Biomimetic Chemistry of Nickel

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I. Introduction

Nickel is now recognized as an essential trace element for bacteria, plants, animals and humans.[1–6] While the role of this metal in animal biochemistry is still not well defined, to date four bacterial enzymes have been found to be Ni dependent: urease (also found in plants), carbon monoxide dehydrogenase (CODH), hydrogenase (H_2-ase), and methyl-*S*-coenzyme-M methylreductase (MCR), which employs a Ni-containing prosthetic group (factor 430). The Ni environment within each protein is different; however, the Ni centers are believed to reside within the active sites of all these enzymes and to be intimately involved in their catalytic cycles. Several aspects of the chemistry of these biological Ni ions are unusual in the context of the known coordination chemistry of nickel: three of the four enzymes are known to contain redox-active nickel centers that can cycle between the +3, +2, and/or +1 oxidation states, in thiolate-rich or tetrapyrrole ligand environments that were not previously thought to favor metal-centered redox processes in Ni complexes. The reactions catalyzed by the enzymes, namely C–S bond cleavage (MCR), the oxidation of H_2 and reduction of H^+ (H_2-ase), and the interconversion of CO and CO_2 and the formation or cleavage of C–S and C–C bonds (CODH), are also highly unusual for nonorganometallic Ni complexes. The exception to this is urease, which is thus far a unique example of the natural employment of the Ni^{2+} ion as a Lewis acid catalyst.

None of the above enzymes has been characterized by X-ray crystallography, and knowledge of their active site structures and modes of activity is therefore limited to that derived from spectroscopic methods and other physicochemical techniques. Despite the plethora of such data now available, many details of the nature and role of the Ni centers in these enzymes are still unclear. This continuing uncertainty has inspired a concurrent growth of interest in the coordination chemistry of nickel; significant

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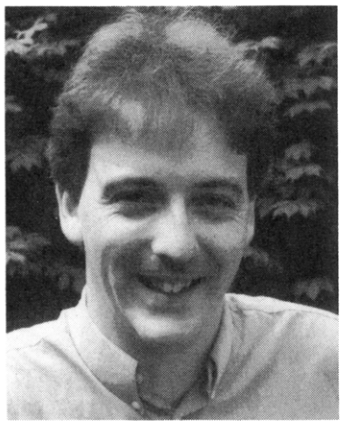
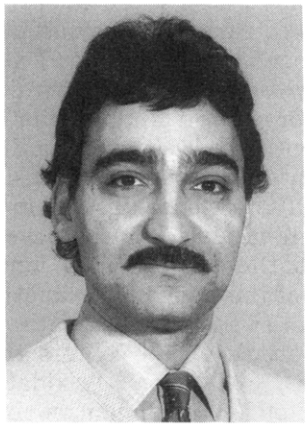


Malcolm Halcrow was born in Liverpool, England, in 1966. He received his Bachelor's degree from the University of Cambridge, and completed his Ph.D. in 1991 under Martin Schröder at the University of Edinburgh, on the crown thioether complex chemistry of nickel, rhodium, and iridium in low oxidation states. He held a one year (1992) Royal Society post-doctoral fellowship with Bruno Chaudret's group at the Laboratoire de Chimie de Coordination du CNRS in Toulouse, France, studying the mechanisms of aromatization reactions of natural products using the electrophilic "Cp*Ru$^+$" fragment and the synthesis of novel ruthenium dihydrogen complexes. At the beginning of 1993 he moved to Indiana University, where he was a Research Associate in George Christou's group at the time of writing this article, investigating the synthesis and structural and magnetochemical properties of polynuclear carboxylate aggregates of manganese and nickel, and the oxidation reactions of molybdenum persulfide complexes. In January 1995 he is taking up a Royal Society research fellowship at the University of Cambridge.



George Christou was born in 1953 on the Mediterranean island of Cyprus and emigrated with his family to London in 1956. He obtained his Ph.D. degree at Exeter University under the supervision of the late H. N. Rydon in the area of bioinorganic chemistry. During 1978–79 he was a post-doctoral fellow with C. David Garner at the University of Manchester and then a NATO post-doctoral fellow with Richard H. Holm at Stanford and Harvard Universities. In 1982 he was appointed to a faculty position at Imperial College, London, where he was also a SERC Advanced Fellow, and in the Fall of 1983 he took up his present position on the faculty of Indiana University, where he is currently Professor of Chemistry. His research interests fall into three areas, namely: (i) the synthesis and detailed characterization of polynuclear carboxylate complexes of manganese and other first row transition metals, with regard to both the elucidation of the mechanism of water oxidation by the tetramanganese cluster of photosystem II and the preparation of novel molecular ferromagnets; (ii) group V metal sulfur chemistry, including its relevance to hydrodemetalation and hydrodesulfurization catalyst poisoning; and (iii) the interactions of 4d metal carboxylates with nucleobases and related ligands, as models for the carcinostatic properties of dinuclear rhodium(II) complexes. He has held both an Alfred P. Sloan Foundation Fellowship (1987–89) and a Camille and Henry Dreyfus Foundation Teacher Scholar award (1987–92), while he has also received the Corday-Morgan medal of the Royal Society of Chemistry (1986) and the 1993 Dwyer medal of the Australian Chemical Society.

efforts toward the synthetic modeling of all of the above nickel biosites have been expended by many research groups worldwide. While we are only beginning to see the development of realistic structural and functional models for all these enzymic Ni centers, results from such work have already showed their importance by allowing early hypotheses about the structures of the H_2-ase and CODH Ni centers to be ruled out. The synthesis of model complexes of increasing sophistication may be anticipated in the near future.

The *raison d'être* of this article is the discussion of the coordination chemistry of nickel relevant to, and inspired by, the properties of Ni enzymes. The enzymology and biochemistry of urease, CODH, MCR, and H_2-ase have been frequently reviewed in the chemical and biochemical literature,[11−44] three comprehensive monographs in this area having appeared during the preparation of this article,[17−19] and we will discuss here only briefly those spectroscopic, structural and mechanistic aspects of interest to the inorganic chemist. The properties of nonnatural Ni-substituted enzymes are also covered, where the data thus derived can shed light on the native Ni-containing systems. In most sections of the article, comprehensive literature coverage between 1988 and early 1994 has been the aim, although earlier work is also cited where appropriate. In some areas, however, notably the discussion of the Ni coordination chemistry of sulfur-containing ligands in sections IX.B and IX.C, the volume of published work has necessitated that we discuss only those compounds of relevance to the modeling of Ni enzymes; we apologize if our value judgements in this regard do not match those of the reader, who is referred to refs 7−10 and 11−19 for earlier discussions of nickel coordination chemistry and bioinorganic chemistry, respectively. Other topics in nickel biochemistry, such as the interaction of Ni complexes with DNA,[45] Ni transport and accumulation *in vivo*[18] and Ni toxicology,[2,4,18,46] are beyond the scope of this review.

Throughout the text, redox potentials and EPR hyperfine coupling constants have been quoted according to the reference standard and units, respectively, employed by the original authors; these data are each converted to a common scale in Table 6, however, to aid comparison. Relevant conversion factors are as follows: for redox potentials $E_{1/2}$(SCE, V) = $E_{1/2}$(Fc/Fc$^+$, V) + 0.40, $E_{1/2}$(SCE, V) = $E_{1/2}$(NHE, V) − 0.24, $E_{1/2}$(SCE, V) = $E_{1/2}$(Ag/AgCl, V) − 0.02, $E_{1/2}$(SCE, V) = $E_{1/2}$(Ag/Ag$^+$, V) + 0.24; for hyperfine coupling constants A (G) = A (MHz) × g/0.7145; A (G) = A (cm^{-1}) × g/(2.1420 × 10^4); A (G) = A (mT) × 10. Note that conversions between redox scales are only approximate, since the potentials of reference electrodes can vary between solvents and different experimental conditions. All magnetochemical exchange interaction constants are given according to the $\mathbf{H} = -2JS_1 \cdot S_2$ convention.

II. Urease

Urease (urea amidohydrolase) catalyzes the hydrolysis of urea to ammonia and carbamate (reaction 1), which then spontaneously degrades *in vivo* to give

a second mole of ammonia and bicarbonate (reaction 2).[20-24] This contrasts with the uncatalyzed aqueous degradation of urea, which affords ammonia and cyanic acid (reaction 3).[75] The enzyme is found in

$$(H_2N)_2C{=}O + H_2O \rightarrow H_2NCO_2^- + NH_4^+ \quad (1)$$

$$H_2NCO_2^- + H_2O \rightarrow HCO_3^- + NH_3 \quad (2)$$

$$(H_2N)_2C{=}O \rightarrow HN{=}C{=}O + NH_3 \quad (3)$$

both plants and bacteria; while several bacterial ureases appear to be involved in the pathology and metabolism of these organisms, urease in plants may play a role in nitrogen metabolism or defense.[23,47] The generation of ammonia from urea fertilizers by soil bacteria has an adverse effect on crop germination and growth,[48] and much effort has been devoted to the study of this phenomenon.

Ureases from the two classes of source differ in their tertiary structures; however, they show extensive sequence homology, and their spectroscopic and catalytic properties are almost indistinguishable. All known ureases contain two moles of redox-inactive Ni per catalytic unit,[19,20,23] which are thought to form a dinuclear center within the active site; urease is thus a member of a growing family of hydrolases employing (mainly Zn^{2+}- or Mg^{2+}-containing) di- or trimetallic active sites.[49] Apourease can be reconstituted with Ni^{2+} *in vivo*[50] and *in vitro*,[51] this process requiring the presence of a series of Ni transport and translocation proteins; replacement of the urease Ni content by growth of Jack beans on soils rich in other first row transition metal ions produces inactive enzyme.[52] The two best characterized ureases are from the Jack bean and *Klebsella aerogenes*; the Ni sites in these enzymes appear to be identical, and data from both sources are cited here.

Although the enzymology of urease continues to receive much attention, the nature of the dinuclear Ni center within the enzyme is still poorly defined. The electronic spectrum of urease shows d−d absorptions at λ_{max} (ϵ_{max}) = 1060 nm (10 M^{-1}·cm^{-1}), 910 (14), 745 (46) and 407 (sh),[53] consistent with octahedral or high-spin five-coordinate Ni ions bound by N- and O-donor ligands.[8] Saturation magnetization measurements[54] and MCD[55] data were interpreted as showing the presence of a mixture of weakly antiferromagnetically coupled ($J = -6.3$ cm^{-1}, $D = -6.9$ cm^{-1}, *ca.* 80% of the total Ni) and either isolated or ferromagnetically coupled (*ca.* 20%) $S = 1$ spins. However, a more comprehensive magnetization study of two ureases at different field strengths was interpreted on the basis of mixtures of magnetically isolated $S = 1$ and $S = 0$ ions with high zero-field splittings ($D \geq -35$ cm^{-1}) and g values ($2.0 \leq g \leq 2.7$), which was taken to imply a mixture of noninteracting six- and five-coordinate Ni centers;[56] the proportion of low-spin Ni^{II} ions in the sample appeared to increase with increasing pH. The earlier analysis did not allow for the presence of an $S = 0$ Ni fraction. In this regard, however, it is noteworthy that both Ni^{II} centers substituted into histidine/carboxylate sites in other enzymes (section III.A), and synthetic mononuclear Ni^{II} carboxylate-containing complexes (section III.B), show almost exclusively high-spin configurations. Given the absence of thiolate ligation to the urease Ni center, the only biological donor that might afford such a diamagnetic Ni^{2+} species would be a deprotonated amide donor from the peptide backbone; the absence of a short (<2 Å) Ni−N vector in the published EXAFS analyses of urease (*vide infra*) appears to rule out this possibility.

Table 1. Electronic Spectra of Urease and Ni-Substituted Enzymes in Histidine- and O-Donor Sites Obtained by UV/Visible or Magnetic Circular Dichroism Spectroscopies

enzymes[b]	coordination sphere[a]	λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1})	ref
urease	5,6?, N/O	1060 (10), 910 (14), 745 (46), 407 (sh)	53
2-Me:urease	5/6?, N/O/S	750, 432 (530), 380 (sh), 322 (2230)	55, 68
Ni-PGM	Oct, O_6?	1300 (5), 730 (7), 410 (23)	104
Ni-FeADH	Oct, $N_{3-4}O_{2-3}$	654 (sh), 621 (12.0), 549 (5.7), 448 (sh)	108
UreE	Oct, $N_{3-5}O_{1-3}$	1000, 615, 360 (<50)	893
Ni-BSA	SqPy, N_4O	480 (sh), 420 (125), 340 (sh)	109
Ni-CPA	N_2O_3	1060 (3), 685 (7), 412 (24)	87
Ni-CA	N_3O_{2-3}	640 (30), 390 (85)	93
NiZn-SOD	N_4O	675 (14), 390 (85)	111
NiCo-SOD	N_4O	393 (100)	111
Ni-LADH	N_2OS	680 (80), 570 (130)	636
Ni-Az	N_2S_2	590 (400), 550 (500)	634
Ni-St	N_2S_2	565 (320), 540 (350)	634

[a] Oct = octahedral; SqPy = square pyramidal. [b] Az = azurin; BSA = bovine serum albumin; CA = carbonic anhydrase; CPA = carboxypeptidase A; FeADH = iron-activated alcohol dehydrogenase; LADH = liver alcohol dehydrogenase; 2-ME = 2-mercaptoethanol; PGM = phosphoglucomutase; SOD = superoxide dismutase; St = stellacyanin; UreE = ureolytic bacterial Ni transport protein E.

Ni *K*-edge EXAFS studies on urease and several model compounds have been interpreted on the basis of either pseudooctahedral[57-59] or five-coordinate[60] enzymic Ni centers, with five or six N/O-donor ligands at Ni−L = 2.06 Å, a weak feature at 3.3 Å being tentatively attributed to an Ni···Ni vector,[60] while the *K* edge shows an enhanced 1s → 3d preedge feature at 8332 eV,[59,60] implying some deviation from an ideal octahedral stereochemistry about the Ni^{II} ions.[61] Mutagenesis studies imply that at least three histidine residues are involved in coordination to Ni,[62] while the aforementioned MCD data suggest predominantly O-coordination about the Ni centers.[55] Finally, the observed inhibition of urease by Et_3O^+ is consistent with a role for at least one carboxylate residue in Ni binding or catalytic turnover.[70] Hence, it seems clear that urease Ni ligation involves both N- and O-donor residues.

Incubation with 2-mercaptoethanol (2-ME), a potent urease inhibitor, causes the appearance of S → Ni charge-transfer absorptions in the electronic spectrum[53,68,69] but little change in the d−d transitions (Table 1),[55] and affords a strongly antiferromagnetically coupled system with $J = -40(10)$ cm^{-1} [54,55] (a high value for coupling between Ni^{II} ions[8]), which was taken to indicate thiolate bridging between the Ni centers (Figure 1). Ni-XAS data on 2-Me-inhibited urease show one Ni−S distance of 2.29 Å, five N/O ligands at 2.07 Å, and a Ni···Ni

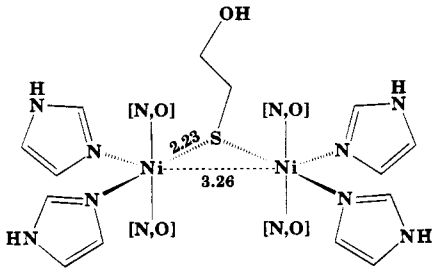


Figure 1. Proposed structure of the dinickel site in 2-mercaptoethanol-inhibited urease. Adapted from ref 60.

