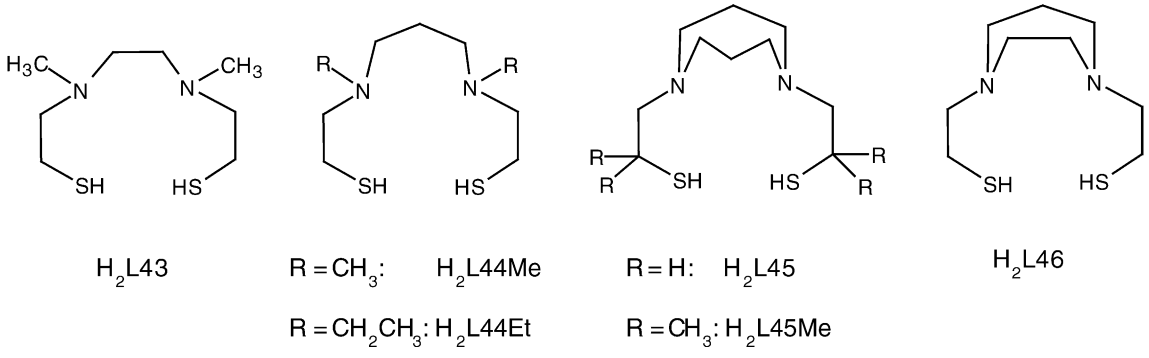


Fig. 26. Tetradentate amine-thiolate ligands.

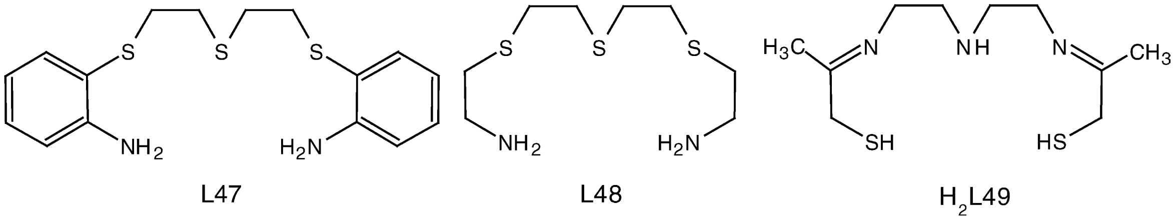


Fig. 27. Mixed-donor ligands used by Kovacs and co-workers [15,110].

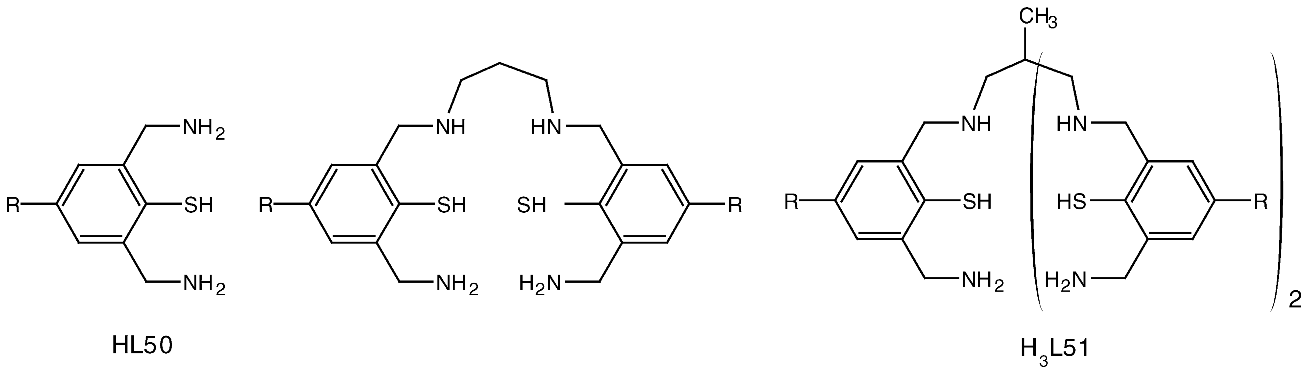


Fig. 28. Dinucleating ligands used by Kersting et al.

the Schiff base ligand favours a mononuclear nickel complex [Ni(L49)], in which the nickel is five-coordinate in a trigonal–bipyramidal geometry. Both in the solid state and in solution the nickel-bound alkylthiolate sulfurs have an affinity for hydrons [110].

The groups of Kersting and Brooker have made use of 2,6-di(aminomethyl)thiophenol as a building block for dinucleating ligands [111,112]. Some examples of the ligands used by Kersting et al. are shown in Fig. 28. Dinuclear Ni(II)Ni(II), as well as mixed-valence Ni(II)Ni(III) complexes, have been isolated and fully characterised [113–115]. The nickel ions in the dinuclear complexes have either square-planar or octahedral coordination geometries, based on the choice of the ligand and the presence of possible co-ligands. Electrochemistry shows that the nickel(III) oxidation state is stabilised, with two reversible oxidations occurring at around +0.64 and +1.14 V versus NHE; in some cases (quasi-) reversible reductions are observed [114]. The oxidations are reported to be metal centred, based on UV–vis and EPR spectroscopy. The one-electron oxidised solution reveals an axial EPR spectrum with $g_\perp = 4.7$ and $g_{||} = 2.1$, indicative of an $S = 3/2$ spin ground state [114]. The complex $[Ni_2(L50)_3]^{2+}$ contains two face-sharing octahedral nickel ions in an N_3S_3 donor set. Distortions from the ideal D_{3h} symmetry suggests that this compound represents a trapped-valence Ni(II)Ni(III) complex [113]. Cyclic voltammetry in DMF shows reversible one-electron reduction and oxidation processes at 0.22 and 0.70 V versus NHE, respectively. A heterodinuclear NiFe complex has been reported with H_3L51 (see Section 5) [116].

Brooker et al. have used the same 2,6-di(aminomethyl)thiophenol building block for the synthesis of macrocyclic, dinucleating ligands shown in Fig. 29 [112,117,118]. Both symmetric complexes with two square-planar nickel(II) ions, and asymmetric complexes containing an octahedral and a square-planar nickel(II) ion have been synthesised and characterised; the average Ni· · ·Ni distance is 3.146 Å [112]. Electrochemistry of the dinuclear nickel complexes shows the possibility of two oxidation processes as well as two reduction processes. According to Brooker et al. the spectroelectrochemical studies of the complex $[Ni_2L52]^{2+}$ (with $R = CH_3$ and $n = 3$) are indicative for metal-centred oxidation. The EPR spectrum of the one-electron oxidised complex is axial with $g_\perp = 2.22$ and $g_{||} = 2.17$, the latter showing hyperfine structure supposedly due to coordinating acetonitrile molecules [112]. Multi-frequency EPR studies on ^{61}Ni enriched samples of the one-electron oxidised $[Ni_2L52]^{3+}$, however, indicate extensive charge delocalisation between the Ni(III) ion and the thiolate donors in the mixed-valence complex, with approximately 30% of the unpaired electron density residing on the bridging thiolate ligands [119].