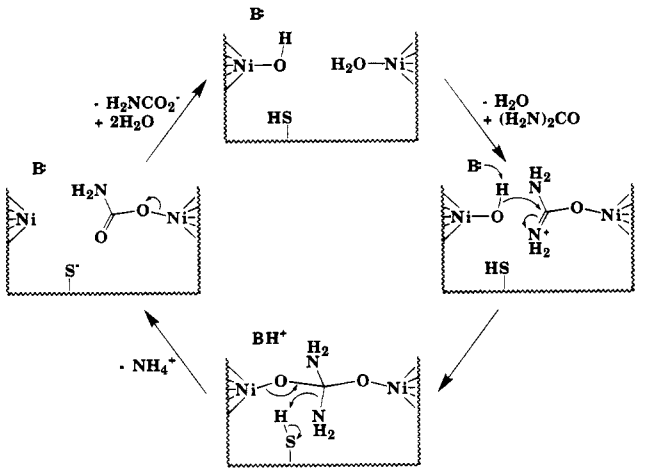


Figure 2. Proposed mechanism of action of urease, based on the work of Zerner and co-workers (ref 70).

distance of 3.26 Å, together with the aforementioned preedge feature, suggesting that thiolate binding to the enzyme occurs by simple ligand substitution at the Ni^{2+} ion(s).[59,60] Several other urease inhibitors, including other thiols, diamidophosphates and acetohydroxamic acid (AHA) derivatives, have also been suggested to bridge between the Ni ions, AHAs being proposed to form stable tetrahedral hydrolysis intermediates bridging the two Ni centers, in the same manner as shown for urea hydrolysis in Figure 2 (*vide infra*):[64,69,70,72] MCD studies on AHA-inhibited urease were consistent with noninteracting octahedral Ni^{2+} ions, however.[76] Urease inhibition by F^- involves terminal Ni−F binding.[69]

While it is clear from the above data that urease Ni is ligated by N- and O-donors only, the coordination geometry about each Ni ion, the distance between the metal centers and the nature of any bridging ligand(s) remain to be determined. On the basis of comparisons with dinuclear Ni complexes containing bridging carboxylate[123,194−196,210] or carbonate ligands,[77,78,96] or by employment of molecular models,[70] the bridged intermediate in the proposed urease hydrolysis mechanism (*vide infra*) is thought to possess a Ni···Ni separation of approximately 3.4, 4.2, or 6 Å depending on the Ni−O−C angle; the presence of a carboxylate or imidazolate bridge between the Ni ions in this species would require a Ni···Ni distance of ≤4.0 and ≥5.3 Å, respectively. Model studies (section III.B) imply that only weak antiferromagnetic exchange interactions ($0 \geq J \geq -5$ cm^{-1}) might be expected between Ni^{II} ions bridging by these functions, such low values being difficult to determine unambiguously for protein samples. An X-ray structural determination of a bacterial urease is in progress.[63]

Urea hydrolysis by urease, which shows $k_{cat} = 5.87 \times 10^3$ s^{-1} at pH 7 and 38 °C,[70] occurs 10^{14} times faster than in the absence of enzyme.[75] In addition to Ni^{2+}, urease activity requires a cysteine residue believed to be ion paired to a histidine residue within the active site[20,22,65,66] and to function as a Brønsted acid. Significantly, this cysteine lies in a histidine-rich region of the polypeptide.[67] A detailed kinetic study of urease hydrolysis of urea and substrate analogues by Zerner and co-workers afforded the proposed mechanism shown in Figure 2,[70] involving nucleophilic attack at a urea molecule O-coordinated to one Ni ion by a hydroxyl moiety which may be coordinated to the second Ni center. The coordinated substrate molecule was suggested to be stabilized and polarized by H-bonding to a carboxylate residue within the active site (not shown).[70,73] The exogenous base ("B") has recently been proposed to be a histidine residue.[74] More recent inhibition data[68] and a molecular modeling investigation[71] have supported this mechanism, which is similar to those proposed for amide and phosphate ester hydrolysis by poly-zinc sites in enzymes such as aminopeptidase, phosphatase, and nuclease;[49,80,81] the molecular modeling study also demonstrated the possibility of an alternative pathway involving nucleophilic attack at a Ni-coordinated urea molecule by a cysteine thiolate group.[71] It is noteworthy, however, that the Zerner scheme does not necessarily require the presence of a dinuclear Ni site or a specific mode of urea binding, model chemistry having demonstrated that the steps involved can also take place at a mononuclear Ni center[22] and at a N-coordinated urea ligand[82,126] (section III.C). The pK_a of any Ni-bound water in the urease active site and its participation as a nucleophile in the catalytic cycle also remain to be conclusively demonstrated.

III. Hydrolysis Catalysis by Nickel Complexes and Nickel-Substituted Enzymes

A. Nickel-Substituted Hydrolytic Enzymes

A large number of enzymes are dependent on a divalent Lewis acid ion such as Ca^{2+}, Mg^{2+}, Fe^{2+}, or Zn^{2+}; these metal ions are often readily removed by a chelating agent such as edta or bpy, and many of the resultant apoenzymes have been reconstituted with nonnative cations. Ni^{2+} can act as both a mechanistic and structural probe in such cases, since the native metal ions often have no available spectroscopic or magnetic handle.[83,84] The fact that the Ni enzymes thus obtained often retain complete or partial activity demonstrates that Ni^{2+} can indeed carry out the roles proposed for it in urease, namely polarization of a carbonyl C=O bond and activation of a coordinated water molecule toward deprotonation.

The best characterized of these synthetic Ni proteins is Ni-carboxypeptidase A (Ni-CPA), whose native enzyme catalyzes the hydrolysis of peptide amide

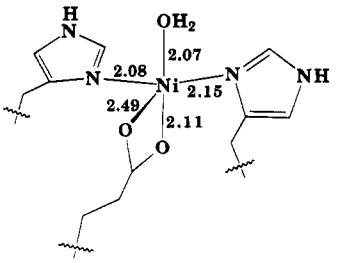


Figure 3. The structure of the active site in Ni-substituted carboxypeptidase A. Adapted from ref 90.

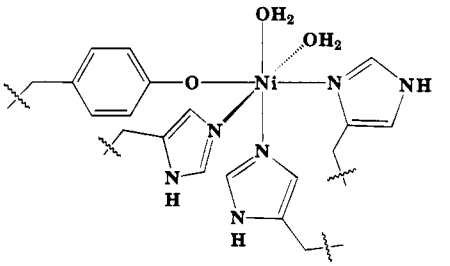


Figure 4. The structure of the active site in Ni-substituted astacin. All Ni–ligand distances are 2.1–2.3 Å. Adapted from ref 98.

bonds (reaction 4) and contains a five-coordinate $[Zn(his)_2(O,O'\text{-glu})(OH_2)]^+$ center within the active site, the carboxylate ligand being asymmetrically bound:[85]

$$RC(O)NHR' + H_2O \rightarrow RCO_2H + H_2NR' \quad (4)$$

Ni-CPA shows *ca.* 50% of the activity of the native enzyme toward amide hydrolysis.[86] The spectroscopic (Table 1)[87–89] and magnetic[54,87] properties of the Ni enzyme were originally thought to arise from an octahedral Ni^{2+} ion, but are also consistent with a high-spin five-coordinate Ni center.[88,89] A single-crystal X-ray structural determination of Ni-CPA showed the Ni complex to exhibit a more regular square pyramidal geometry (Figure 3) compared with the native Zn site.[90] Carboxylate inhibitors bind directly to the Ni^{2+} ion in Ni-CPA;[89] the precise role played by metal ions in amide hydrolysis by CPA is still unclear, however.[85]

In contrast to the above results, Ni-substituted carbonic anhydrase (Ni-CA) shows greatly reduced activity for CO_2 hydration (reaction 5).[91] The elec-

$$CO_2 + H_2O \rightarrow HCO_3^- + H^+ \quad (5)$$

tronic spectral (Table 1),[92–94] ^1H NMR[92,95] and magnetic[54] properties of this enzyme have been interpreted on the basis of an octahedral Ni^{II} ion containing at least one aqua ligand, with a five-coordinate species possibly being observed at higher pH[93] or in the presence of inorganic anions;[94] this contrasts with the tetrahedral $[Zn(his)_3(OH_2)]^{2+}$ site in the native enzyme. The low activity of Ni-CA has been rationalized on the basis of the preferred bidentate mode of coordination of the CO_2 hydrolysis product bicarbonate to a Ni^{II} center (*cf.* approximately monodentate to Zn^{2+}).[96,97]

In the light of the above hypothesis, the recently reported single-crystal X-ray structural characterization of Ni-substituted astacin is of interest.[98] Astacin is a peptidase, containing a trigonal bipyramidal Zn^{2+} ion with a $[Zn(his)_3(tyr)(OH_2)]^+$ geometry; the role of the Zn center in catalysis is uncertain. Ni-astacin, by contrast, shows an octahedral stereochemistry about the Ni^{2+} ion, the sixth coordination site being occupied by a second aqua ligand (Figure 4). The observed inactivity of the Ni-substituted enzyme toward peptide cleavage was rationalized on the basis of this expanded coordination sphere at Ni, which was suggested to block access of the substrate to the active site pocket or to interfere sterically with the transition state(s) during catalysis. Given that a similar change from tetrahedral to five- or six-coordination is also believed to occur upon Ni substitution of Zn^{2+} in carbonic anhydrase,[92–95] this should also be considered as an alternative explanation for the inactivity of Ni-CA.

In addition to the above, other Lewis acid metal ion-dependent enzymes that have been substituted by Ni^{2+} with little or partial loss of activity include examples of collagenase[99] (native metal ion Zn^{2+}, in a $[Zn(his)_3(OH_2)]^{2+}$ site,[100] role of the metal ion unclear), alcohol dehydrogenase[101] (Zn^{2+}, $[Zn(cys)_2(his)(OH_2)]$ site, coordinates and activates a substrate hydroxyl group[102]), phosphotrieasterase[103] (Zn^{2+}, N/O ligation, activates a bound H_2O molecule), phosphoglucomutase[104] (Mg^{2+}, octahedral O_6-donor site, facilitates phosphate transfer to and from the substrate), phosphoenolpyruvate carboxylase[105] (Mg^{2+}, ligation unknown, stabilizes enolate through O-coordination), ribulose-1,5-bisphosphate-carboxylase[106] (Mg^{2+}, O- and possibly N-ligated, orients and activates substrate by carbonyl O-coordination), and 3-deoxy-D-*arabino*-heptulosonate 7-phosphate synthase[107] (Fe^{2+}, octahedral geometry, coordinates and activates a carbonyl group). An alcohol dehydrogenase possessing a six-coordinate Fe^{II} site with N/O-donor ligation has also been Ni-substituted;[108] interestingly, the UV/visible spectra of the resultant inactive Ni enzyme and of the octahedral sites in Ni-phosphoglucomutase[104] and the UreE Ni protein (section X),[893] are quite distinct from that described for urease (Table 1).

Although not a hydrolase, both Cu^{2+} and Zn^{2+} sites in superoxide dismutase, whose native enzyme contains a heterobimetallic $[\{Cu(his)_3(OH_2)\}(\mu\text{-his}^-)\{Zn(his)_2(asp)\}]$ active site (**6**),[110] have been selectively substituted by Ni^{2+}.[111–114] While the dinickel-substituted enzyme is not yet available, the spectroscopic and magnetic properties of the resultant $[Ni_2(\mu\text{-his}^-)]$ site would be of great interest to establish the presence or absence of such an imidazolate-bridged dinickel moiety in urease.

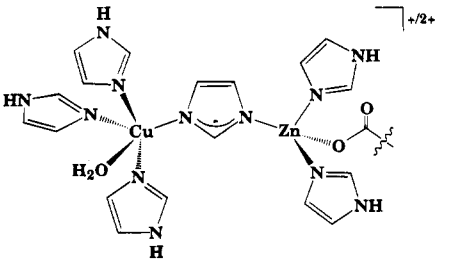


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Table 2. Structural Data for Selected Mononuclear Nickel Complexes or Binuclear Complexes Containing Isolated Ni^{II} Ions Bearing Nitrogen-Donor and Carboxylate Ligands (Includes Amino Acid Complexes)