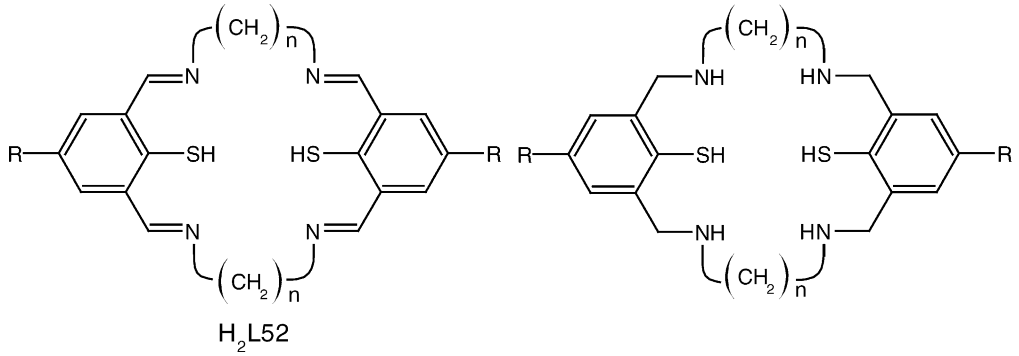


Fig. 29. Dinucleating ligands used by Brooker et al.

3. Iron complexes

Soon after it became known that Nature has made use of an unusual iron carbonyl dicyanide unit in the active site of [NiFe] hydrogenases [2], intensive renewed investigations into classical organometallic iron complexes were undertaken. Interesting reinvestigations into the reactions of iron with cyanide and carbon monoxide resulted in the isolation and characterisation of the new "classic" complexes $[Fe^{II}(CN)_5(CO)]^{3-}$, *trans*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$, *cis*-$[Fe^{II}(CN)_4(CO)_2]^{2-}$, and *fac*-$[Fe^{II}(CN)_3(CO)_3]^{-}$. With the aid of these compounds improved insight has been obtained regarding the stability of this type of complexes, as well as the sensitivity of the CN and CO stretching vibrations for oxidation states and the degree of hydrogen bonding in solution [120–122].

Considering the nickel cysteine part of the enzyme active site as a ligand for iron, Darensbourg et al. have synthesised and reported the crystal structure of $K[(\eta^5\text{-}C_5H_5)Fe(CN)_2(CO)]$ [124]. Its structural and spectroscopic characterisation conforms with the enzymatic $Fe(CN)_2(CO)$ part and therefore permits exploration of solvent and counter ion effects on the IR-spectra of the iron-bound diatomic molecules. In the typical piano stool complex, the average Fe–CN distance was found to be 1.91 Å and the Fe–CO distance is 1.73 Å. The potassium counter ion interacts with six cyanides from symmetry related molecules in an octahedral geometry. Three absorptions in the infrared spectrum of this complex in the region 2100–1900 cm^{-1} are due to the symmetric and asymmetric stretching vibrations of the cyanides and the carbonyl-stretching mode. In acetonitrile the data match remarkably well with the native enzyme; 2094, 2088 and 1949 cm^{-1} for the complex and 2093, 2083 and 1947 cm^{-1} for hydrogenase from *D. gigas*, respectively. The studies have been extended to another six-electron ligand, the bulkier pentamethylcyclopentadienyl, of which the complexes $K[(\eta^5\text{-}C_5Me_5)Fe(CN)_2(CO)]$, $[(\eta^5\text{-}C_5Me_5)Fe(CN)(CO)_2]$, as well as the hydronated complex $H[(\eta^5\text{-}C_5Me_5)Fe(CN)_2(CO)]$ have been prepared and characterised [123]. The crystal structure of the hydronated complex $H[(\eta^5\text{-}C_5H_5)Fe(CN)_2(CO)]$, of which the anion is reproduced in Fig. 30, shows that the hydron is present in the lattice, bridging between cyanide groups of symmetry-related molecules [123]. The similarities of the spectroscopic data suggests that the six-electron cyclopentadienyl ligand has the same donor abilities as the $Ni(\mu\text{-}SCys)_2(\mu\text{-}O)$ or $Ni(\mu\text{-}SCys)_2(\mu\text{-}OH)$ donor set in the enzyme. However, the quasi-reversible $Fe^{III/II}$ redox couple of +0.66 V versus NHE is significantly different from redox couples found for the hydrogenases that are known to be in the range −0.1 to −0.45 V [124].

Koch et al. have modelled the $[Fe(CO)(CN)_2]$ part of the hydrogenases using the tripodal phosphane based ligands discussed in Section 2.2 (Fig. 12) [51,125]. The trigonal–bipyramidal complexes $[Fe^{II}(L17)(CN)]^{2-}$, $[Fe^{III}(L17Ph)(CN)]^{-}$, and $[Fe^{II}(L17Ph)(CO)]^{-}$, as well as the octahedral complex $[Fe^{II}(L17)(CO)(CN)]^{2-}$ were synthesised and fully characterised. The structures of the trigonal bipyramidal Fe(II) and Fe(III) cyanide complexes are nearly similar, only with significantly shorter iron–thiolate distances in the latter (2.29 Å versus 2.17 Å) [125]. The CN stretching frequency in the infrared spectra shifts to lower energy and also gains intensity upon reduction from Fe^{III} (2094 cm^{-1}) to Fe^{II} (2070 cm^{-1}). Electrochemistry shows that for the cyanide complex also the Fe(IV) oxidation state is accessible; the Fe(II)/Fe(III) and Fe(III)/Fe(IV) half-wave potentials are found at −0.588 and +0.63 V versus NHE [125]. Reaction of the complex $[Fe^{II}(L17)(CN)]^{2-}$ with carbon monoxide results in the formation of the octahedral complex $[Fe^{II}(L17)(CO)(CN)]^{2-}$ shown in Fig. 31, in which the cyanide ligand remains located *trans* to the phosphorous donor atom. The IR spectrum of this octahedral complex reveals absorption bands at 2079 and 1904 cm^{-1} for the CN and CO stretches, respectively, and electrochemistry shows the occurrence of a reversible oxidation couple $Fe^{II/III}$ at −0.24 V versus NHE [125]. The CO stretching frequency of $[Fe^{II}(L17Ph)(CO)]^{-}$ is the same in the solid state and in solution (1940 cm^{-1}); the complex exhibits a reversible oxidation at +0.32 V versus NHE, bulk oxidation of the carbonyl complex, however, results in loss of CO [51].

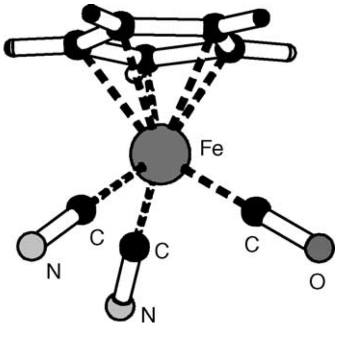


Fig. 30. Molecular structure of $[(\eta^5\text{-}C_5H_5)Fe^{II}(CO)(CN)_2]^{-}$ [123].

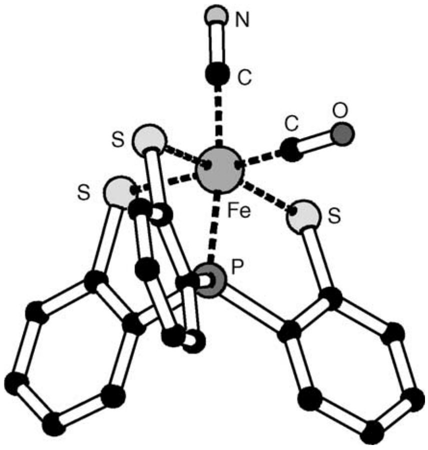


Fig. 31. Molecular structure of $[Fe^{II}(L17)(CO)(CN)]^{2-}$ [125].

Davies et al. have used the similar tetradentate tripodal NS_3 ligand tris(mercaptoethyl)amine (H_3L27, see Fig. 18) in the synthesis of iron complexes [126,127]. Reduction of the Fe(III) complex $[Fe^{III}(L27)Cl]^-$ under CO results in the paramagnetic trigonal-bipyramidal iron(II) complex $[Fe^{II}(L27)(CO)]^-$, which structure is comparable to that of $[Fe^{II}(L17Ph)(CO)]^-$ described above, but which has a notably lower CO stretching frequency of 1885 cm^{-1} [127]. Reaction of the ligand H_3L27 with iron salts in the presence of NO results in the complex anion $[Fe^{II}(L27)(NO)]^-$. The chemistry of this complex is extremely rich, in different conditions resulting in various dinuclear, trinuclear and tetranuclear iron complexes, which were characterised with Mössbauer spectroscopy and magnetic measurements [126].

The group of Liaw studied the reactivity of iron carbonyl and iron cyanide adducts for oxidative addition reactions, as well as for substitution and hydronation reactions [128–130]. Oxidative addition of various organic disulfides to $[HFe(CO)_4]^-$ results in the iron(II) complexes $[Fe(CO)_4(SR)]^-$, and a subsequent reaction with the disulfide yields the complexes *fac*-$[Fe(CO)_3(SR)_3]^-$ [131]. The compounds *fac*-$[Fe(CO)_3(SR)_3]^-$ may serve as ligands to other metal ions and in this respect are suitable candidates for further reaction with nickel ions; in fact, a reaction with simple nickel salts result in the linear trinuclear complex $[\{Fe(CO)_3(SR)_3\}_2Ni]$ [131]. A reaction of bis(2-aminophenyl)disulfide with $(PPN)[Fe(CO)_4(CN)]$ results in the air-stable 16-electron iron(II) complex $(PPN)[Fe(CO)_2(CN)(atp)]$, in which the ligand atp is the dianionic ligand derived from 2-aminothiophenol (H_2atp) by dehydronation of both the thiolate and the amine function [128]. The IR spectrum of this complex in acetonitrile shows a weak absorption for the cyanide ligand and two strong absorptions for the carbonyl groups at 2099, 1997, and 1933 cm^{-1}, respectively [128]. The complex $[Fe(CO)_2(CN)(atp)]^+$ can be reversibly hydronated with 2-aminothiophenol resulting in a six-coordinate complex $[Fe(CO)_2(CN)(Hatp)_2]$ in which one of the ligands is bound through sulfur only. Reaction of $[Fe(CO)_2(CN)(atp)]^+$ with 1,2-benzenedithiol (H_2L3) or 2-mercaptopyrimidine (Hmpm) results in dinuclear $[Fe(CO)_2(CN)(L3)]_2{}^{2-}$ and mononuclear *cis*-$[Fe(CO)(CN)(mpm)_2]$, respectively [128]. Similar studies have been performed with thioxanthate derivatives and 2-mercaptopyridine as the ligands [129]. Very recently, Chen et al. reported the structure of $[Fe(CO)_2(CN)(bmes)]^-$ in which the dianionic ligand bmes (H_2bmes: bis(2-mercaptoethyl)sulfide) binds facially to the iron(II) centre with the cyanide bound *trans* to the thioether sulfur [130]. From these studies Liaw et al. conclude that particular combinations of iron(II) with carbonyl, cyanide and thiolate groups apparently are stabilised as a result of the combination of σ-donor and π-acceptor properties of these ligands [130].

Already in 1990, Sellmann et al. reported on the chiral iron(II) complex of the ligand H_2L7 (see Fig. 5) with carbonyl ligands. The complex *cis*-$[Fe(L7)(CO)_2]$ and the dinuclear $[Fe(L7)(CO)]_2$ were synthesised as speculative models for oxidoreductases, such as nitrogenase and hydrogenase, and were further studied using Mössbauer spectroscopy [133]. Renewed investigations using the ligand H_2L8 (see Fig. 5) have resulted in the synthesis and characterisation of $[Fe(CO)(CN)_2(L8)]^{2-}$ shown in Fig. 32, the first model complex with two thiolate groups containing two cyanides and only one carbonyl group [132]. The complex in the solid state is relatively stable, but in solution it is rapidly oxidised by air resulting in loss of CO. In cyclic voltammetry the complex shows two irreversible oxidation processes at −0.098 and +0.489 V versus NHE, but the first oxidation becomes quasi-reversible when the scan is reversed at +0.1 V [132]. The influence of possible hydrogen bonds in solution on the IR frequencies of the carbonyl and cyanide groups has also been investigated; large blue shifts were found for the CO stretch (1929 cm^{-1} in acetonitrile versus 1973 cm^{-1} in water), whereas smaller (10 cm^{-1}) changes were found for the CN vibrations [132].

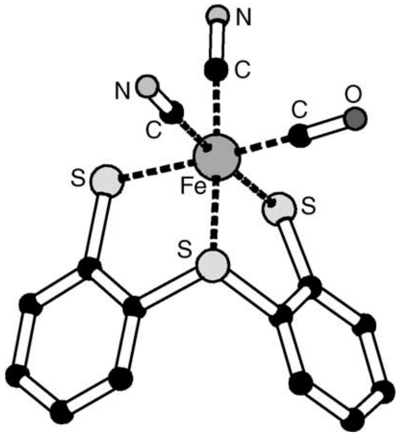


Fig. 32. Molecular structure of $[Fe(L8)(CO)(CN)_2]^{2-}$ [132].

4. Dinuclear [NiFe] complexes

The number of (dinuclear) [NiFe] complexes bridged by (alkyl or aryl) thiolate groups that have been reported is relatively low, given the fact that a tremendous effort has been put in this field of research since the report of the crystal structure of [NiFe] hydrogenase in 1995. The structures present in the Cambridge Structural Database are rather diverse and it is difficult to find a common theme to describe these different complexes.

The group of Kersting has succeeded to isolate and characterise a heterodinuclear complex with the ligand H_3L51 (see Section 2.4, Fig. 28) [116]. A solution of the ligand H_3L51 was first treated with an equimolar amount of a nickel salt and a slightly substoichiometric amount of base, followed by a solution of iron(II) chloride and air oxidation [116]. It is remarkable that this procedure results in a high yield of the complex $[Ni^{II}Fe^{III}(L51)]^{2+}$ with the nickel ion residing at the capped end of the ligand. The two metal ions in the structure are both in N_3S_3 octahedral geometries that are face sharing through the three bridging thiolate groups. Assignments of the metal sites have been made considering the bond lengths. Electrochemistry in DMF solution revealed two reversible one-electron processes at half-wave potentials of +0.69 and −0.19 V versus NHE, assigned to the oxidation Ni(II)/Ni(III) and the reduction Fe(III)/Fe(II), respectively. The electrochemical behaviour of the heterodinuclear complex is significantly different from that of the homodinuclear nickel or iron analogues, confirming the presence of both metals [116].

Glaser et al. have used the hexadentate ligand 1,4,7-tris(4-*tert*-butyl-2-mercaptobenzyl)-1,4,7-triazacyclononane (H_3mbtacn) for the synthesis of (mixed) metal clusters with magnetic interactions [134]. The linear heterotrinuclear complexes $[\{Fe(mbtacn)\}_2Ni]^{n+}$ show remarkable similarities to the dinuclear complex of Kersting described above, and reveals three reversible one-electron processes in cyclic voltammetry for the 4+/3+/2+/1+ series of overall charge; X-ray structures have been obtained for the 2+ and 3+ charged species. The electronic structures were studied with several techniques, showing that these compounds cannot be described with localised valences [134].

The reaction of [Ni(L44Me)] (see Section 2.4, Fig. 26) with iron(II) perchlorate resulted in a tetranuclear cluster $[\{Ni(L44Me)\}_3Fe]^{2+}$. Two of the mononuclear nickel complexes acts as didentate ligands with both thiolate sulfurs bridging to the iron centre, the third nickel complex acts as a monodentate ligand; consequently, the high-spin iron(II) centre is in a distorted square–pyramidal geometry of five sulfur-donor atoms [135]. The Ni···Fe distances are in the range of 2.98–3.27 Å.