complexes[f]	coordination geometry[a]	donor set[b]	d(Ni···N), Å	d(Ni···O), Å	ref
[Ni(hmpmgg)]	SqPl	c-N_2O_2	1.806(4), 1.830(4)	1.829(3), 1.870(3)	129
[Ni(dachd)]	SqPl	c-N_2O_2	1.86(2), 1.96(2)	1.88(2), 1.91(2)	130
[Ni(datnbn)]	SqPl	c-N_2O_2	1.907(7), 1.911(7)	1.842(5), 1.846(5)	131
[Ni(bpaas)]	SqPl	N_3O	1.849(5), 1.851(5), 1.961(5)	1.835(5)	132
[Ni(bpambs)]	SqPl	N_3O	1.837(2), 1.857(3), 1.937(3)	1.874(2)	133
[Ni(bpaebu)]	SqPl	N_3O	1.829(6), 1.855(6), 1.943(7)	1.866(5)	134
[Ni(mbacbg)]	SqPl	N_3O	1.86(1), 1.86(1), 1.93(1)	1.84(1)	135
[Ni(bpabdp)]	SqPl	N_3O	1.849(9), 1.856(9), 1.961(9)	1.868(9)	136
[Ni(bdabhp)]	SqPl	N_3O	1.849(5), 1.871(5), 1.951(5)	1.878(4)	137
[Tp*Ni(O,O'-O_2CR)][c]	5	N_3O_2	–	–	138
[Ni(DACO-Ac)(OH_2)]	SqPy	N_2O_3	2.025(7), 2.030(7)	1.983(6), 1.997(7), 2.011(7)	139
[Ni(Brsaltry)(OH_2)$_3$]	Oct	NO_5	1.993(5)	1.996(5), 2.063(5), 2.066(5), 2.071(5), 2.139(5)	140
[Ni(Menida)(OH_2)$_3$]	Oct	NO_5	2.120(1)	2.002(1), 2.037(1), 2.042(1), 2.081(1), 2.115(1)	141
[Ni(mmmpeg)(OH_2)$_2$]$_x$	Oct	NO_5	2.013(5)	1.976(5), 2.024(4), 2.058(5), 2.092(4), 2.163(4)	142
[Ni(tmen)(O-urea)$_2$(O,O'-O_2CMe)]$^+$	Oct	c-N_2O_4	2.093(4), 2.142(4)	2.055(3), 2.095(4), 2.097(3), 2.146(3)	123
[Ni(ser)$_2$(OH)$_2$]	Oct	c-N_2O_4	2.100(5)	2.012(5), 2.135(5)	143
[Ni(2-MePy)$_2$(O,O'-O_2CPh)$_2$]	Oct	c-N_2O_4	2.072(8), 2.087(6)	2.096(7), 2.103(8), 2.119(5), 2.127(7)	144
[Ni$_2$(2,6-pydta)]	Oct	c-N_2O_4	2.215(4), 2.237(4)	2.010(4), 2.022(4), 2.032(4), 2.051(4)	145
[Ni(edta)]$^{2-}$	Oct	c-N_2O_4	2.064, 2.080	2.027, 2.064, 2.077, 2.091	146
[Ni(edtaH)(OH_2)]$^-$	Oct	c-N_2O_4	2.08(1), 2.13(1)	2.03(1), 2.04(1), 2.08(1), 2.16(1)	147
[Ni(oro)(OH_2)$_2$(NH_3)]$_x$	Oct	c-N_2O_4	2.08(1), 2.10(2)	2.08(1), 2.08(2), 2.10(1), 2.11(1)	148
[Ni(phen)(O-phth)(OH_2)$_3$]	Oct	c-N_2O_4	2.080(4), 2.082(4)	2.065(3), 2.070(3), 2.080(4), 2.082(4)	149
[Ni(bpy)(O-phth)(OH_2)$_3$]	Oct	c-N_2O_4	2.058(6), 2.087(6)	2.047(5), 2.071(5), 2.091(5), 2.101(5)	149
	Oct	c-N_2O_4	2.053(2), 2.059(1)	2.045(1), 2.068(1), 2.087(1), 2.128(1)	150
[Ni({R}-ala)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.089(4), 2.095(4)	2.040(4), 2.067(4), 2.094(4), 2.095(4)	151
[Ni({RS}-ala)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.053(8), 2.092(8)	2.052(6), 2.061(6), 2.096(5), 2.101(5)	152
[Ni(pro)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.058(3)	2.046(2), 2.150(3)	153
[Ni(tyr)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.08(1), 2.11(1)	2.00(1), 2.05(1), 2.11(1), 2.11(2)	154
[Ni(β-ala)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.096	2.140, 2.167	155
[Ni(α-aib)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.064(4), 2.092(4)	2.044(4), 2.046(3), 2.079(4), 2.112(4)	156
[Ni(α-daib)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.10, 2.11	2.01, 2.11, 2.14, 2.24	157
[Ni(achCO_2)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.054(7), 2.082(7)	2.059(4), 2.059(4), 2.095(4), 2.098(4)	158
[Ni(quin)$_2$(O,O'-O_2CPh)$_2$]	Oct	t-N_2O_4	2.080(4)	2.083(3), 2.096(3)	144
[Ni(py)$_2$(OH_2)$_2$(O-OCMe)$_2$]	Oct	t-N_2O_4	2.100(6)	2.050(5), 2.102(5)	159
[Ni({O_2CCH$_2$}$_2$NH)$_2$]$^{2-}$	Oct	t-N_2O_4	2.079(2)	2.038(2), 2.065(2)	160
[Ni(pydcH)$_2$]	Oct	t-N_2O_4	1.951(3), 1.959(3)	2.096(4), 2.098(4), 2.168(4), 2.194(3)	161
	Oct	t-N_2O_4	1.97(1), 1.98(2)	2.104(8), 2.11(2), 2.17(1), 2.207(6)	162
[Ni(pydc)$_2$]$^{2-}$	Oct	t-N_2O_4	1.95(1), 1.96(1)	2.09(1), 2.12(1), 2.15(1), 2.16(1)	163
[Ni(pyrval)$_2$]	Oct	t-N_2O_4	2.02(1)	2.03(1), 2.14(1)	164
[Ni(gly)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.077(2)	2.067(2), 2.098(2)	165
[Ni(sarc)$_2$(OH_2)$_2$]	Oct	t-N_2O_4	2.046(7)	1.880(6), 2.263(6)	166
[Ni(pdg)$_2$]	Oct	t-N_2O_4	1.98(2), 2.04(2)	2.01(2), 2.05(2), 2.07(2), 2.07(2)	167
[Ni(hmbmda)(OH_2)]	Oct	f-N_3O_3	2.051(4), 2.072(4), 2.203(4)	2.063(4), 2.069(4), 2.107(4)	168
[Ni(gly)$_3$]$^-$	Oct	f-N_3O_3	2.088(3), 2.091(3), 2.095(3)	2.044(2), 2.047(2), 2.060(2)	169
[Ni(bzN_3O_2AcH)(OH_2)]	Oct	f-N_3O_3	2.165(3), 2.173(3), 2.175(3)	2.013(2), 2.013(3), 2.074(3)	170
[Ni(tacnta)]$^-$	Oct	f-N_3O_3	2.04	2.07	171
[Ni(bbiea)(O,O'-O_2CMe)(HOMe)]$^+$	Oct	f-N_3O_3	2.041(3), 2.050(3), 2.111(2)	2.107(2), 2.119(3), 2.216(2)	172

[Ni(pydc)(tmen)(OH_2)]	Oct	*m*-N_3O_3	1.979(3), 2.101(4), 2.178(4)	2.097(3), 2.140(3), 2.144(3)	173
[{Ni(bpy)$_2$}$_2$(μ-*O*,*O*′,*O*″,*O*‴-tpha)]$^{2+}$	Oct	*c*-N_4O_2	2.049(4), 2.051(4), 2.059(4), 2.063(4)	2.112(3), 2.144(3)	174
[Ni(tet-b)(*O*,*O*′-O_2CMe)]$^+$	Oct	*c*-N_4O_2	2.09(1), 2.11(3), 2.14(1), 2.16(1)	2.103(9), 2.116(9)	175
[Ni$_2$(tet-b)$_2$(OH_2)(μ-*O*,*O*′,*O*″-tart)][d]	Oct	*c*-N_4O_2	2.072(5), 2.087(4), 2.140(4), 2.142(6)	2.148(4), 2.191(5)	176
	Oct	*c*-N_4O_2	2.100(5), 2.112(4), 2.154(5), 2.165(5)	2.102(4), 2.160(5)	
[Ni(gly)$_2$(bpy)]	Oct	*c*-N_4O_2	2.042(4), 2.064(4), 2.065(4), 2.145(5)	2.079(4), 2.083(4)	177
[Ni(gly)$_2$(ImH)$_2$]	Oct	*c*-N_4O_2	2.060(4), 2.086(3), 2.102(4), 2.104(4)	2.071(3), 2.108(3)	178
[Ni(glygly)$_2$]$^{2-}$	Oct	*c*-N_4O_2	1.990(3), 2.136(3)	2.172(3)	179
[Ni(his)$_2$]	Oct	*c*-N_4O_2	2.08(1), 2.08(1), 2.09(1), 2.10(1)	2.10(1), 2.13(1)	180
[Ni(asp)(ImH)$_3$]	Oct	*c*-N_4O_2	2.076(9), 2.09(1), 2.09(1), 2.129(9)	2.10(1), 2.134(8)	181
[Ni(Pyala)$_2$]	Oct	*c*-N_4O_2	2.081(7), 2.087(7), 2.105(7), 2.111(7)	2.058(6), 2.066(6)	182
[Ni(dotaH$_2$)]	Oct	*c*-N_4O_2	2.114(7), 2.177(6)	2.025(6)	183
[Ni(hmteda)]	Oct	*c*-N_4O_2	2.072(3), 2.073(3), 2.091(3), 2.107(3)	2.065(3), 2.199(3)	184
[Ni(sda)$_2$(*O*-O_2CCH$_3$)$_2$]	Oct	*t*-N_4O_2	2.082(4), 2.127(4)	2.133(3)	185
[Ni(pn)$_2$(*O*-O_2CR)$_2$][e]	Oct	*t*-N_4O_2	2.105(2), 2.121(2)	2.128(2)	186
[Ni(Mepn)$_2$(*O*-O_2CCCl$_3$)$_2$]	Oct	*t*-N_4O_2	2.063(5), 2.080(4)	2.103(4)	187
[Ni(hmtca)(OH_2)]$^+$	Oct	*t*-N_4O_2	2.070(3), 2.093(3), 2.097(3), 2.103(3)	2.065(2), 2.223(2)	188
[Ni(dmta)(ImH)$_2$]$^+$	Oct	N_5O	2.061(3), 2.095(3), 2.105(3), 2.113(3), 2.121(3)	2.134(3)	221

[a] SqPl = square planar; SqPy = square pyramidal; Oct = octahedral; 5 = 5-coordinate. [b] *c* = *cis*; *t* = *trans*; *f* = *fac*. [c] R = Me, Ph. Metric parameters not available. [d] Contains two octahedral Ni ion asymmetrically bridged by a tartrate ligand bound in bidentate fashion to one Ni ion and monodentate to the other. [e] R = aryl, several examples reported. Data quoted are for R = 4-NO_2-C_6H_4. [f] achCO_2H = 1-aminocyclohexanecarboxylic acid; α-aibH = α-aminoisobutyric acid; [*R*]-alaH = (*R*)-alanine; {*RS*}-alaH = (*RS*)-alanine; β-alaH = β-alanine; aspH$_2$ = (*R*)-aspartic acid; bbiea = bis(2-benzimidazol-2-ylethyl)amine; bpaasH$_2$ = (*S*)-(*N*-benzylprolyl)aminoacetophenonyl-(*S*)-serine; bpabdpH$_2$ = (*R*)-*N*-[2-[(*N*′-benzylprolyl)amino]benzophenonyl]dehydroaminobut-2-enoic acid; bdabhpH$_2$ = (2*S*,3*S*)-3-[[α-[2-(1-benzyl-6-oxo-1,7-diazacyclo[3.2.0]heptadecan-7-yl)phenyl]benzylidene]amino]-2-(hydroxybenzyl)propionic acid; bpaebuH$_2$ = (*S*)-2-[[*o*-[(*N*-benzylprolyl)amino]phenyl]ethylidenimino]-3-methylbutanoic acid; bpambsH$_2$ = 2-[(*N*-benzylprolyl)amino]-*o*-methylbenzylideneserine; bpy = 2,2′-bipyridine; BrsaltryH$_2$ = *N*-(5-bromosalicylidene)-(*R*)-tryptophan; bzN_3O_2AcH$_3$ = 1,12,15-triaza-3,4:9,10-dibenzo-5,8-dioxocycloheptadecane-*N*,*N*′,*N*″-triacetic acid; dachdH$_2$ = 1,4-diazacycloheptane-*N*,*N*′-diacetic acid; α-daibH = di-α-aminoisobutyric acid; datnbnH$_2$ = 3*N*,7*N*-(1,3,5,7-tetraazabicyclo[3.3.1]nonyl)diacetic acid; DACO-ACH$_2$ = 1,5-diazacyclooctane-*N*,*N*′-diacetic acid; dmtaH = diethylenetriamine-*N*′-acetic acid; dotaH$_4$ = 1,4,7,10-tetraazacyclododecane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid; edtaH$_4$ = 1,2-diaminoethane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid; glyH = glycine; glyglyH$_2$ = glycylglycine; hisH = (*R*)-histidine; hmbmdaH$_2$ = *N*-(hydroxymethyl)-*N*-benzimidazol-2-ylmethylenediaminediacetic acid; hmpmggH$_2$ = *N*-(*N*-[[(3-hydroxy-5-(hydroxymethyl)-4-pyridyl)methylene]glycyl]glycine; hmtcaH = 5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*′,*N*‴-diacetic acid; hmtcdaH$_2$ = 5,5,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane-*N*-acetic acid; ImH = imidazole; mbacbgH$_2$ = γ-methyl-*N*-[[*o*-[[(*N*-benzylazolidin-2-yl)carbonyl]amino]phenylene]-α-benzylidene]-(2*S*,4*R*)-4-methylglutamic acid; MenidaH$_2$ = *N*-methyliminodiacetic acid; Mepn = 2-methyl-1,3-diaminopropane; mmmpegH$_2$ = [(5-(hydroxymethyl)-4-methylene-2-methylpyridin-3-yl)oxy]-α,α-ethanoglycine; oroH$_2$ = 2,6-dioxo-1,2,3,4-tetrahydro-4-pyrimidinecarboxylic acid; pdgH = pyridoxylideneglycine; phen = 1,10-phenanthroline; phthH$_2$ = phthalic acid; pn = 1,3-diaminopropane; proH = (*RS*)-proline; py = pyridine; PyalaH = (*S*)-β-2-pyridyl-α-alanine; pydcH$_2$ = pyridine-2,6-dicarboxylic acid; pydtaH$_4$ = pyridine-2,6-diaminetetraacetic acid; pyrvalH = pyridoxalyl-(*RS*)-valine; quin = quinoline; sarcH = sarcosine; sda = *meso*-stilbene-1,2-diamine; serH = (*R*)-serine; tacntaH$_3$ = 1,4,7-triazacyclononane-1,4,7-triacetic acid; tartH$_2$ = *d*-tartaric acid; tet-b = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; tmen = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane; tphaH$_2$ = terephthalic acid; Tp*$^-$ = tris(3,5-dimethylpyrazolyl) borate; tyrH = (*R*)-tyrosine; 2-MePy = 2-methylpyridine; 2,6-pydtaH$_4$ = pyridine-2,6-diamine-*N*,*N*,*N*′,*N*′-tetraacetic acid.

Table 3. Structural and Magnetic Data for Selected Binuclear Ni^{II} Complexes Containing Biologically Relevant Bridging Ligands