A reaction of the mononuclear complex [Ni(L45)] (see Section 2.4, Fig. 26) with iron(II) chloride also resulted in a tetranuclear cluster, but with a different composition, namely $[\{Ni(L45)\}FeCl_2]_2$ [136]. The linear tetranuclear cluster is centrosymmetric, the central core consists of two iron(II) ions bridged by two chloride ions, each iron ion having one terminal chloride ion. The peripheral square-planar nickel complexes act as didentate ligands to the iron centres, resulting in a five-coordinate FeS_2Cl_3 chromophore in a distorted square–pyramidal geometry [136]. The nickel–iron distance in this complex is 3.10 Å, the iron–iron distance is 3.73 Å.

More recently, Verhagen et al. reported a similar structure for a nickel complex of the tetradentate S_4 ligand H_2L10 (see Section 2.1, Fig. 6) [137]. Both the nickel–iron and the iron–iron distances are slightly smaller than those in the complex with L51, being 3.04 and 3.69 Å, respectively. The magnetic moment of 5.35 μ_B per iron centre is consistent with isolated high-spin Fe(II) ion [137], but this value is in contrast with the value of 3.49 μ_B per iron centre reported for the L51 complex; the latter low value was explained by assuming an antiferromagnetic coupling being present between the iron centres [136]. Electrochemistry of $[\{Ni(L10)\}FeCl_2]_2$ shows only irreversible processes [137]. It has been proposed, based on spectroscopic and analytical data, that the mononuclear N_2S_2 complex [Ni(L43)] in a reaction with $FeCl_2$ forms a similar linear tetranuclear compound [138].

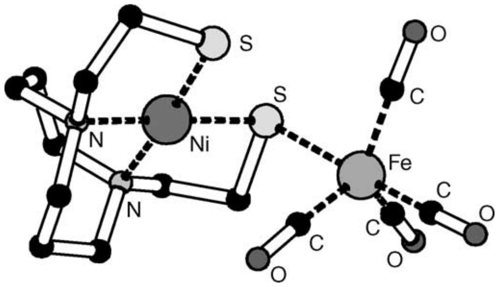


Fig. 33. Molecular structure of $[Ni(L45)Fe(CO)_4]$ [139].

The group of Darensbourg [139] was the first to report a reasonably accurate model system for the [NiFe] active site after the publication of the crystal structure in 1995. Reaction of two equivalents of the nickel complex [Ni(L45)] with $Fe_2(CO)_9$ resulted in the heterodinuclear complex $[Ni(L45)Fe(CO)_4]$ in which the square-planar nickel complex is bridged by one thiolate sulfur at the apex of the trigonal bipyramidal Fe(0) centre, as is shown in Fig. 33 [139]. Because of the single bridge between the metal ions, the nickel–iron distance in this complex is rather long (3.76 Å). Chemical oxidation of this dinuclear compound resulted in the linear trinuclear cluster $[\{Ni(L45)\}_2Fe(CO)_2]^{2+}$, in which the nickel complex is now acting as a didentate ligand to iron using both thiolate sulfurs, thereby reducing the nickel–iron distance to 3.09 Å. The central iron(II) ion is in a *cis* S_4C_2 environment [139].

Chalbot et al. have shown that the nickel complex [Ni(L43)] of the similar, but more flexible N_2S_2 ligand H_2L43, reacts in a totally different manner with $Fe_2(CO)_9$; a trinuclear, triangular complex of formula $[Ni(L43)Fe_2(CO)_6]$ was obtained, which is shown in Fig. 34 [140]. NMR spectroscopy showed that the structure is diamagnetic and is C_2-symmetric in solution. The diamagnetism can be explained by the formation of the triangular metal core with three two-centre two-electron bonds. The ligand folding around the nickel(II) ion has changed from square-planar to "helical" with the two thiolate groups occupying *trans* positions

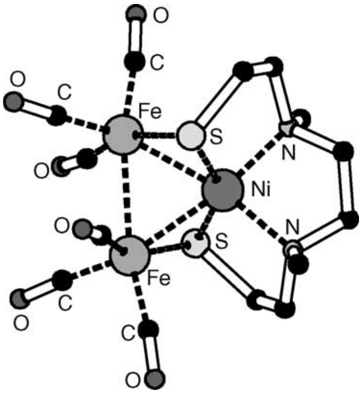


Fig. 34. Molecular structure of $[Ni(L43)Fe_2(CO)_6]$ [140].

(S–Ni–S = 145°); the nickel ion is in a distorted geometry that can be described as octahedral when also the nickel–iron interactions are taken into account. Each of the thiolate groups bridges the nickel ion to one of the iron centres [140].

Very recently, a comprehensive crystallographic, spectroscopic and DFT analysis has been reported by Wang et al. on similar trinuclear complexes containing the same $NiFe_2$ core but in which nickel is in an all-sulfur coordination environment of derivatives of the ligand H_2L5 (see Fig. 5) [141]. These clusters were obtained by a reaction of the mononuclear nickel complex with $Fe_3(CO)_{12}$ and they undergo chemical reversible reduction to generate EPR-active monoanions. The results of detailed studies of the EPR parameters in combination with IR studies and DFT calculations suggest that the SOMO of the reduced cluster is delocalised over all three metal centres with little participation of the sulfur atoms [141].

The reaction of [Ni(L43)] with the complex $K[HFe(CO)_4]$ resulted in even more surprises: as the main product the tetranuclear compound $[Fe(L43)Ni(CO)_3]_2$ was obtained, as a side product the novel diiron complex $[Fe(L43)Fe(bmes)(CO)_2]$ was formed [138]. The latter complex could only have been formed by partial decomposition of the ligand L43 to form bmes, and substitution of the nickel ion by iron, explaining the low yields; it could, however, be reproduced in high yields from a reaction of the complex $[Fe(L43)]_2$ with $K[HFe(CO)_4]$ in the presence of a stoichiometric amount of H_2bmes [142]. The unusual dinuclear iron complex with mixed spin states was reported to be a first speculative model for iron-only hydrogenases [142]. The flexibility of the ligand H_2L43 is reflected in the ease with which the nickel ion is released and replaced by iron, as well as by the fact that it is able to change its binding mode from square-planar with two *cis* thiolates, to “helical” with the two thiolate groups in *trans* positions. This flexibility is also apparent from the tetranuclear cluster $[Fe(L43)Ni(CO)_3]_2$; in this case the metal ions have not only exchanged ligand sites, but also oxidation states [143].

Osterloh et al. have used both the N_2S_2 complex [Ni(L44Et)] and the S_4 containing complex [Ni(ttn)] (see Section 2.1) in their search for new [NiFe] model compounds [144–146]. Reaction of [Ni(L44Et)] with $[Fe(NO)_2(CO)_2]$ resulted in the heterodinuclear complex $[Ni(L44Et)Fe(NO)_2]$, in which the nickel ion is bridged by both thiolate groups to the iron centre. The NO groups are linearly coordinated and therefore must be regarded as NO^+; the formal oxidation state of the tetrahedral iron centre then is −II. The IR spectrum of this complex shows two intense absorption bands at 1663 and 1624 cm^{-1}, that are assigned to the symmetrical and asymmetrical stretching vibration of the nitrosyl ligands [145]. The electrochemistry of $[Ni(L44Et)Fe(NO)_2]$ in acetonitrile shows a quasi-reversible oxidation at +0.120 V versus NHE, which has been tentatively assigned to the Fe^{-II}/Fe^{-I} redox couple. Based on spectroscopic and analytical data, it has been proposed that the mononuclear complex [Ni(L43)] in a reaction with $[Fe(NO)_2(CO)_2]$ forms a similar dinuclear [NiFe] nitrosyl compound, but no crystal structure was reported [138].

Reaction of the cubane cluster $[Fe_4S_4I_4]^{2-}$ with either one of the mononuclear complexes [Ni(L44Et)] or [Ni(ttn)] results in cubane clusters to which one or two mononuclear nickel complexes are bound either in a monodentate or in a didentate fashion. The electrochemistry and NMR spectra of these clusters have been reported; such compounds are of interest as possible models for the active site of CO dehydrogenase and acetyl-CoA synthase [144,146].

Liaw et al. have used a different approach to obtain a dinuclear nickel–iron nitrosyl complex [147]. As starting complexes the compounds $[Ni^{II}(bmes)]_2$ and $[Fe(NO)_2(SePh)_2]^-$ were used (SePh: selenophenolate); reaction of these complexes in the presence of NO_2^- results in the neutral heterodinuclear compound $[(NO)Ni(bmes)Fe(NO)_2]$. Both metals in this structure have a distorted tetrahedral geometry; the nickel centre is coordinated by the tridentate dithiolate ligand and a linearly bound nitrosyl group, the iron centre is coordinated to the two bridging thiolates and two linearly bound nitrosyl ligands. This $\{Fe(NO)_2\}^9$ odd-electron species shows an isotropic EPR signal with $g = 2.02$, and it can be reversibly reduced by one electron at −0.97 V versus NHE [147].

Whereas all attempts described above to synthesise [NiFe] complexes were taking a starting point from mononuclear nickel thiolate complexes, more recently new routes were followed, and interesting results have been obtained by making use of iron thiolate precursors [148,149]. As described in Section 3, the complex *fac*-$[Fe(CO)_3(SR)_3]^-$ may serve as a ligand to other metal ions. A reaction of the complex in which HSR is 2-methyl-3-mercaptofuran with nickel perchlorate resulted in the linear trinuclear complex $[\{Fe(CO)_3(SR)_3\}_2Ni]$ containing an octahedral nickel ion in an S_6 coordination environment capped with terminal $Fe(CO)_3$ groups [131].

The anionic complexes $[Fe(L27)(CO)]^-$ (see Section 3) and $[Fe(L27)(NO)]^-$ have been used by the group of Evans as ligands to nickel; a series of heterodinuclear nickel–iron complexes with bridging thiolate groups has been obtained [150]. The dinuclear compounds $[\{Fe(L27)(CO)_2\}NiCl(dppe)]$, $[\{Fe(L27)(CO)\}NiCl(dppe)]$, $[\{Fe(L27)(NO)\}NiCl(dppe)]$, $[\{Fe(L27)(NO)\}Ni(CH_3)(dppe)]$, and the trinuclear complex $[\{Fe(L27)(CO)\}_2Ni]$ have been described (dppe: 1,2-bis(diphenylphosphanyl)ethane) [150]. As already mentioned in Section 2.2, the chelating diphosphane dppe in these complexes is a capping ligand used as a measure to prevent oligomerisation. Crystal structures of the complexes $[\{Fe(L27)(CO)_2\}NiCl(dppe)]$ and $[\{Fe(L27)(NO)\}NiCl(dppe)]$ show similar coordination environments for the nickel(II) ion, which has a square pyramidal NiS_2P_2Cl chromophore (Fig. 35). The low-spin iron(II) ion in $[\{Fe(L27)(CO)_2\}NiCl(dppe)]$ is in an octahedral geometry with two *cis* carbonyl groups [150]. The iron centre in $[\{Fe(L27)(NO)\}NiCl(dppe)]$ is formally a high-spin Fe(III) ion, the bent binding of the nitrosyl group is in agreement with NO^-. Antiferromagnetic coupling of the iron $S = 5/2$ state with the $S = 1$ of the nitrosyl group results in an overall

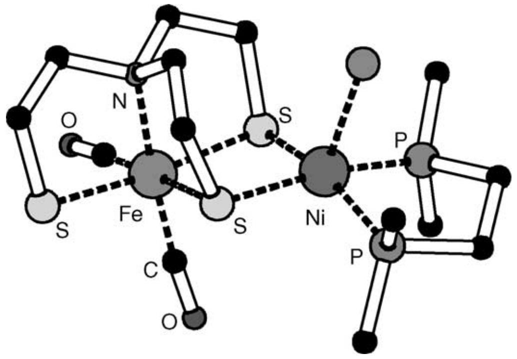


Fig. 35. Structure of [{Fe(L27)$(CO)_2$}NiCl(dppe)] [148].

spin of 3/2 for the $\{FeNO\}^7$ complex [150]. A crystal structure of the complex [{Fe(L27)(NO)}$Ni(CH_3)$(dppe)] shows a remarkable difference as in this compound only one thiolate group bridges the two metal ions, and the nickel ion is square planar with a NiP_2SC chromophore. The Fe–nitrosyl unit in this complex is bent at 152°, again indicating an NO^-, with the iron being formally high-spin Fe(III) [151]. When the "auxiliary" capping ligand dppe is not used, indeed oligomerisation results in the formation of the trinuclear cluster [$\{Fe(L27)(CO)\}_2Ni$]. In this cluster the two peripheral iron(II) ions are in a trigonal bipyramidal geometry, each binding through two thiolate groups to the central nickel(II) ion, which is in a nearly regular tetrahedral S_4 environment [152].

Sellmann et al. have used the dinuclear iron(II) compound [$Fe(L8)(CO)_2]_2$ as a starting complex. Reaction of this compound in tetrahydrofuran with two equivalents of [$Ni(L3)(PMe_3)_2$] results in the formation of the novel dinuclear complex [(L3)Ni(L8)Fe(CO)$(PMe_3)_2$] shown in Fig. 36 [149]. The nickel(II) ion in this complex is surrounded by four thiolate groups in an essentially planar geometry; the iron(II) ion is in an octahedral environment of three sulfur-donors of the ligand L8 in a facial arrangement, one carbonyl group trans to one of the bridging thiolates and two phosphane donors. The nickel-to-iron distance is 3.32 Å, similar to distances found in other thiolate-bridged [NiFe] complexes. The dinuclear complex is diamagnetic, in accordance with both metals being in a low-spin state [149].

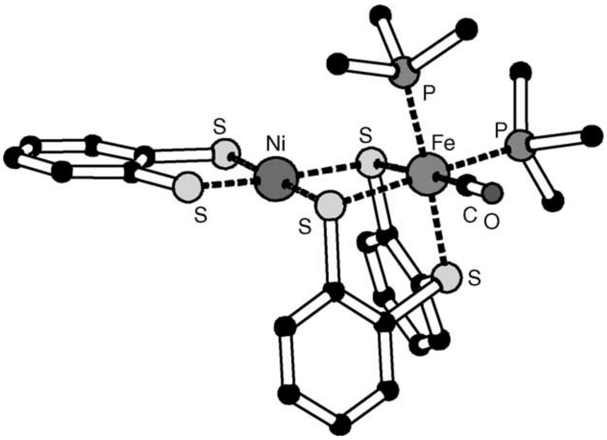


Fig. 36. Molecular structure of [(L3)Ni(L8)Fe(CO)$(PMe_3)_2$] [149].