complexes[i]	bridging ligands	d(Ni··Ni), Å	Ni−(μ-O)−Ni, deg	J,[a] cm^{-1}	g	ref
$[Ni_2(OH)_2(HB\{3,5\text{-}Pr^iPz_2\}_3)_2]$	$2(OH^-)$	3.204(3)	106.1(3)	–	–	96
$[Ni_2(OH)(O_2CMe)_2(Me_3[9]aneN_3)_2]^+$	OH^-, $2(O,O'\text{-}O_2CMe^-)$	3.400(3)	115.2(1)	−4.5(1)	2.17(1)	194
$[Ni_2(O_2CMe)_2(bimp)]^+$	OAr^-, $2(O,O'\text{-}O_2CMe^-)$	3.422(4)	116.7(5)	−1.9	2.2	195
$[Ni_2(O_2CEt)_2(BPMP)]^+$	OAr^-, $2(O,O'\text{-}O_2CEt^-)$	–	–	−1.2(2)	2.19(4)	196
$[Ni_2(O_2CMe)_3(urea)(tmen)_2]^+$	$O,O\text{-}O_2CMe^-$, $2(O,O'\text{-}O_2CMe^-)$	3.4749(6)	–[b]	−0.9	2.38	123
$[Ni_2(OH_2)(O_2CR)_4(tmen)_2]^c$	OH_2, $2(O,O'\text{-}O_2CR^-)$	3.48−3.68	117−118	>−4[d]	–	197, 198
$[Ni_2(OH_2)(O_2CC_2H_4\text{-}o\text{-}OH\text{-}C_6H_4)_4(py)_4]$	OH_2, $2(O,O'\text{-}O_2CR^-)$	3.607(5)	116.9(4)	–	–	199
$[Ni_2(Phsal)_4(O_2CMe)]^-$	$2(OAr^-)$, $O,O'\text{-}O_2CMe^-$	3.101(2)	97.3(2)	−4.66(4)	2.30(5)	200
$[Ni_3(ips)_4(NO_3)_2]$	$2(OAr^-)$	–	–	≤15	–	201
$[Ni_2(Phsal)_2(NO_3)_2(2\text{-pic})_2]$	$2(OAr^-)$	–[b]	98.7(1)	8.7(1.0)	2.12(2)	202
$[Ni_2(ips)_2(NO_3)_2(EtOH)_2]$	$2(OAr^-)$	3.010(1)	96.4(1)	16.0(1.0)	2.15(2)	202
$[Ni_2(ips)_2(NO_3)_2(DMF)_2]$	$2(OAr^-)$	3.083(1)	99.0(1)	−9.2(5)	2.31(2)	202
$[Ni_2(dpdfp)(py)_4]^{2+}$	$2(OAr^-)$	≤3.10[e]	–	−23	2.13	203
$[Ni_2(dpdfp)(Cl)_2]$	$2(OAr^-)$	≤3.10[e]	–	−27	2.19	203
$[Ni_2(dhmpen)(O_2CMe)_2]$	$2(OAr^-)$	–	–	2.1	2.14	204
$[Ni_2(dfpen)(O_2CMe)_2]$	$2(OAr^-)$	3.005(2)	95.6(2)	10.1	2.15	204
$[Ni_2(\{OH\}_2\text{-dpdfp})(OH_2)_2X_2]^f$	$2(OAr^-)$	3.10	101.5(3)	−23 to −27	–	205
$[Ni_2(\{OH\}_2\text{-dpdfp})(O_2CMe)_2]$	$2(OAr^-)$	≈3.3	–	−3	–	205
$[Ni_2(dhmpen)(HOMe)_2(ClO_4)_2]$	$2(OAr^-)$	3.135(2)	101.3(1)	−29.5	2.29	206, 209
$[Ni_2(dhmpen)(py)_2]^{2+}$	$2(OAr^-)$	3.206(5)	105.7(2)	−67.1	2.24	207, 209
$[Ni_2(dhmpen)(OH_2)_2(NCS)_2]$	$2(OAr^-)$	3.113(3)	99.2(1)	−21.3	2.19	209
$[Ni_2(dhmpen)(O_2CCH_2NH_3)(OH_2)_2]^{2+}$	$2(OAr^-)$, $O,O'\text{-}O_2CR$	3.066(8)	92.6(3), 95.0(3)	−1.1	2.21	208, 209
$[Ni_2(PhphenO)_2(O_2CMe)(NCMe)_2]^+$	$2(OAr^-)$, $O,O'\text{-}O_2CMe^-$	3.011	93.7(2), 93.9(2)	–	–	210
$[Ni_4(dfpdap)(OH)(MeO\text{-}H\text{-}OMe)(O_2CMe)_2]$	OAr^-, OMe^-, OH^-	2.788(1)	83.5(2)	−33.3[g]	2.17	211, 212
	OAr^-, $O,O'\text{-}O_2CMe^-$, OH^-	2.936(1)	95.6(2)			
$[Ni_4(dfpdap)(OH)(MeO\text{-}H\text{-}OMe)_3]$	OAr^-, OMe^-, OH^-	2.758(4)[h]	83.0(5)[h]	−30.0[g]	2.17	212
	OAr^-, OH^-	3.026(3)[h]	98.1(6)[h]			
$[Ni_4(dfpdap)(OH)(MeO\text{-}H\text{-}OMe)(N_3)_2(OH_2)_2]$	OAr^-, OMe^-, OH^-	2.771(1)	83.2(2)	−28.5[g]	2.17	212
	OAr^-, OH^-	3.058(2)	99.9(3)			
$[Ni_4(OMe)_4(O_2CMe)_2(DMB)_2]$	$2(OMe^-)$, $O,O'\text{-}O_2CMe^-$	2.998(1)	93.2(2)	18	2.00	213
	$2(OMe^-)$	3.193(1)[h]	100.9(2)[h]	−9.1		
$[Ni_4(OH)_4(tzdt)_4(py)_4]$	$2(OH^-)$	3.06(4)	95.6(4)	17.5	2.0	214
	$2(OH^-)$	3.20(3)	103.2(4)	−22		
$[Ni_4(OH)_4(chta)_4(NO_3)_4]$	$2(OH^-)$	3.164(1)−3.196(3)	98.3(2)−99.7(2)	0.95, −0.80, −1.16	2.20	216
$[Ni(hipp)_2(OH_2)_3]_x$	OH_2	3.942	137.2	−12.9	2.2	218
$[Ni(asp)(OH_2)_3]_x$	$O,O'\text{-}O_2CR^-$	5.255	–	≈0[i]	–	219
$[\{Ni(edta)\}\{Ni(OH_2)_4\}]_x$	$O,O'\text{-}O_2CR^-$	5.517(3)	–	−2.86	2.09, 2.21	220
$[Ni(dmta)(ImH)]_x$	$O,O'\text{-}O_2CR^-$	5.652(1)	–	0.16	2.12	221
$[Ni_2(O_2CMe)_2(\eta^2,\sigma\text{-Meanb})_2]^j$	$2(O,O'\text{-}O_2CMe^-)$	2.984(1)	–	–	–	222
	$2(O,O'\text{-}O_2CMe^-)$	3.064(2)	–	–	–	222
$[Ni_2(O_2CCF_3)_2(\eta^2,\sigma\text{-Meanb})_2]$	$2(O,O'\text{-}O_2CCF_3^-)$	3.151(2)	–	–	–	223
$[Ni_2(O_2CPh)_2(Me)_2(PMe_3)_2]$	$2(O,O'\text{-}O_2CPh^-)$	2.865(2)	–	–	–	224
$[Ni_2(O_2CPh)_4(quin)_2]$	$4(O,O'\text{-}O_2CPh^-)$	–	–	−125	2.5	225
$[Ni_2(O_2CCMe_3)_4(quinald)_2]$	$4(O,O'\text{-}O_2CPh^-)$	2.754(3)	–	−160	–	226
$[Ni_2(O_2CCMe_3)_4(2,4\text{-lu})_2]$	$4(O,O'\text{-}O_2CR^-)$	2.7080(5)	–	−224	2.72	227
$[Ni_2(O_2CCMe_3)_4(2,5\text{-lu})_2]$	$4(O,O'\text{-}O_2CR^-)$	2.7202(8)	–	−128	2.38	227, 228
$[Ni_2(O_2CCMe_3)_4(2\text{-EtPy})_2]$	$4(O,O'\text{-}O_2CR^-)$	2.7227(7)	–	−221	2.85	227, 228
$[Ni_2(tren)_2(BiIm)]^{2+}$	$N,N',N'',N'''\text{-BiIm}^{2-}$	–	–	−2.9	2.082	229
$[Ni_2(pmads)(O_2CMe)_2]^{2+}$	$S,S'\text{-RSSR}$, $2(O,O'\text{-}O_2CMe^-)$	4.134(2)	–	≈0[k]	–	644

[a] $\mathbf{H} = -2JS_1S_2$ convention. [b] Not reported. [c] Several examples published. [d] Reference 194. [e] References 205 and 714. [f] $X^- = Cl^-, Br^-, N_3^-$. Structure reported for $X^- = Cl^-$. [g] Interpreted as an isolated "pair of dimers". [h] Averaged value. [i] Curie–Weiss behavior observed, $\theta = -0.4K$. [j] Two isomers structurally characterized. [k] Curie–Weiss behavior observed, $\theta = -4K$. [l] $aspH_2$ = (*R*)-aspartic acid; $BiImH_2$ = 2,2′-biimidazole; bimpH = 2,6-bis[bis[(1-methylimidazol-2-yl)methyl]amino]methyl]-4-methylphenol; BPMPH = 2,6-bis[bis(2-pyridylmethyl)amino]methyl]-4-methylphenol; chta = cyclohexane-*r*-1, *c*-3, *c*-5-triamine; dfpdapH$_4$ = 2 × 2 condensation product of 2,6-diformyl-4-methylphenol with 2,6-bis(aminomethyl)-4-methylphenol; dfpenH$_2$ = 2 × 2 condensation product of 1,2-diaminoethane and 2,6-bis(dihydroxymethyl)-4-methylphenol; dhmpenH$_2$ = 2 × 2 condensation product of 1,3-diaminopropane and 2,6-bis(hydroxymethyl)-4-methylphenol; DMB = 2,5-dimethyl-2,5-diisocyanohexane; dmtaH = diethylenetriamine-*N*′-acetic acid; dpdfpH$_2$ = 2 × 2 condensation product of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol; edtaH$_4$ = 1,2-diaminoethane-*N*,*N*′,*N*″,*N*‴-tetraacetic acid; HB{3,5-Pr^{i}Pz$_2$}$_3^-$ = tris(3,5-diisopropylpyrazolyl) borate; hipp$^-$ = hippurate [$C_6H_5C(O)N{=}CHCO_2^-$]; ImH = imidazole; ipsH = *N*-isopropylsalicylaldimine; MeanbH = 2-methylallyl-3-norbornane; Me$_3$[9]aneN$_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane; {OH}$_2$-dpdfpH$_2$ = 2 × 2 condensation product of 1,3-diaminopropan-2-ol and 2,6-diformyl-4-methylphenol; PhphenOH = 2-(2-hydroxyphenyl)-1,10-phenanthroline; PhsalH = *N*-phenylsalicylaldimine; 2-pic = 2-methylpyridine; pmads = bis[2-[*N*,*N*-bis(2-pyridylmethyl)aminolethyl] disulfide; py = pyridine; quin = quinoline; quinald = quinaldine; tmen = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane; tren = 2,2′,2″-triaminotriethylamine; tzdtH = 1,3-dithiazolidine-2-thione; 2,4-lu = 2,4-lutidine; 2,5-lu = 2,5-lutidine; 2-EtPy = 2-ethylpyridine.

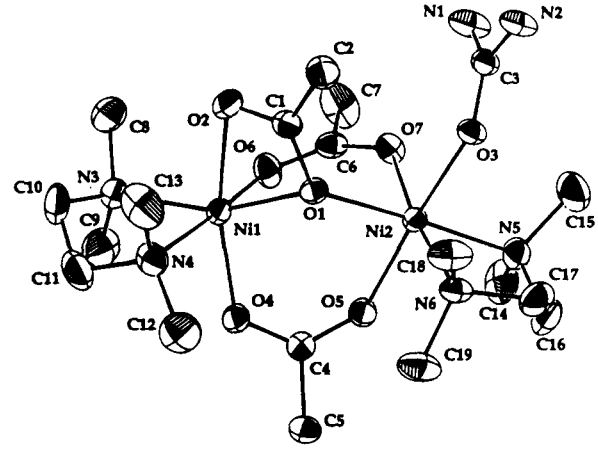


Figure 5. Structure of $[Ni_2(\mu\text{-}O_2CMe)_3(urea)(tmen)_2]^+$ (tmen = *N*,*N*,*N*′,*N*′-tetramethyl-1,2-diaminoethane). (Reprinted from ref 123. Copyright 1993 the American Chemical Society.)

B. Structural Models for Urease

Notwithstanding the large number of octahedral Ni^{II} complexes of amines, pyridyls and similar ligands,[8] relatively few complexes designed as structural urease models have been reported. Several mononuclear and halide-bridged dinuclear octahedral nickel amine compounds have been characterized by EXAFS, yielding edge features and structural parameters very similar to those derived for urease (Ni^{II}–N = 2.06–2.10 Å).[115–119] No well-resolved Ni···Ni distances were observed in these studies for those species known to be dimeric, such as $[Ni_2(en)_4Cl_2]^{2+}$ (en = 1,2-diaminoethane), although similar studies on thiolate-bridged $Ni^{II/II}$ dimers only showed recognizable Ni···Ni peaks at low temperatures.[581]

Four Ni^{II} urea complexes have been structurally characterized, all of which contain O-donating urea ligands (Figure 5), with metric parameters typical of metal-coordinated organic carbonyl groups [Ni–O = 2.06–2.10 Å and Ni–O–C = *ca.* 135°].[121–123] This is the most commonly observed mode of coordination of urea and carboxylic acid amide derivatives to Ni^{2+} and other transition metal ions,[124,125] although N-coordinated Ni^{II} complexes of a series of substituted chelating ureas (**7**) have been synthesized.[126] A polymeric Ag^+ complex containing μ-O,N-coordinated urea ligands has been structurally characterized.[127] pH-induced linkage isomerism in $[M^{III}(NH_3)_5(urea)]^{3+}$ (M = Cr, Co, Ru, Rh) derivatives is well established,[82,128] the N-bound deprotonated urea ligands rapidly converting to O-bound ureas below pH 2 via an observable N-coordinated intermediate (reaction 8), although this phenomenon has not been noted for

$$[ML_n(\text{–NHC\{O\}NH}_2)]^{(m-1)+} + H^+ \rightleftharpoons [ML_n(\text{–NH}_2\text{C\{O\}NH}_2)]^{m+} \rightleftharpoons [ML_n(\text{–O=C\{NH}_2\}_2)]^{m+} \quad (8)$$

Ni^{II} urea complexes. Interestingly, tetramethylurea (tmu) forms a square-pyramidal $[Ni(tmu)_5]^{2+}$ complex in neat tmu, with a Ni–O distance of 2.00(1) Å and showing electronic absorptions at $\lambda_{max}(\epsilon_{max})$ = 1250 nm (45 M^{-1} cm^{-1}), 943 (13), 719 (1), 534 (sh), and 456 (79).[120]

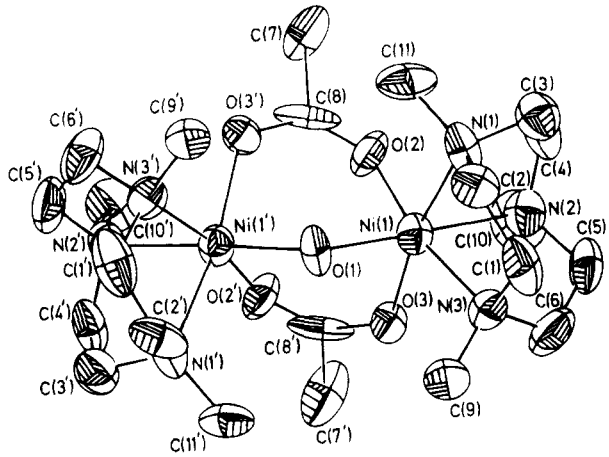


Figure 6. Structure of $[Ni_2(\mu\text{-}OH)(\mu\text{-}O_2CMe)_2(Me_3[9]aneN_3)_2]^+$ ($Me_3[9]aneN_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane). (Reprinted from ref 194. Copyright 1988 the Royal Society of Chemistry.)

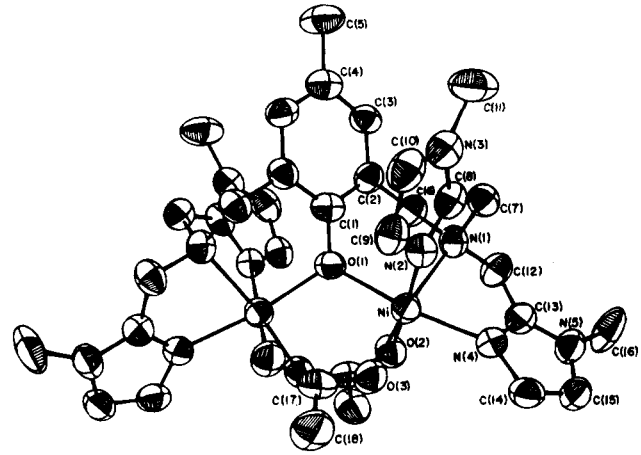


Figure 7. Structure of $[Ni_2(\mu\text{-}O_2CMe)_2(bimp)]^+$ (bimpH = 2,6-bis{[bis({1-methylimidazol-2-yl}methyl)amino]methyl}-4-methylphenol). (Reprinted from ref 195. Copyright 1989 the American Chemical Society.)