5. Model complexes and reactivity

5.1. General reactivity of the nickel complexes

Over the past decade the reactivity of mononuclear nickel thiolate complexes has been studied extensively. Basically three types of reactivity have been investigated, all related to the nucleophilicity of the complex:

1. binding to other metal ions (aggregation);
2. reaction with alkylating agents (alkylation); and
3. reaction with hydrogen peroxide or dioxygen (oxidation or oxygenation).

Alkylation and oxidation of thiolate sulfur atoms are processes that may account for deactivation of enzyme active sites. Alkyl-group transfer to a metal-bound cysteine thiolate is a significant reaction in metallobiochemistry and is mediated by a number of zinc-containing enzymes [153]. The X-ray crystal structure of the nitrosylated Fe-nitrile hydratase revealed cysteine oxygenates, in both sulfenic (RSO) and sulfinic (RSO_2) forms, coordinated to the iron atom in the active site. A similar environment has been suggested for the Co-containing nitrile hydratase [154].

The mononuclear nickel thiolate complexes show affinity for binding to other metal ions, which is the origin of (undesired) cluster formation or oligomerisation, but which is also necessary to obtain the desired heterodinuclear [NiFe] complexes, as has been discussed in Section 4. The effect of metallation on the redox potential of the nickel(II) ion has been discussed using a series of hetero-oligometallic complexes derived from [Ni(L45)] [155]. Recently, the X-ray structure of acetyl coenzyme-A synthase (ACS) revealed an unusual dinuclear site connected to a [4Fe–4S] cubane cluster. Initially the nature of the central metal ion in this cluster was unknown, it was suggested that this metal could either be a zinc, copper or nickel ion [156–158]. These reports have initiated studies to the reactivity of mononuclear nickel thiolate complexes with various metal salts. A large number of interesting aggregates have recently been reported, which, however, fall outside the scope of the present review, but are reviewed elsewhere in this issue.

Fundamental investigations of the alkylation reactivity of synthetic metal–thiolate complexes have provided insight into the nucleophilic character of such species. The group of Darensbourg has been very active in this field; they have studied the reactivity of the complexes [Ni(L45)] and [Ni(L45Me)] with a large number of alkylating agents, such as methyl iodide [106], 1,3-dibromopropane, bis(2-iodoethyl)ether [159], and iodoacetic acid [160,161]. In all reactions the alkylated ligand, containing either one or two thioether groups, remains coordinated to the nickel(II) ion in a square-planar mode. The effects of these alkylation reactions on the spectroscopic and electrochemical properties of the nickel complexes have been reported [159,160,162]. The crystal structure for the dimethylated complex $[Ni(L45(SMe)_2)]I_2$ shows that the thioether donors remain coordinated, as they were in the *cis*-dithiolate complex [Ni(L45)], thereby keeping the nickel ion in a low-spin square-planar geometry [106].

In contrast, Kaasjager et al. have shown that the complex [Ni(L43)] with a more flexible N_2S_2 ligand in a reaction with methyl iodide forms the octahedral high-spin nickel(II) complex $[Ni(L43(SMe)_2)I_2]$. In the structure of this complex the thioether-sulfur-donors are coordinating in the axial positions, the binding of the ligand has changed to a “helical” mode, thereby allowing the complex to change to a high-spin state [163]. During this change of folding of the tetradentate ligand from square-planar to “helical” the position of the methyl groups at the nitrogen donor atoms have changed from “*cisoid*” to “*transoid*”, i.e. from the same side of the molecule to opposite sides [163]. This change is necessary to allow the mercaptoethyl arms to occupy axial positions in the octahedral complex. These results indicate that the cyclic backbone of the ligand L45 exerts a considerable strain to the flexibility of the ligand, preventing the twist of the ligand and thereby precludes the formation of high-spin octahedral complexes.

Other groups have also investigated the reactivity of selected nickel thiolate complexes for alkylation reactions. The template-type reactions invariably result in extended ligand systems or macrocyclic ligands. The complex $[Ni(L3)_2]$ in a reaction with one equivalent of bis(2-bromoethyl)amine resulted in $[Ni(L6NH)]_2$ (see Section 2.1, Fig. 5); the use of two equivalents of the reagent resulted in the isolation of the nickel complex of the macrocyclic ligand 1,10-diaza-4,7,13,16-tetrathia-5,14-dibenzooctadecane [164,165].

In a recent report Fox et al. [166] demonstrate that metal(II) complexes coordinated by an N_4-donor ligand and with an axially bound phenylthiolate are alkylated by benzyl bromide according to a common, bimolecular mechanism, but with rates that are governed by the identity of the central metal ion. This type of metal–ion dependence has not been previously described for alkylations of metal–thiolate complexes that retain their integrity in solution [166].

The air sensitivity of transition-metal thiolate complexes typically results in ligand-based oxidation of RS^- to $RS^\bullet$, with subsequent complex degradation. Nevertheless, a growing number of examples is known of reactions of O_2 or other O-atom sources with metal thiolate complexes in which complex integrity is retained.

The group of Maroney was the first to report a nickel sulfinato (RSO_2) complex that was the result of aerobic oxidation of the mononuclear dithiolate complex $[Ni(L27Me)(CN)]^-$ [82]. The dinuclear complex $[Ni(L27Me)]_2$ in DMF reacts with two equivalents of cyanide to form the mononuclear $[Ni(L27Me)CN]^-$ [82]. Chemical oxidation of this dimer with I_2 results in the formation of the cyclic disulfide; the resulting oxidised ligand remains coordinated to nickel with its nitrogen donor, the thioether sulfur and one of the disulfide sulfur atoms. The coordination sphere of the mononuclear nickel(II) ion is completed by two iodide ions, resulting in a square–pyramidal geometry [82]. Dioxygen, however, leads to oxygenation of one of the thiolate groups to a sulfinato group, which in the product remains coordinated through sulfur to the low-spin, square-planar nickel(II) ion. A study of the related complexes $[Ni(L26)]_2$ and the seleno-derivative showed similar oxidation for the thiolate complex, whereas the selenoato complex appeared to be more resistant to oxidation [81].

The dioxygen uptake in the complexes [Ni(L45)] and [Ni(L45Me)] resulted in the isolation of S-oxygenates ranging from monosulfenates (RSO) to the disulfinato species, all S-bound to nickel [107,167]. Reaction of the [Ni(L45)] complexes with isotope labeled $^{18}O_2$ showed that the monosulfinato complex was formed by molecular O_2 addition at a single thiolate sulfur, whereas the disulfinato complex is formed by a cross-site molecular O_2 addition with a disulfenato species as an intermediate [168]. Both products are derived from the initial Ni-bound $RS–O–O^-$ persulfoxide species and the divergent mechanistic pathway accounts for the two products. Higher oxygenation levels of L45 up to sulfonate products have not been reported as yet.

Again in contrast with the studies described above, the complex [Ni(L43)] with the acyclic N_2S_2 ligand in a reaction with H_2O_2 did yield the disulfonato species $[Ni\{L43(–SO_3)_2\}(H_2O)_2]$, in which the sulfonato groups are bound to nickel through oxygen, as shown in Fig. 37 [169]. The increased O-atom uptake of the more flexible ligand resulted in a change from a low-spin to a high-spin nickel ion accompanied by a geometry change from square planar to octahedral. Later studies showed that this high level of oxygenation could even be reached using air. The dithiolate complex [Ni(L43)] reacts with molecular oxygen or H_2O_2 to produce the mixed sulfinato/thiolato complex $[Ni\{L43(–SO_2)\}]$ and

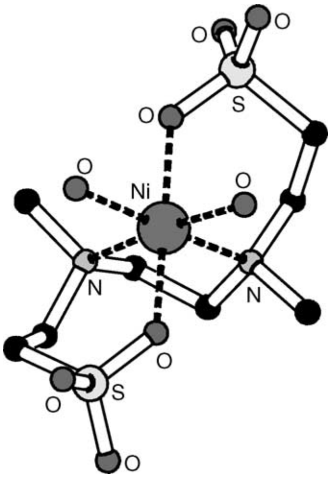


Fig. 37. Molecular structure of $[Ni\{L43(–SO_3)_2\}(H_2O)_2]$ [169].

the fully oxidized product [Ni{L43(–SO_3)$_2$}(H_2O)$_2$]. X-ray analysis of [Ni{L43(–SO_2)}] revealed a square-planar nickel ion coordinated by two *cis* amine nitrogens, one thiolate sulfur-donor and one sulfinato sulfur-donor. This complex is the only intermediate in the oxygenation reaction that could be isolated, and it was shown to be further reactive towards O_2 to yield the fully oxidized product (i.e. the disulfonate species), a hitherto unprecedented reactivity [163].