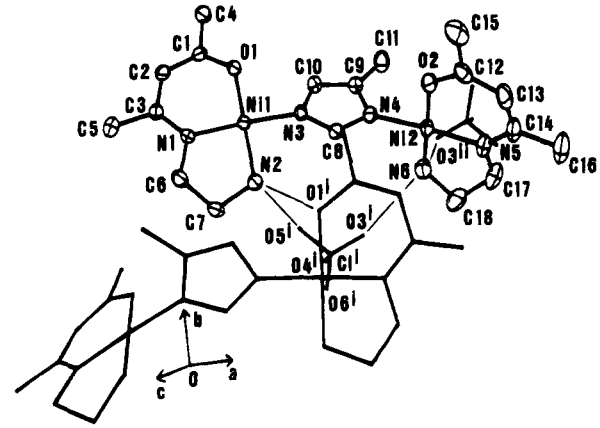


Figure 8. Structure of $[Ni_2(\mu\text{-}4\{5\}Me\text{-}Im)(AE)_2]^+$ (AEH = 7-amino-4-methyl-5-aza-3-hepten-2-one; 4Me-ImH = 4-methylimidazole). (Reprinted from ref 231. Copyright 1991 the American Chemical Society.)

A variety of mononuclear mixed nitrogen/carboxylate donor complexes of Ni^{II} that might mimic the Ni^{2+} coordination environment of urease are known, although these have not been systematically studied; relevant examples, almost all of which show high-spin configurations, are listed in Table 2. The number of structurally characterized mononuclear Ni^{II} carboxylate complexes is far greater than the number of reported di- and polynuclear Ni carboxylate species (Table 3, *vide infra*), suggesting that Ni^{II} carboxylates may have a lower tendency toward aggregation to di- or polynuclear species via the formation of carboxylate bridges compared to those of other first row transition metal ions such as $Mn^{II/III/IV}$,[189] $Fe^{II/III}$,[190] and Cu^{II}.[191] The prevalence of monodentate carboxylate coordination to Ni^{II}, and the pronounced asymmetry in Ni−O(carboxylate) distances shown by most Ni^{II} complexes containing chelating carboxylate ligands,[123,144,172,174,176,750] are also noteworthy. The only synthetic low-spin Ni^{II} carboxylate complexes not containing strong field donors such as alkyls, deprotonated amides, or thiolates are formed from constricting, tetradentate chelate ligands;[129−137] an example of a biochemical ligand of this type is albumin, which is the major Ni carrier in mammalian blood and forms a low-spin square-pyramidal Ni^{II} complex with one histidine, one amide, and two deprotonated amide N-donors, and one axial carboxylate ligand.[192]

A very limited magnetic database exists for di- or polynuclear complexes of high-spin Ni^{II} with biologically relevant O-donor bridging ligands,[193] which is summarized in Table 3. In most cases, antiferromagnetic coupling with $J > -5$ cm^{-1} is observed between Ni^{II} ions bridged by both hydroxide/alkoxide and carboxylate groups (Figures 5−7), which rises to $J > ca.$ -70 cm^{-1} in complexes containing bridging alkoxo, phenoxo, or aqua ligands only. Large antiferromagnetic exchange couplings ($-20 > J > -67$ cm^{-1}) in phenoxo-bridged dinickel complexes arise from ligand-enforced planarity of the bridging O-donors;[203,205,209,212] Ni^{II} complexes bridged by pyramidal phenolates exhibit weaker antiferromagnetic interactions.[205,208,209,212] The only reported examples of ferromagnetic behavior are associated with a coincidental orientation of phenoxo bridges that allows orthogonal Ni−(μ-O) overlap for the two Ni^{2+} ions,[201,202] or unusually acute Ni−O−Ni angles ($\leq ca.$ 98°) imposed by a constrained binucleating macrocyclic ligand[204,209] or by the formation of a $[Ni_4(OR)_4]^{4+}$ cubane core.[213−216] In addition to the examples in Table 3, the structure determination of a complex containing the core motif $[Ni^{II}_2(\mu\text{-}OR)(\mu\text{-}O,O'\text{-}O_2CMe)]$ has been communicated, although no structural parameters were given.[217] No molecular $Ni_2(\mu$-oxo) species has been described.

A small number of $Ni_2(\mu$-imidazolate) complexes have been prepared,[229−234] only two of which have been structurally characterized: $[Ni_2(AE)_2\{\mu\text{-}4\{5\}\text{-}MeIm)]$ (AEH = 7-amino-4-methyl-5-aza-3-hepten-2-one; 4-MeImH = 4-methylimidazole; Ni···Ni = 5.84 Å; Figure 8)[231] and $[Ni_2(bzimdt)_2(\mu\text{-}N,N',O,O'\text{-}bzimCO_2)]^{2+}$ (bzimdt = 1,6-dibenzimidazol-2-yl-2,5-dithiahexane; $bzimCO_2H_2$ = 2-benzimidazolylcarboxylic acid; Ni···Ni = 5.397 Å; Figure 9).[233] Magnetic data from the biimidazolate-bridged Ni^{II} dimer $[Ni_2(tren)_2(\mu\text{-}BiIm)]^{2+}$ have been reported;[229] the observed J of -2.7 cm^{-1} should represent a maximum value for coupling between two imidazolate-bridged Ni^{II} ions. Only four dinuclear thiolate-bridged complexes containing high-spin Ni^{II} ions have been described (Table

Table 4. Structural Data for Selected Thiolate-Bridged Ni^{II}–M {M = Ni^{II}, Ni^{III}, Fe^{II}} Complexes[a]

complexes[g]	bridging ligands	d(Ni···μ-S), Å	d(Ni′···μ-S), Å [d(Fe···μ-S), Å][h]	d(Ni···Ni′), Å [d(Ni···Fe, Å][h]	Ni–(μ-S)–Ni, deg [Ni–(μ-S)–Fe, deg][h]	dihedral angle,[b] deg	ref
$[Ni_2(memta)_2]$	2(RS^-)	2.189(3), 2.210(2)	2.214(2), 2.176(2)	2.635(1)	73.50(8), 73.84(7)	105.2	672
$[Ni_2(\{SC_2H_4\}_2PC_2H_4SH)_2]$	2(RS^-)	2.215, 2.225	—[c]	2.647	73.2	—[d]	480
$[Ni_2(peeta)_2]^{2+}$	2(RS^-)	2.30(2), 2.35(2)	2.21(2), 2.28(2)	2.69(1)	71.9(6), 72.3(5)	—[d]	739
$[Ni_2(Ph_2PC_2H_4S)_2Br_2]$	2(RS^-)	2.168(1), 2.232(1)	—[c]	2.695(1)	75.5(1)	100.7(2)	481
$[Ni_2(\{SC_2H_4\}_2S)_2]$	2(RS^-)	2.183(5), 2.220(5)	2.217(5), 2.183(5)	2.733(5)	76.8(2), 76.7(2)	111.3	695
$[Ni_3(SC_2H_4NH_2)_4]^{2-}$	2(RS^-)	2.154(3), 2.156(3)	2.212(3), 2.212(3)	2.733	77.5(2), 77.5(2)	109	731
$[Ni_2(peaet)_2]^{2+}$	2(RS^-)	2.169(1), 2.186(1)	—[c]	2.739(1)	77.94(5)	110	732
$[Ni_3(dmeda)_2]^{2+}$	2(RS^-)	2.144(1), 2.160(1)	2.216(1), 2.219(1)	2.748(1)	78.10(4), 77.71(4)	107.84(7)	733
$[Ni_6(1,3\text{-ptd})_7]^{2-}$	2(RS^-)	2.200(2), 2.204(2)	2.186(2), 2.192(2)	2.750(2)	77.7(7), 77.5(7)	109.5	674
	2(RS^-)	2.175(2), 2.188(2)	2.247(2), 2.226(2)	2.822(2)	79.5(7), 79.3(7)	—[d]	
	2(RS^-)	2.185(3), 2.188(2)	—[c]	2.843(2)	81.2(1), 81.1(1)	119.8	
$[Ni_2(SEt)_2(S_2CSEt)_2]$	2(RS^-)	2.179(4), 2.184(3)	2.196(3), 2.186(4)	2.763(2)[e]	78.3(1), 78.4(1)	110.2	482
$[Ni_2(SEt)_2(CS_3)_2]^{2-}$	2(RS^-)	2.185(4), 2.189(5)	2.199(4), 2.184(4)	2.767(3)	—[d]	111.1(2)	673
$[Ni_3(SCH\{Me\}CO_2)_4]^{2-}$	2(RS^-)	2.137(2), 2.141(2)	2.228(2), 2.228(2)	2.783(1)	79.2(1), 79.1(1)	115	736
$[Ni_2(SBz)_2(S_2CSBz)_2]$	2(RS^-)	2.188(4), 2.190(4)	—[c]	2.795(3)	79.5	115.5[e]	483
$[Ni_3(edt)_4]^{2-}$	2(RS^-)	2.175(3), 2.177(3)	2.210(3), 2.223(2)	2.830(1)	80.04(8), 80.38(9)	113.19	669
$[Ni_2(pemta)_2]^{2+}$	2(RS^-)	2.186(3), 2.206(3)	2.198(1), 2.193(1)	2.848(2)	81.04(9), 80.70(9)	99.2[f]	738, 739
$[Ni_3(edt)_4]^{2-}$	2(RS^-)	2.174(1), 2.179(1)	2.189(1), 2.210(1)	2.856(1)	81.3(1), 81.6(1)	116.8	670, 674
$[Ni_3(1,2\text{-pdt})_4]^{2-}$	2(RS^-)	2.167(3), 2.165(3)	2.189(3), 2.208(2)	2.896	83.34(9), 82.94(9)	125	671
$[Ni_2(edt)_3]^{2-}$	2(RS^-)	2.167(2), 2.178(3)	2.225(3), 2.207(2)	2.941(2)	83.83(9), 84.50(8)	119.07	669
$[Ni_3(xdt)_4]^{2-}$	2(RS^-)	2.219(2), 2.229(2)	2.193(2), 2.208(2)	3.016(1)	86.26(7), 85.66(7)	123.4	674
	2(RS^-)	2.226(2), 2.228(2)	2.192(2), 2.206(2)	3.131(1)	90.26(7), 89.84(7)	131.6	
$[Ni_3(SEt)_8]^{2-}$	2(RS^-)	2.19–2.23		3.04	87	<180	675
$[Ni_2(peapt)_2]^{2+}$	2(RS^-)	2.167(2), 2.180(2)	2.170(2), 2.166(2)	3.047(1)	89.27(8), 89.02(8)	136.1	737
$[Ni_3(SC_3H_6NH_2)_4]^{2-}$	2(RS^-)	2.185(5), 2.202(5)	2.182(6), 2.182(6)	3.104(2)	90.2(3), 90.7(3)	139	728
$[Ni_2(dpet)_2]^{2+}$	2(RS^-)	2.169(2), 2.180(2)	—[c]	3.134(2)	92.5(1), 91.9(1)	145.2	740
$[Ni_2(dpdft)]^{2+}$	2(RS^-)	2.171(6), 2.181(6)	—[c]	3.163(4)	—[d]	144.4	714
$[Ni_2(dmdnN_4S_2)]^{2+}$	2(RS^-)	2.176(2), 2.177(2)	—[c]	3.182(2)	93.9(1), 94.0(1)	162.8[f]	484
$[Ni_3(SEt)_4(C_6F_5)_4]^{2-}$	2(RS^-)	2.199(3), 2.208(3)	2.216(5), 2.211(3)	—[d]	94.0(1), 94.1(1)	149	485
$[Ni_2(SPh)_2(dppe)_2]^{2+}$	2(RS^-)	2.251(2), 2.254(2)	—[c]	3.254(2)	92.50(6)	180	486
$[Ni_2(S\text{-}p\text{-}Cl\text{-}C_6H_4)_6]^{2-}$	2(RS^-)	2.212(1), 2.220(2)	—[c]	3.273(1)	95.22(5)	180	672
$[Ni_2(SC_3H_6NMe_2)_2(dppe)_2]^{2+}$	2(RS^-)	2.236(1), 2.237(1)	—[c]	3.310(1)	95.5(1)	180	487
$[Ni_2(SEt)_6]^{2-}$	2(RS^-)	2.214(2), 2.224(1)	—[c]	3.355(2)	98.2(1)	180	675
$[Ni_2(mpdea)_2]$	2(RS^-)	2.376(3), 2.495(2)	—[c]	3.587(2)	94.8(1)	—	741
$[Ni_2(terpy)_2(SPh)_4]$	2(RS^-)	2.410(2), 2.519(2)	—[c]	3.920(1)	105.3(1)	—	529
$[Ni_2(S\text{-}2,4,5\text{-}Pr^i_3\text{-}C_6H_2)_5]^-$	3(RS^-)	2.267(4)–2.324(4)	2.282(4)–2.324(4)	2.607(3)	68.2(1)–69.4(2)	—	660
$[Ni_2(P\{o\text{-}S\text{-}C_6H_4\}_3)_2]^-$	2(RS^-)	2.251(2), 2.260(2)	—[c]	2.501(2)	67.32(7)	—	715
$[\{Ni(dmpn)\}_3Fe]^{2+}$	2(RS^-)	2.160(6), 2.168(5)	[2.619(6), 2.459(7)][h]	[2.976(4)][h]	76.4(2), 79.8(2)	—	477
	2(RS^-)	2.166(5), 2.167(6)	[2.484(5), 2.581(5)][h]	[3.123(3)][h]	84.1(2), 81.8(2)	—	
	RS^-	2.160(6)	[2.477(7)][h]	[3.269(4)][h]	89.4(2)	—	
$[\{Ni(BME\text{-}DACO)FeCl\}(\mu\text{-}Cl)]_2$	2(RS^-)	2.172(3), 2.165(3)	[2.552(3), 2.462(3)][h]	[3.100(1)][h]	81.6(1), 83.9(1)	—	476

[a] Doubly thiolate-bridged dimers of square planar Ni^{II} ions are listed in order of increasing (shortest) Ni···Ni distance; toroidal Ni thiolate clusters have not been included. [b] Dihedral angle between adjacent Ni(μ-S)$_2$L$_2$ square planes. [c] Crystallographic center of symmetry or 2-fold axis present at the center of the $Ni_2(SR)_2$ bridge. [d] Not reported. [e] Reference 672. [f] Ni ions show square pyramidal coordination, with a long apical Ni–X (X = O, S) distance of 2.78 Å. The dihedral angle given is the angle between basal ligand planes about each Ni center. [g] H_2BME-DACO = *N*,*N*′-bis(2-mercaptoethyl)-1,5-diazacyclooctane; H_2dmdnN_4S_2 = 3,13-dimethyl-3,13-dinitro-1,5,11,15-tetraazacycloeicosane-8,18-dithiol; dmedaH_2 = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,2-diaminoethane; H_2dmpn = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine; dpdftH_2 = 2 × 2 condensation product of 1,3-diaminopropane and 2,6-formyl-4-methylbenzenethiol; dpetH = 1,5-diamino-3-pentanethiol; dppe = 1,2-bis(diphenylphosphino)ethane; edtH_2 = 1,2-ethanedithiol; memtaH_2 = bis(2-mercaptoethyl)[2-(methylthio)ethyl]amine] mpdeaH_2 = 2,2′-bis[(2-mercaptophenyl)thio]diethylamine; peaetH = 2-[2-(2-pyridyl)ethylamino]ethanethiol; peaptH = 3-[2-(2-pyridyl)ethylamino]propanethiol; peetaH = *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(2-ethylthio)ethyl]-2-aminoethanethiol; pemtaH = *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(2-methylthio)ethyl]-2-aminoethanethiol; terpy = 2,2′,6′,2″-terpyridine; xdtH_2 = *o*-xylene-α,α′-dithiol; 1,2-pdtH_2 = 1,2-propanedithiol; 1,3-pdtH_2 = 1,3-propanedithiol. [h] Bracketed values correspond to the bracketed column head.