The group of Riordan has reported some unusual reactivity of nickel complexes with the thioether ligands L13 towards dioxygen (L13^{t}Bu with *R* = *tert*-butyl; L13ad with *R* = adamantyl; see Fig. 7). Reaction of the nickel(I) complex [Ni^I(L13^{t}Bu)(CO)] with dioxygen in toluene at −78 °C led to the thermally unstable species that was formulated as [{Ni^{III}(L13^{t}Bu)}$_2$(μ-O)$_2$] based on its spectroscopic features [170]. The nickel(I) complex [Ni^I(L13ad)(CO)] reacts with dioxygen to form a 1:1 species identified as the side-on dioxygen adduct [Ni^{III}(L13ad)(O_2)]; this formulation is based on the observed reactivity and spectroscopic properties [40].

5.2. Functional model systems; activation of dihydrogen

It may be self-evident that the huge interest in the possibilities of a hydrogen economy, based on the cheap and sustainable generation of H_2, and the clean and efficient oxidation of H_2 in fuel cells has given an impetus to the research for functional models of hydrogenases [171]. It has been shown that dimetallic iron complexes with two thiolate bridges are excellent functional models for the Fe-only hydrogenase that are able to (electro-) generate dihydrogen gas from acidic solutions [172]. Hydronation mechanisms of nickel complexes and the relevance to hydrogenases, as well as industrial catalysts have recently been reviewed [173]. A number of studies have been reported in which the functional model is based on metals other than nickel, such as rhodium [174] or ruthenium [175], but these fall outside the scope of this review.

In the search for active functional models for [NiFe] hydrogenases several of the structural models described in the previous sections have been tested on hydrogenase activity. Mainly three types of activity can be distinguished: H_2/D^+ exchange (scrambling), activation of H_2 (oxidation to H^+), and reduction of H^+ to H_2. For functional models of the [NiFe] hydrogenases the first two activities are of importance.

Zimmer et al. have studied the catalytic activity of the complex [Ni(H_2L21)$_2$]Cl_2 (see Section 2.3, Fig. 17) for D_2/H^+ exchange in ethanol [63]. A 0.1 M solution of this complex in a dmso/EtOH mixture (90:10) resulted in 7.5 turnovers of H/D exchange in five minutes at 25 °C and a D_2 pressure of 1 bar. Similar complexes lacking one or both phenolic hydrons did not show any activity in H/D exchange, leading to the conclusion that both phenolic hydrons are required for activity. It has been suggested that hydrogen bonding might increase the affinity of the complex for D_2 and thus promote exchange [63]. Similar dinuclear complexes with substituted dianionic ligands L22 and L23 have been used in other catalytic studies, namely silane alcoholysis [176], and reduction of methylviologen [62]. The group of Crabtree has also studied the electrocatalytic generation of dihydrogen from hydrons by a nickel(II) complex of the macrocyclic N_4 ligand obtained by the condensation of 2,6-diacetylpyridine with bis(3-aminopropyl)amine [177]. In an aqueous solution containing this nickel(II) complex, catalytic currents resulting from H_2 evolution are observed. Controlled-potential electrolysis of solutions at pH 2 of the nickel complex has resulted in a yield of 14.2 ml of H_2 after 12 h, whereas a blank electrolysis experiment in the absence of the catalyst resulted in only 0.3 ml of dihydrogen [177].

In the group of Mascharak the reactivity of the complexes [Ni(terpy)(SR)$_2$] and [Ni(dapa)(SR)$_2$] towards hydride-donors and dihydrogen has been studied (see also Section 2.4). The dapa complexes bind H^- more readily than the terpy analogues and can they can even be reduced by H_2 to produce the hydride complex, [Ni^I(dapa)(EPh)$_2$(H)]$^{2-}$, with E = S or Se [72]. Enhancement of the intensities of the EPR signals of the hydride adduct in the presence of a base indicates heterolytic cleavage of dihydrogen at the nickel site [72].

Interesting reactivity was observed for the complex [Ni(NHP^{n}Pr$_3$)(L8)] synthesized by Sellmann et al., shown in Fig. 38 (see also Section 2.1). The nickel(II) ion in this complex is coordinated by three sulfur-donors of the tridentate ligand and one nitrogen donor originating from a phosphorane imine group in a severely distorted square-planar arrangement with *trans* angles of 160° [29]. When this complex is treated with D_2 gas at a pressure of 10 bar, the imine hydron is exchanged for a deuteron with the concurrent formation of HD. This reaction is slow and could be monitored using ^{1}H and ^{2}H NMR spectroscopy, confirming the formation of the deuterated imine, as well as a triplet for HD. Isolation of the complex after treatment with 30 bar of D_2 for 96 h, resulted in a complex for which the IR spectrum shows a ν(ND) band at 2427 cm^{-1}, whereas the starting complex has a ν(NH) band at 3273 cm^{-1}. In the proposed mechanism, it is suggested that D_2 binds to the nickel centre in an apical position and is

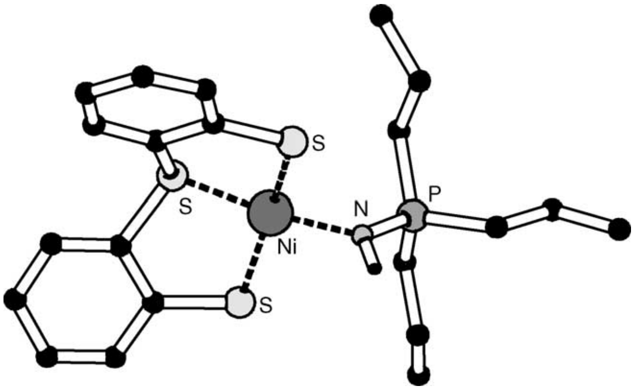


Fig. 38. Molecular structure of [Ni(L8)(NHP^{n}Pr$_3$)] [27].

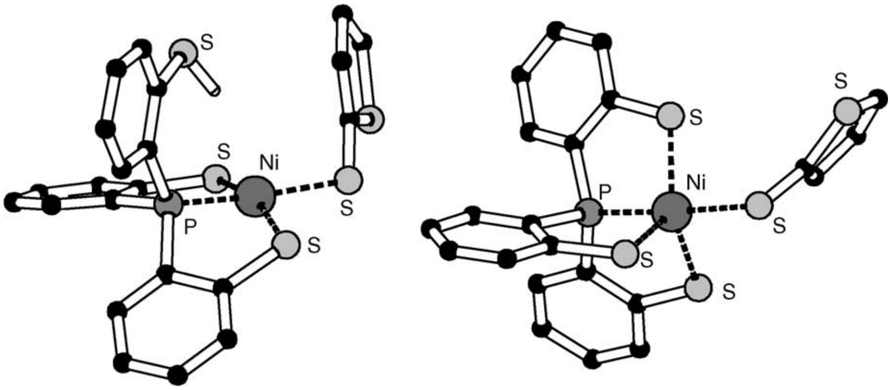


Fig. 39. Molecular structures of $[Ni^{II}(HL17)(SR)]^-$ and $[Ni^{III}(L17)(SR)]^-$ [178].

heterolytically cleaved by the concerted action of the Lewis-acidic nickel centre and one Brønsted-basic thiolate donor. After scrambling of the acidic thiol deuteron with the acidic phosphorane imine hydron, HD is recombined and released [29]. Recently, the group of the late Prof. Sellmann has reported that the complexes $[Ni(^{R}L8)(S^{t}Bu)]^-$ are also capable of D_2/H^+ exchange under a pressure of 18 bar D_2 [33]. These are the first nickel complexes in a sulfur-only coordination environment that can be regarded as active functional models of the [NiFe] hydrogenases.

Lee et al. have recently reported a nickel(II) complex of the tripodal ligand H_3L17 in which one of the thiol groups is hydronated [178]. In the complex $[Ni^{II}(HL17)(SR)]^-$ shown in Fig. 39, the nickel ion is in a distorted square-planar PS_2S' chromophore, formed by a tridentate chelate of the ligand HL17 and a thiolate donor from 2-mercaptothiophene. The hydron residing on the non-coordinating arm of the tripodal ligand is at a distance of 2.55 Å from the nickel ion, and is 2.89 Å away from one of the thiolates of HL17. The related compound $[Ni^{II}(HL17)(SeR)]^-$ (SeR: selenophenol) shows H/D exchange with D_2O; the IR spectra show a shift of the 2273 cm^{-1} S–H vibration to 1676 cm^{-1} for S–D. Instead of a ligand-based oxidation to form disulfide and the dinuclear complex $[Ni^{II}(L17)]_2{}^{2-}$, in a reaction with dry dioxygen the complex is oxidized to form $[Ni^{III}(L17)(SR)]^-$, in which the nickel(III) ion is in a trigonal–bipyramidal geometry (Fig. 39) [178]. In the oxidation reaction a molecule of water is produced as the by-product, as has been confirmed with ^1H and ^2H NMR spectroscopy using the deuterated complex $[Ni^{II}(DL17)(SR)]^-$. The EPR spectrum of the Ni(III) complex is rhombic, with *g* values of 2.304, 2.091 and 2.0 [178].

Bis(diphosphane)nickel complexes have been reported that show heterolytic splitting of dihydrogen [179]. The complex $[Ni(PNP)_2](BF_4)_2$, in which PNP is $Et_2PCH_2N(Me)CH_2PEt_2$, possesses both hydride and hydron acceptor sites. When dihydrogen gas is passed through a solution of $[Ni(PNP)_2]^{2+}$ in acetonitrile or dichloromethane the solution bleaches during the formation of the hydride species $[HNi(PNHP)(PNP)]^{2+}$. In this reaction, one of the central nitrogen atoms of the ligands is hydronated. In the ^1H NMR of the complex $[HNi(PNHP)(PNP)]^{2+}$ at lower temperatures two resonances are observed at −15.2 and 7.4 ppm. These resonances have been assigned to the hydride and to the NH-proton, respectively. The hydride and the NH hydron undergo rapid intramolecular exchange with each other and with hydrons in solution. After addition of a base, the complex $[HNi(PNP)_2]^+$ is formed. Hydronation of the corresponding Ni(0) complex $[Ni(PNP)_2]^0$ with NH_4PF_6 yields the complex $[HNi(PNP)_2](PF_6)$. The observation of a resonance at −14.8 ppm in the ^1H NMR spectrum of this complex confirmed the presence of a hydride species. A comparison has been made with other bis(diphosphane)nickel complexes, resulting in the conclusion that larger tetrahedral distortions of the nickel ions lead to better hydride acceptors. When the bis(diphosphane)nickel complexes do not have a nitrogen atom available as hydron acceptor site, the complexes do not show hydride exchange. Based on these observations it was suggested that the nitrogen atom of the bridging di(sulfanylmethyl)amine bridging ligand in [Fe] hydrogenases is necessary for activity [179].

Kinetic studies have been performed on the hydronation of various thiolate donors in the complexes $[Ni(triphos)(SR)]^+$ in acetonitrile solution (triphos: bis(1-diphenylphosphanyl-2-ethyl)phenylphosphane) [180]. The measured pK_a values in acetonitrile correspond to values in the range of 7–8 in water, suggesting that in physiological conditions a thiolate group is always the initial site of hydronation. Unexpected differences in the behaviour of the complexes containing either benzenethiolate or ethanethiolate groups are indicative of the formation of an η^2 H–SEt interaction in the latter. This side-on coordination may be an intermediate in partial intramolecular hydron transfer of the thiol group to the nickel centre [180].

6. Concluding remarks

A variety of complexes have been synthesised to structurally model the active site of hydrogenases. The earlier views on the possible active site indeed has generated a large variety of interesting new coordination compounds, which no doubt has greatly contributed to the increased understanding of nickel coordination chemistry. The survey described above of the successful syntheses of thiolato complexes of nickel with simple starting materials, has not only illustrated a rich chemistry, but also a number of important features. Homoleptic nickel thiolate complexes tend to form oligonuclear clusters due to the tendency of thiolates to form bridges between metals. A proper choice of reaction conditions, such as the solvent and the stoichiometry, may prevent oligomerisation, but also the use of capping ligands such as phosphanes have proved useful in this respect. The use of chelating ligands that include thioether functions, have reduced the tendency for polynucleation. Such thioether groups are equally relevant as ligands in these complexes, because in hydrogenases often hydrogen bridges exist between the peptide chain and the thiolate sulfurs, making the reactivity and properties of the cysteine thiolates resemble that of thioethers. The chemistry becomes even richer when other donor atoms are part of the chelating ligands, such as O, N or P. This is not only true for Ni thiolate complexes, but also for the heteronuclear Ni–Fe complexes; they at least also contribute to the stability of the Ni geometry. The redox potentials of the various nickel complexes reported in the several studies have been shown to vary quite dramatically.

Excellent progress has been made in the synthesis of complexes modelling the iron centre of the [NiFe] hydrogenase active site. Deceptively simple iron complexes, in fact, show high resemblance with the active site, considering the IR vibrations of the carbon monoxide and cyanide molecules. The quest for heterodinuclear [NiFe] complexes resembling the hydrogenase active site has proven to be difficult, but some breakthroughs have recently been reported. The use of restricting ligands such as phosphanes also in this case seems to be of crucial importance.

In recent years it has become clear that the biomimetic systems that have been developed for the nickel-containing enzymes [NiFe] hydrogenases are also relevant for the study of mimics for acetyl-coenzyme-A-synthase/CO-dehydrogenases. The intense study of such systems in recent years, both by biomimetics and as the enzymes has another important driving force, in addition to the fundamental interest and exciting coordination chemistry. In fact, a more practical driving force for such studies is the reactivity of nickel enzymes in the generation or consumption of dihydrogen. This property is of great significance because future world energy problems may be reduced, or perhaps even solved by the development of a sustainable hydrogen economy. So the rational design and synthesis of structural and functional models for hydrogenases, as well as their characterisation and reactivity studies might contribute to the development of new catalysts for practical use in, e.g. fuel cells, as has been expertly described by Cammack et al. [181]. In a number of countries and cities, in fact, already public transport is partly using dihydrogen gas as a fuel.

Acknowledgement

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