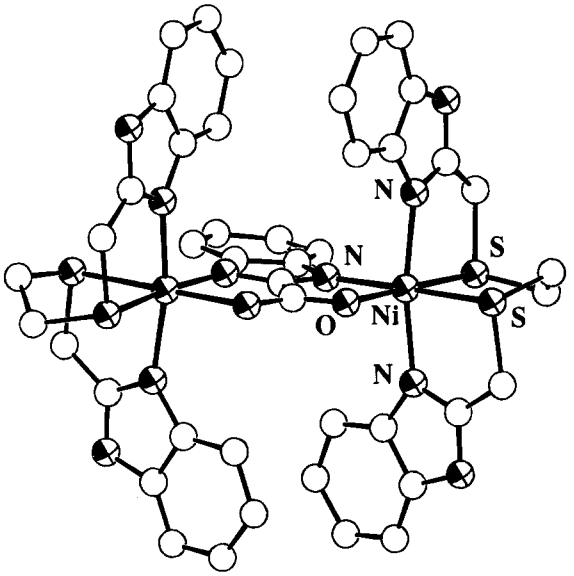


Figure 9. Structure of $[Ni_2(\mu\text{-bzim}CO_2)(bzimdt)_2]^{2+}$ (bzimCO_2H_2 = 2-benzimidazolylcarboxylic acid; bzimdt = 1,6-bis{2-benzimidazolyl}-2,5-dithiahexane). Atomic coordinates taken from ref 233.

4), and for none of these are magnetic susceptibility data available.[529,660,741,829] Hence, given the uncertainty regarding the interpretation of structural and magnetic data obtained from urease and its inhibited derivatives, there is a definite need for the synthesis of additional structural model complexes for this enzyme.

C. Synthetic Ni^{II} Complexes as Lewis Acid Catalysts

The hydrolysis of amides, esters, phosphate esters, and nitriles by transition metal cations such as Zn^{2+}, Cu^{2+}, Ni^{2+}, $Co^{2+/3+}$, and Fe^{2+} has been well investigated,[235-240] and many mechanistic data are available. Relatively few studies have been designed to model urease reactivity, however, most such work being oriented toward the functional modeling of carboxypeptidase A and other Zn^{2+} enzymes,[235-239] while recent attention has focused on metal-promoted hydrolyses of phosphate esters to model DNA cleavage reagents.[240]

A metal ion Lewis acid catalyst can play either one or both of two possible mechanistic roles. Interaction of a metal ion with the substrate electrophile (*e.g.* a carbonyl group) can activate the substrate to nucleophilic attack by polarization of the target bond (Figure 10). This polarization may occur by direct complexation of the electrophilic functionality to the metal center, or simply from inductive effects arising from the proximity of the electrophile to the metal ion when the former is attached to a metal-bound ligand. In the latter case, a driving force for nucleophilic attack is provided by the conversion of a weakly basic carbonyl moiety into a strongly coordinating tetrahedral intermediate, as in Figures 2 and 12. Alternatively, the metal ion may coordinate the attacking nucleophile (*e.g.* H_2O), thus increasing the basicity and nucleophilicity of the latter, which may in the limiting case be deprotonated (Figure 11). Model studies have shown that Ni^{2+} can perform both processes, albeit with often modest efficiency.

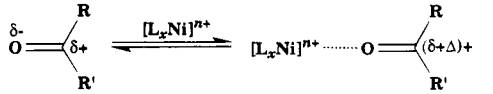


Figure 10. Activation of a polar substrate to nucleophilic attack by a Lewis acidic metal ion.

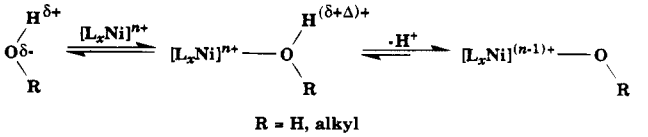


Figure 11. Activation of a nucleophile by a Lewis acidic metal ion.

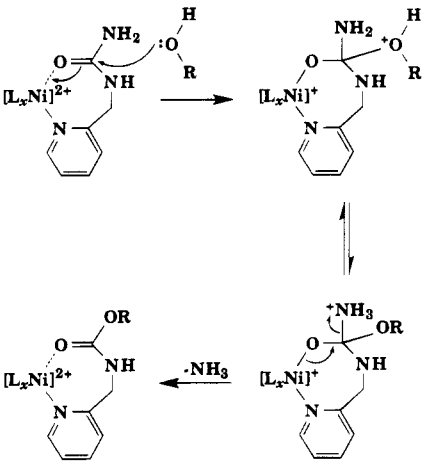
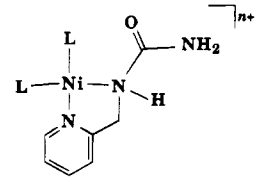


Figure 12. Proposed mechanism for the Ni^{2+}-catalyzed hydrolysis of *N*-(2-pyridylmethyl)urea. Adapted from ref 75.

The first kinetic investigation of a reaction designed to mimic urease involved the activation of *N*-(2-pyridylmethyl)urea by $NiCl_2$.[75] Zerner *et al.* showed that both the hydrolysis and ethanolysis of this ligand are first order in substrate and nucleophile, each reaction exhibiting $\Delta H^{\ddagger} \approx 26$ kcal mol^{-1}, suggesting that they follow similar mechanisms. UV/visible spectroscopy showed that octahedral Ni complexes were formed by the substrate in solution, which led to the proposed mechanism shown in Figure 12; this closely parallels the mechanism of action of urease proposed by the same authors (Figure 2). The second-order rate constants of $k_{obs} \approx 10^{-5}$ M^{-1} s^{-1} correspond to rate enhancements of *ca.* 7×10^4 over the uncatalyzed reactions. Broadly similar mechanisms involving substrate polarization and activation to attack by an external nucleophile have been demonstrated for the Ni-activated intramolecular attack of a carboxylate group at a Ni-coordinated ester linkage,[241,242] and ester,[244,245] amide,[242,246,247] and nitrile[248] hydrolysis by Ni complexes; the latter reaction shows rate enhancements of up to 10^7, the highest recorded for a Ni^{2+} hydrolysis catalyst. Interestingly, the N-coordinated Ni^{2+} urea complex (**7**) undergoes intermolecular hydrolysis with a rate enhancement of 10^3, whereas the O-coordinated Zn^{2+} complex does not.[126] The pentaammine urea derivatives $[M^{III}(NH_3)_5(O\text{-urea})]^{3+}$ (M = Cr, Co, Rh) are inert to hydrolysis, which has led to the suggestion that efficient hydrolysis of urea may require a dinuclear metal catalyst.[249]



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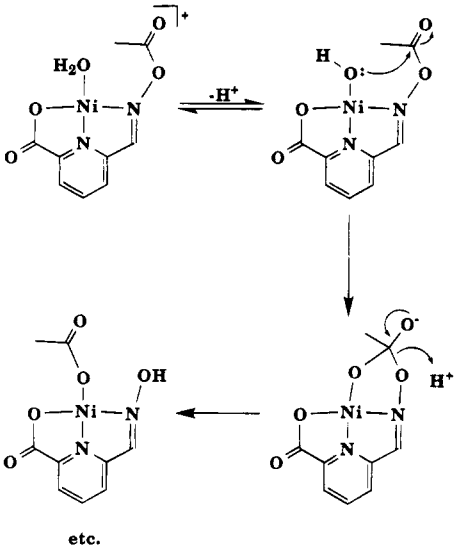
L = Cl⁻, EtOH

No example of urea or intermolecular amide hydrolysis by a Ni^{2+}-activated aqua nucleophile has been described, although amide hydrolysis by water-derived hydroxo moieties bound to Zn^{2+}, Cu^{2+}, and Co^{3+} is well known.[250,251] The intramolecular hydrolysis of several ester and amide chelates assisted by Ni^{2+} and other metal ions[247,250-254] have been shown to follow this mechanism, however, with rate enhancements of up to 10^5 being observed for Ni^{2+} catalysts.[247] A detailed kinetic analysis of one such reaction by Wells and Bruice[252] demonstrated no rate dependence on the pK_a of the leaving alcohol for the metal-catalyzed reactions, a lack of inhibition of the reaction by a competing external nucleophile, and differences in the kinetically and thermodynamically determined metal–ligand dissociation constants and pK_a's. All these observations were rationalized on the basis of attack of a metal-bound hydroxyl at a neighboring carbonyl group, followed by acid-catalyzed cleavage of the resultant tetrahedral intermediate (Figure 13). Groves and Chambers demonstrated that the rate of intramolecular attack at a dangling amide by a M^{2+}-bound hydroxyl (M^{2+} = Ni^{2+}, Cu^{2+}, Zn^{2+}) is enhanced when the metal ion is constrained to lie above the plane of the amide group, thus preventing competing metal–carbonyl interactions.[250]

Catalysis of the aqueous hydrolysis of phosphate diesters by $[Ni(tren)]^{2+}$ has been shown to involve both substrate and nucleophile coordination at the same Ni ion (Figure 14).[255] Nucleophilic attack at coordinated substrate by the activated nucleophile is the rate-determining step for the reaction, which is first order in substrate, catalyst, and hydroxide ion and shows rate enhancements of 10^3 on the basis of the concentration of deprotonated $[Ni(tren)(OH)(OH_2)]^+$ at pH = 8.6, but only of 34 on the basis of total Ni. Other Ni^{II} complexes examined showed minimal rate enhancements for this reaction at all pH's.[255] This mechanism is also well known for the hydrolysis of phosphate esters bound to Cu^{2+} [256] and Co^{3+} [258] centers, which show rate enhancements of up to 10^6. In contrast, transition metal-catalyzed hydrolysis of di- and triphosphates involves coordination of two metal ions to the polyphosphate chain, one of which provides the attacking nucleophile in the manner described above for phosphate ester hydrolysis (Figure 14) while the other, which binds to an adjacent O–P–O chelate ring, facilitates expulsion of the PO_4^{3-} leaving group.[259-261,267] Ni^{2+} proved a poor catalyst for this reaction, again showing overall rate enhancements of ≤30, suggesting that this inactivity may be related to the high pK_a of Ni-coordinated water and resultant low concentration of the catalytically active species $[Ni(L)_x(OPO_y\{OR\}_{3-y})(OH)]^{n+}$ (*vide infra*).[261]



etc.

Figure 13. Proposed mechanism for the intramolecular Ni^{2+}-catalyzed hydrolysis of esters. Adapted from ref 253.

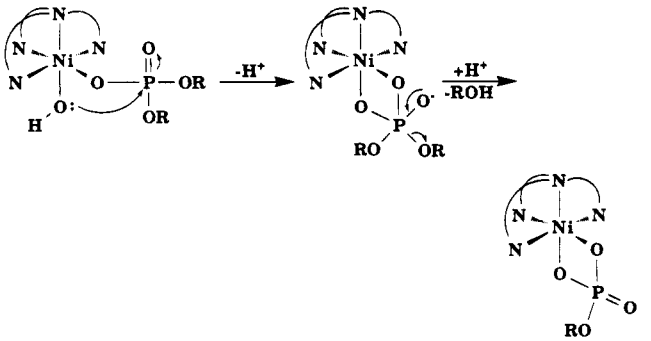
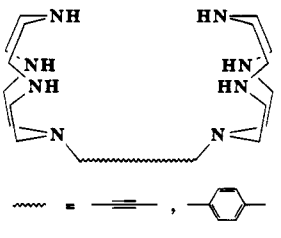


Figure 14. Proposed mechanism of phosphate ester hydrolysis by $[Ni(tren)]^{2+}$. Adapted from ref 255.

Burrows and co-workers have employed binucleating ligands containing rigid spacers (**9** and **10**) to prepare a series of acetate- or imidazolate-bridged and unbridged binuclear N-ligated Ni^{II} complexes with Ni···Ni separations of *ca.* 3.5 Å (**9**)[262] and 5.9 Å (**10**).[232] Preliminary results have shown these compounds to catalyze phosphate ester and ester hydrolysis, respectively, at rates superior to those shown by mononuclear Ni catalysts. In one case



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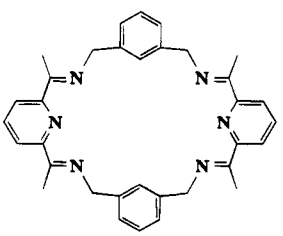


10

where mechanistic data are available, however, ester hydrolysis by an acetate-bridged complex of ligand **10** was second order in Ni complex,[232] suggesting that the initial dinuclear bridged species may not be the active catalyst in solution. Several other dinuclear Ni^{II} complexes with this type of rigid binucleating ligand have been structurally characterized, but none has been examined as a functional urease model.[263]

It is noteworthy that no synthetic hydrolytic catalyst, whether containing Ni^{2+} or another metal ion, has achieved the rate enhancement of 10^{14} observed for urea hydrolysis by urease; enhancements of $\leq 10^{11}$ are typical in synthetic systems, the most efficient transition metal catalysts generally involving Cu^{2+}, Zn^{2+}, or Co^{3+}. While model studies involving Ni are limited, the results described above show that the most efficient hydrolysis catalysis by Ni^{II} complexes appears to occur for substrate (Figure 10), rather than nucleophile (Figure 11), coordination to the Ni^{2+} ion. Examples of Ni^{II}–aqua complexes with pK_a values for deprotonation of the coordinated water molecule within the range of 9–12 have been reported,[244,249,252,253,255,268] compared to *ca.* 7–9 for Cu^{2+},[250,256,257] 7–10 for Zn^{2+},[236,250,264,266] 2–10 for Fe^{3+},[243,268] and 5–8 for Co^{3+};[267] the tendency of a given complex $[M(L)_n(OH_2)]^{m+}$ to form a hydroxo species follows the order $M = Cu^{2+} > Zn^{2+} > Ni^{2+} > Mn^{2+}$, consistent with the Irving–Williams series.[268] The acidity of a Zn-coordinated aqua ligand in Zn^{II} amine complexes varies significantly with the coordination geometry about the Zn center, however, with physiological pK_a values of 7–8[265] only being observed for tetrahedral $[Zn(L)_3(OH_2)]^{2+}$ species whose structures correspond closely to those observed for the Zn^{2+} sites in enzymes such as carbonic anhydrase.[236,266] In addition, both substrate and nucleophile activation by metal ions have been enhanced in several model systems by the presence of a noncoordinated acid or base functionality on the ancillary ligands of the metal catalyst, which can assist in protonation of the leaving group or deprotonation of the metal-bound nucleophile.[242,251,269]

In conclusion, assuming the validity of the Zerner mechanism for urea hydrolysis (Figure 2), the discrepancy between hydrolytic rate enhancements observed in biological and synthetic Ni catalysts may reflect: the presence in the former of at least three basic residues adjacent to the Ni site,[62] which may participate in the deprotonation of Ni-bound water; differences in coordination environment and charge between the model complexes examined and the enzymic Ni site; and the orientation of the urea substrate molecule within the active site so as to maximize the rate of nucleophilic attack by a Ni-bound hydroxyl.

IV. Methyl-S-coenzyme-M Methylreductase and Factor 430

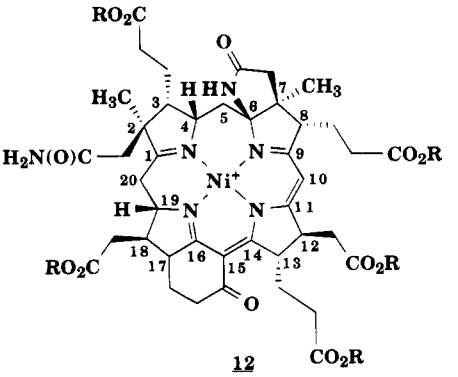
A. Methyl-S-coenzyme-M Methylreductase

Methyl coenzyme-M methylreductase (2-(methylthio)ethanesulfonic acid reductase, MCR, "component C") is an enzyme in the respiratory cycle of all known methanogens, whose function is to catalyze the elimination of CH_4 from the methyl carrier MeSCoM by the reductant (7-mercaptoheptanoyl)threonine phosphate (HS-HTP, "component B"; reaction 11).[25–32]

$$CH_3\text{-S-CoM} + \text{HS-HTP} \rightarrow CH_4 + \text{CoM-S-S-HTP} \quad (11)$$

The resultant disulfide is subsequently cleaved by a separate enzyme, this reduction being coupled to the generation of a trans-membrane proton gradient, thus completing the bacterial respiratory cycle.[30,270] Most methanogens are believed to contain two distinct forms of MCR, although the structural and functional differences between the two enzymes have not been defined.

In addition to ATP (in most cases) and a series of activating proteins collectively termed "component A", the enzyme requires a Ni-containing prosthetic group, known as Factor 430 (F_{430}) because of an intense absorption maximum exhibited at $\lambda_{max} = 430$ nm ($\epsilon_{max} = 23\,300\ M^{-1}\ cm^{-1}$); while no crystal structure is available, a series of biosynthetic, NMR, and structural studies by Eschenmoser and coworkers identified F_{430} as the dodecahydroporphyrin (corphin) complex **12**,[271] an assignment confirmed by



12

R = H; F_{430}
R = Me; F_{430M}

a 2-D NMR investigation[272] and an X-ray structural determination of the F_{430M} 12,13-diepimer (**12**).[271] The mode of binding of F_{430} within the enzyme is unclear, although the magnetic[273,274] and resonance Raman[275] properties of the inactive enzymic Ni^{II} center suggest it to be axially coordinated by N- or, more likely, O-donor ligands. A Ni XAS investigation of as-isolated MCR showed five or six Ni–(N/O) vectors of 2.09 Å, with no distinct pre-K-edge features.[276]

Until 1991, *in vitro* preparations of MCR possessed specific activities of below 5% of that shown in whole cells;[283,284] an improved method of purification has since afforded enzyme showing 30% of physiological activity,[277,286] this activity only being observed under reducing conditions.[277,306] The isolated reduced enzyme exhibits two distinct sets of EPR signals, termed MCR-red1 ($g_{\|} = 2.24$, $g_{\perp} = 2.05$) and MCR-red2 ($g_1 \approx g_2 = 2.24$, $g_3 = 2.18$; $A_{1,2,3}\{^{14}N\} = ca.$ 10 G; $A_{\|}\{^{61}Ni\} = 44$ G),[277–280] which arise from active enzyme molecules[286] and are believed to derive from a Ni^{I} F_{430} center within the enzyme with weak axial ligation. These signals were also detected from intact methanobacteria,[279,280] along with the other Ni-derived EPR signals that were only observed under aerobic conditions and could not be assigned.[280] Treatment of active enzyme with HSCoM causes quantitative ingrowth of the MCR-red2 signal at the

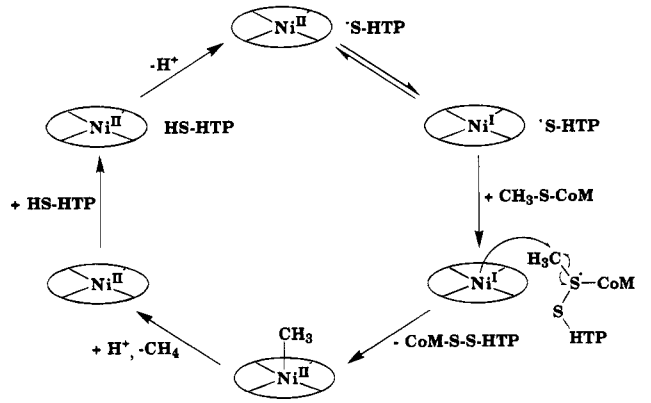


Figure 15. Proposed mechanism of methanogenesis by MCR, involving initial formation of a disulfide radical. Adapted from ref 386.

expense of MCR-red1, while incubation with MeSCoM corresponding factors MCR-red1 over MCR-red2.[277,281] Chloroform and O_2 are potent inhibitors of MCR, causing oxidation of the reduced cofactor,[26,277] while inactive MCR can be partially reactivated by irradiation ($400 < \lambda < 515$ nm), presumably via photolytic reduction of the Ni^{II} center;[282] these data also support the involvement of Ni^{I} in the catalytic cycle. Several substituted alkanesulfonate CoM analogues are also enzyme inhibitors, although these may not bind to the Ni center.[281,283-285]

Mechanistic studies of CH_4 generation by MCR have been hampered by the low activity level of the purified enzyme and few data have been reported. A recent labeling study of the MCR-catalyzed reduction of EtSCoM showed ethanogenesis to involve net inversion of configuration at the α-carbon atom, supporting a mechanism involving nucleophilic attack at the propanoyl-CoM α-C atom,[288] while the unstable adduct [$Ni^{II}F_{430M}$-CH_3] has been detected in solutions containing F_{430M} (**12**) and $(CH_3)_2Mg$.[287] Interestingly, an increased rate of difluoromethane evolution compared to the native methanogenesis reaction was observed during incubation of MCR with CF_2H-S-CoM, despite the known strengthening of C–S bonds upon fluorination of an α-carbon atom (CF_3-S-CoM was not cleaved by MCR), which was taken to be consistent with the increased stability expected for a [Ni-CF_2H] intermediate species compared to the corresponding methyl derivative.[283] In addition, axial ligation to macrocyclic Ni^{I} complexes, as observed in protein-bound F_{430}, is known to enhance the nucleophilicity of the Ni ion.[493]

In the light of these data, it has been proposed that C–S activation might proceed via nucleophilic attack of reduced F_{430} at Me-S-CoM to afford a [Ni^{II}-CH_3] intermediate (reaction 13), from which CH_4 would be eliminated by protonation (reaction 14).[288] A related

$$[Ni^{I}] + CH_3\text{-S-CoM} \rightarrow [Ni^{II}\text{-}CH_3] + \text{CoM-S}^{\bullet} \quad (13)$$

$$[Ni^{II}\text{-}CH_3] + H^{+} \rightarrow [Ni^{II}] + CH_4 \quad (14)$$

catalytic cycle has been proposed by Berkessel, which is shown in Figure 15.[386] The prior formation of a disulfide radical, as suggested here, would activate the CH_3–S bond to cleavage, thus avoiding the difficulty that F_{430} does not cleave thioethers *in vitro* (section V.B).[301] In the absence of HS-HTP, however, MeSCoM reduction by MCR affords CH_4 and HSCoM, the resultant thiol not being covalently bound to Ni,[289] suggesting that the enzymic C–S cleavage step does not require the presence of HS-HTP; this question remains to be resolved. It should also be noted that model studies have shown that Ni^{I}-induced C–S bond cleavage can also occur via a Ni → S electron transfer process (section V.B),[384] and a role for such a step in the MCR catalytic cycle cannot be ruled out. There is as yet little evidence for the nature of any direct interaction of MeSCoM or HS-HTP with the Ni site; it has recently been suggested that MeSCoM binding to an axial site of F_{430} within MCR might be regulated by the presence or absence of a sixth, *trans*-axial donor.[387]

B. Isolated F_{430}

Given the belief that the MCR Ni center plays an integral part in the catalytic cycle of this enzyme, much attention has focused on the structural and chemical properties of F_{430}. It is noteworthy, however, that almost all such studies have been performed on the isolated cofactor, rather than the intact enzyme. Since F_{430} is known to be axially ligated within the enzyme cavity,[273-276] while isolated F_{430} does not reduce MeSCoM,[301] caution should be exercised in relating data from these investigations to the *in vivo* system. In addition, spectroscopic studies reported prior to 1987 employed stereochemically heterogeneous samples of F_{430} (*vide infra*), and many of these data have since required reinterpretation.

F_{430} is extracted from the MCR enzyme as a Ni^{II} complex containing a mixture of the native form and its 12,13-diepimer (**12**), which interconvert on heating[290,291] but can be chromatographically separated;[292] at equilibrium, aqueous solutions of F_{430} contain only 4% of the naturally occurring epimer.[290] For reasons of improved solubility, the methanolysis product F_{430M} (**12**) is often employed in chemical studies. The UV/visible,[292,300] MCD,[274] Raman,[293] and XAS[292-294] spectra, and structural[275,293,294] and redox[295,300] properties of F_{430} and its diepimer in both Ni^{II} and Ni^{I} oxidation states show small but significant differences. Aqueous solutions of F_{430} exist in temperature-dependent equilibrium between four- and six-coordinate forms, the latter dominating at low temperatures;[296] in the presence of exogenous base five- or six-coordinate adducts are rapidly formed,[275,293] the diepimer exhibiting a lower affinity for adduct formation than the native cofactor.[292,293,374] The EXAFS-derived Ni–N distance of 1.90(2) Å for F_{430} and its 12,13-diepimer[275,276,292-294] increases to *ca.* 2.1 Å on coordination of two axial 1-methylimidazole ligands;[293] it is likely that these changes are permitted by puckering of the corphin ring (section V.A.ii). The Ni K-edge derived from $Ni^{II}F_{430}$ in aqueous solution shows no pronounced features, suggesting predominantly octahedral coordination about Ni in this solvent, while that shown by the 12,13-diepimer is typical of a square planar Ni ion, with an enhanced $1s \rightarrow 4p_z$ preedge feature at 8336 eV.[292,293] Interestingly, a conformational analysis of F_{430} showed that the macrocycle is sufficiently flexible to accommodate

a trigonal bipyramidal geometry about the Ni ion,[297] although such a species has yet to be observed experimentally.

Uniquely for a Ni tetrapyrrole, pentamethyl and pentaalkylamide derivatives of F_{430} undergo reversible electrochemical oxidation ($E_{1/2}$ = +0.83 V *vs* Fc/Fc$^+$ in MeCN)[298] and reduction ($E_{1/2}$ = −1.32 V *vs* Fc/Fc$^+$ in THF or DMF)[295,299] to afford metal-centered Ni^{III} ($g_\perp$ = 2.211, $g_{||}$ = 2.020) and Ni^I (g_1 = 2.250, g_2 = 2.074, g_3 = 2.065, $A_{1,2,3}\{^{14}N\}$ = 9.5 G) species, respectively. A recent study in alkaline aqueous solution showed that F_{430M} has a Ni$^{II/I}$ potential of −0.65 V *vs* NHE, that distinct EPR and electronic spectra are observed for reduced F_{430M} and its 12,-13-epimer, and that both reduced species interact weakly with H_2O, as evidenced by the ESEEM detection of a solvent-exchangeable proton at 13 MHz;[300] the EPR spectra obtained here and in nonaqueous solvents are almost identical to the MCR-red1 signal observed in intact methanobacteria.[279,280] EXAFS data from reduced F_{430M} suggest the presence of two distinct Ni−N distances of 1.88(3) and 2.03(3) Å, while the near Ni K-edge lies at 2−3 eV lower energy than that for Ni$^{II}F_{430M}$ and retains features consistent with four coordination at Ni^I.[294] Aerial oxidation of F_{430} leads to (reversible) dehydrogenation of the corphin framework.[290,291]

Although reduced F_{430M} does not react with MeS-CoM or other thioethers, in the presence of sulfonium ions methane is evolved according to eq 15.[301] This reaction is first order in F_{430M} and substrate, consistent with nucleophilic attack of the Ni^I center on the sulfonium ion being the rate-determining step, although the presence of a preequilibrium for activation of Ni$^IF_{430M}$ (reaction 16, *e.g* coordination of an axial ligand) could not be ruled out.[302] Reduced F_{430M} was also found to reduce CH_3I to CH_4,[301,303] and 1,2-$C_2H_4Cl_2$ to C_2H_5Cl or C_2H_4,[304] leading to the recently confirmed[305] suggestion that MCR may catalyze dehalogenation reactions.

$$R_2SMe^+ + 2Ni^IF_{430M} + HX \rightarrow CH_4 + R_2S + 2Ni^{II}F_{430M} + X^- \quad (15)$$

$$[Ni^IF_{430M}]_{inactive} \rightleftharpoons [Ni^IF_{430M}]_{active} \quad (16)$$

V. Structural and Functional Models for Factor 430

A. Structural and Electrochemical Investigations of Nickel Tetrapyrroles

The redox behavior of Ni porphyrins is complex and was well studied even before the characterization of F_{430}.[307] Recently, there has been renewed interest in this area, particularly with the aims of identifying Ni porphyrin and hydroporphyrin derivatives capable of metal-centered rather than ligand-centered redox chemistry, the structural characterization of these species and their redox products in solution and the solid state, and identifying their reactivity patterns (section V.B).

i. Redox Studies

Several redox schemes for Ni tetrapyrroles have been identified. The most commonly observed oxidation behavior involves the reversible electrogeneration of ligand-centered singly and doubly oxidized species, which may undergo intermolecular electron transfer to give metal-centered radicals at lower temperatures (reaction 17).[307−314] These ligand- and metal-centered oxidation products are readily distinguished by their EPR, electronic and resonance Raman spectra.[315] This complex behavior is due to the similarity in energy between the porphyrin-based HOMO and the Ni d_{z^2} orbital, a balance that can be disturbed by electron-donating or -withdrawing macrocycle substituents,[308,310,311,337] by sterically induced ruffling of the porphyrin ring,[317,318,358] by partial hydrogenation of the porphyrinic π-system (thus varying the hole size and conformational flexibility of the tetrapyrrole ring, as well as the ligand π-orbital energies),[318] by axial ligation of the Ni atom,[319,320] or by the solvent employed.[316] Few Ni porphyrin derivatives form [Ni^{III}(porph)]$^+$ one-electron oxidation products at ambient temperatures, examples being limited to some di-β-oxoporphyrins ($\langle g \rangle$ = 2.24 at 77 K; Figure 16).[316,319] For these complexes, no correlation in oxidation potential was observed between metal- and ligand-based first oxidations, which occurs at +0.34 ≤ $E_{1/2}$ ≤ +0.78 V *vs* SCE, although significant variations in metal-centered oxidation potentials did arise between donor (MeCN) and nondonor (CH_2Cl_2) solvents; binding of imidazole to these Ni^{II} di-β-oxoporphyrins in CH_2Cl_2 significantly shifts their oxidation potentials to less positive values.[319] Recently, the first Ni^{IV} π-cation (reaction 18; porph = meso-α,α,α,α-tetrakis(*o*-pivalamidophenyl)porphyrin)[321] and Ni^{III} π-dication (reaction 19; porph = 2,3,6,7,12,13,16,17-octaethylporphycene and some octaalkyltetraphenyl porphyrin derivatives) triply oxidized products have been identified.[322] Only ligand-based one- or two-electron oxidative behavior has been described for Ni porphycene,[323] porphyrazine,[324,520] chlorin,[318,325,326] oxophlorin,[327] and corrin[328] derivatives (Figure 16); [Ni^{II}(OEiBC)] forms [Ni^{II}(OEiBC$^{\bullet+}$)]$^+$ and [Ni^{III}(OEiBC$^{\bullet+}$)]$^{2+}$ on successive oxidations.[318] While the oxidized and partially oxidized [Ni(oep$^{\bullet+}$)]$_2^{n+}$ (n = 1, 2) cations have been

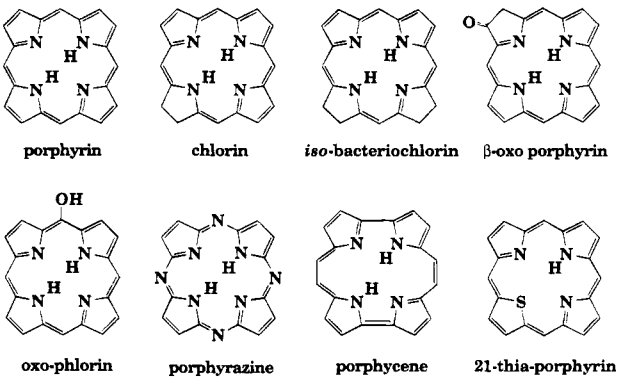


Figure 16. Structures of the tetrapyrrole ligands referred to in section V.A.

$$[Ni^{II}(porph)] \overset{-e^-}{\rightleftharpoons} [Ni^{II}(porph^{\bullet+})]^+ \overset{-e^-}{\rightleftharpoons} [Ni^{II}(porph^{2+})]^{2+} \quad (17)$$

$$\Delta \uparrow\downarrow$$

$$[Ni^{III}(porph)]^+ \overset{-e^-}{\rightleftharpoons} Ni^{III}(porph^{\bullet+})]^{2+}$$

structurally characterized[329,330] and exhibit dimeric structures in the solid state with Ni–N distances little changed from their neutral congener,[331] no crystallographic or EXAFS study of a Ni^{III} porphyrin or hydroporphyrin has been reported.

$$[Ni^{II}(porph)] \overset{-2e^-}{\rightleftharpoons} \text{“}[Ni(porph)]^{2+}\text{”} \overset{-e^-}{\rightleftharpoons} [Ni^{IV}(porph^{\bullet+})]^{3+} \quad (18)$$

$$[Ni^{II}(porph)] \overset{-e^-}{\rightleftharpoons} [Ni^{II}(porph^{\bullet+})]^{+} \overset{-e^-}{\rightleftharpoons} [Ni^{II}(porph^{2+})]^{2+} \overset{-e^-}{\rightleftharpoons} [Ni^{III}(porph^{2+})]^{3+} \quad (19)$$

The reductive behavior of Ni porphyrins is similarly complicated. While ligand-based reductive processes are often observed,[307,332–335,345,421] metal-centered reduction products have also been detected, the site of reduction depending on the tetrapyrrole ligand and experimental conditions;[336,337] for example, [Ni(oep)] has been reported to form both metal- ($\langle g \rangle = 2.083$)[336] and ligand-centered ($\langle g \rangle = 2.003$)[332] one-electron reduction products in DMF and MeCN, respectively. Reduced species of intermediate character have also been observed for several Ni porphyrins[337] and hydroporphyrins,[335] while coordination of CO, MeCN, or DMF to Ni^{II} porphyrin radical anions has been shown to afford five-coordinate Ni^{I} adducts (reaction 20).[337] The triply reduced derivative $[Ni^{I}(oep^{2-})]^{3-}$ has been detected.[338]

$$[Ni^{II}(porph^{\bullet-})]^{-} + CO \rightarrow [Ni^{I}(porph)(CO)]^{-} \quad (20)$$

Two studies of the electroreductive behavior of a variety of Ni complexes of porphyrins and their di-, tetra-, hexa-, and octahydro analogues found that genuine Ni^{I} species were only obtained for isobacteriochlorins (iBC, Figure 16), which are reduced at more negative potentials compared to that of F_{430} in organic solvents ($E_{1/2} = -1.3$ to -1.5 V *vs* SCE).[332,335] The reduced $[Ni(iBC)]^{-}$ derivatives exhibit EPR spectra very similar to that of reduced F_{430} (*e.g.* for $[Ni(OEiBC)]^{-}$, $g_{\parallel} = 2.20$, $g_{\perp} = 2.07$, $\langle A\{^{14}N\} \rangle = 9$ G[332]). This behavior was rationalized on the basis that the iBC rings were the most flexible of those examined, thus permitting the structural distortions about the Ni center concomitant with a metal-centered reduction. Interestingly, although molecular mechanics calculations suggested that the saturated meso carbon atoms C(5) and C(20) (**12**) contribute particularly to the flexibility of the corphin ring,[297] and hence by inference to the metal-centered redox chemistry shown by F_{430}, these two positions are unsaturated in the iBC ligand (Figure 16). Reduction of [Ni(OEiBC)] with Na/Hg or sodium naphthalide in protic solvents leads to ligand–hydrogenation products.[339]

The reduction of Ni^{II} 21-thiaporphyrin complexes (Figures 16 and 17) affords species characterized as metal-centered Ni^{I} radicals,[340–343] although even in this case EPR parameters imply a substantial thiaporphyrin ligand contribution to the singly occupied orbital of the reduced products.[342] Unusually for a (formally) Ni^{I} complex, $[Ni^{I}(STPP)]$ (STPPH = 5,10,15,20-tetraphenyl-21-thiaporphyrin, Figure 17) coordinates two axial Me_2Im (Me_2Im = 1,2-dimethylimidazole) ligands; the changes in EPR spectra between the four-coordinate [Ni(STPP)] ($g_1 = 2.109$, $g_2 = 2.039$, $g_3 = 2.031$) and six-coordinate $[Ni(STPP)(Me_2Im)_2]$ ($g_1 = 2.238$, $g_2 = 2.198$, $g_3 = 2.136$) parallel the MCR-red1 to -red2 transition (section IV.A), if one allows for the reduction in g values associated with the presence of the thiaporphyrin S-donor.[340] Reduction of Ni^{II} porphycenes affords ligand radical anions.[323,334]

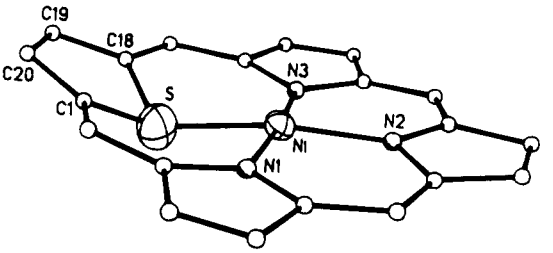


Figure 17. Structure of $[Ni^{I}(SDPDTP)]$ (SDPDTPH = diphenyl-di-*p*-tolyl-21-thiaporphyrin). (Reprinted from ref 341. Copyright 1989 American Chemical Society.)

Pulse radiolysis studies on the chemical generation of monooxidized and reduced Ni porphyrin derivatives in solution showed that the initial site of electron transfer varies with the substituents on the porphyrin ligand and with the solvent employed.[344] In all cases, rapid decay to ligand-centered two-electron redox products was observed.

ii. Structural and Conformational Studies

The structural characterization of Ni tetrapyrroles in solution and the solid state, particularly with regard to the factors influencing macrocyclic flexibility and axial ligand binding, has received much recent attention. An extensive Raman study of Ni^{II} porphyrins and hydroporphyrins by Shelnutt and coworkers has shown that four-/six-coordination equilibria occur in coordinating solvents, and that several four-coordinate structures can be observed corresponding to different tetrapyrrole conformations.[346–348] Raman and electronic spectroscopies can be used to determine the extent of ligand ruffling[347–361] and the degree of axial ligation[346,347,353,362] in Ni tetrapyrroles; axial Ni histidine binding in Ni hemoglobin has been detected by the former technique.[363] One-electron oxidation of Ni^{II} β-oxoporphyrins (Figure 16) has been shown to increase the affinity of these complexes for axial imidazole binding by a factor of *ca.* 107.[364]

The single-crystal X-ray structures of sterically hindered Ni^{II} porphyrins show the macrocycles to exhibit severe S_4 ruffling to a saddle-shaped conformation, giving Ni–N bond lengths of 1.90–1.92 Å, approximately 0.05 Å shorter than those in planar Ni porphyrins.[356,358,365–370] EXAFS data show that these Ni–N distances are maintained in solution, supporting the assertion that short Ni–N bonds in such complexes may be taken to indicate ligand nonplanarity.[358] Analogous studies of Ni complexes of hydroporphyrins showed similar trends in decreasing Ni–N distances with increased ruffling,[319,335,361,362,371–373] although here the observed distortions are controlled by hole size considerations and increased core flexibility.[374] Increased macrocycle ruffling has been suggested by different authors

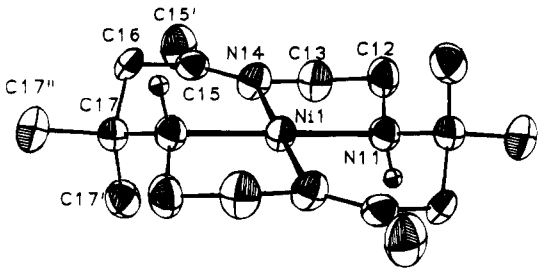


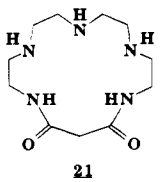
Figure 18. Structure of $[Ni^{I}(tetb\text{-}H_4)]^+$ (tetb-H_4 = 5,7,7,-12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). (Reprinted from ref 378. Copyright 1991 American Chemical Society.)

to increase[319,362] or have little effect on[375] axial ligand binding by Ni tetrapyrroles; different axial ligand binding affinities were observed for two stereoisomers of [Ni(OEiBC)][376] (*cf.* F_{430}, section IV.B).

An EXAFS study of a Ni iBC derivative showed that reduction of the Ni center results in a distortion of the macrocyclic framework rather than a simple lengthening of the Ni–N bonds, affording two distinct sets of Ni–N distances of 1.85(5) and 2.00(3) Å [*cf.* for $[Ni^{II}(iBC)]$ Ni–N = 1.93(2) Å].[335,377] This pattern of two short, two long Ni–N distances at 1.8–1.9 and 1.9–2.1 Å has been observed in every inplane Ni^{I} aza complex to be structurally characterized by EXAFS or X-ray diffraction[335,341,377–379] (Figures 17 and 18), including reduced F_{430} (section IV.B);[294] it is unclear whether this distortion is electronic in nature or a consequence of the ligands examined. Reduction of square planar Ni tetraaza complexes causes a pronounced shift in Ni K-edge to lower energy, by 2–3 eV; this shift is reduced to 0.5–1 eV by axial ligand binding to the reduced species.[335,378] Binding of CO to a series of square-planar Ni^{I} tetraazamacrocyclic complexes was shown to afford five-coordinate adducts, with little change in Ni–N distances, and a short Ni–C bond of *ca.* 1.80 Å.[378] Ni-EXAFS and XANES data for reduced $[Ni^{II}(porph^{\bullet-})]^-$ species (porph = chlorin, porphycene) were identical to those from the corresponding nonreduced precursors.[377]

B. C–S and C–X (X = Halide) Bond Cleavage by Nickel Complexes

While C–S bond formation and cleavage by organonickel reagents are well-established reactions,[380] very few examples of C–S activation involving Ni coordination compounds have been described, and only one synthetic complex has been reported to react directly with MeSCoM. [Ni(hdN_5)] (hdN_5H_2 = 1,4,7,-10,13-pentaazacyclohexadecane-14,16-dione, **21**) was



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shown to stoichiometrically convert MeSCoM to CH_4 and coenzyme M in H_2O, *via* a process that becomes catalytic upon addition of an external oxidant.[381,382] Mechanistic studies showed the reaction to be first order in [Ni(hdN_5)] and in MeSCoM at near-stoichiometric reactant ratios, and to involve concomitant oxidation of H_2O to O_2; deactivation of the catalyst in the absence of oxidant was due to formation of $[Ni(hdN_5)(SCoM)]^-$.[382]

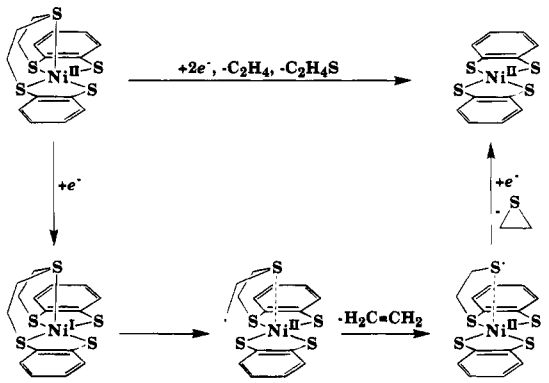
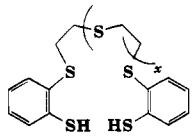


Figure 19. Proposed mechanism for the reductive formation of $[Ni(bzdt)_2]^{2-}$ from [Ni(mptds)] (mptdsH_2 = 2,2′-bis-{(2-mercaptophenyl)thio}diethyl sulfide, **22**; bzdtH_2 = benzene-1,2-dithiol). Adapted from ref 384.

The reductive dealkylation of [Ni(mptds)] (**22**) to afford $[Ni(bzdt)]^{2-}$ (bzdtH_2 = benzene-1,2-dithiol) was noted by Sellmann *et al.*[383] A recent mechanistic



22
x = 1; mptdsH_2

study of this reaction[384] showed the organic byproduct to be C_2H_4 and ethylene sulfide, and that at least two EPR-active intermediates are involved; the first of these (g_1 = 2.199, g_2 = 2.094, g_3 = 2.028) was assigned to the initial reduced $[Ni^{I}(mptds)]^-$ species, which is observable by cyclic voltammetry. A mechanism involving transfer of the Ni^{I} $d_{x^2-y^2}$ unpaired electron to a C–S σ^*-orbital, inducing homolytic C–S cleavage, was proposed (Figure 19). A related S → Ni electron-transfer mechanism was also proposed for the oxidative cleavage of a [CH_2SPh] pendant arm from a series of substituted Ni(dihydrosalen) derivatives;[385,386] while no reaction was observed for C–S cleavage from the free ligands by [Ni(salen)],[386] indicating an important proximity effect for this reaction, a recent NMR study showed no evidence for axial thioether coordination to the unoxidized Ni center in solution for these complexes.[387]

C–S bond cleavage about a Ni center has also been reported to occur via Ni → S hydride transfer,[388] oxidative addition to a Ni^0 complex[389] and by deprotonation of an α-CH_2 group,[390] although these mechanisms are unlikely to be relevant to F_{430} chemistry.

A related reaction that has been much more extensively studied is the reduction of alkyl halides by square planar Ni^{I} complexes (reaction 23; X^- = Cl^-, Br^-, I^-). This is a radical reaction, generating

$$R\text{–}X + [Ni^{I}(L)]^{(n-1)+} \rightarrow X^- + [Ni^{II}(L)]^{n+} + [R\text{–}H + R\text{–}R + R_{-H} + ...] \quad (23)$$

R• transients and/or Ni alkyls, which then decay to form alkanes, alkenes and dimeric or cyclic organ-

ics: the identity and distribution of the observed products varies dramatically with organic substrates and nickel catalysts, and with the substrate:catalyst ratio employed. There is conflicting mechanistic evidence for the initial C–X activation step, however, with several schemes being proposed.

A detailed mechanistic study by Bakac, Espenson, and co-workers of the aqueous electroreduction of alkyl halides by $[Ni(tmc)]^{2+}$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetraaazacyclotetradecane)[391-399] showed that the rate-determining step for the reaction was electron transfer from the reduced $[Ni(tmc)]^{+}$ to R–X, probably via an inner-sphere atom-transfer mechanism (reactions 24 and 25).[399] This was suggested by the observed reactivity trends for R of benzyl > allyl > secondary > primary > methyl > cyclopropyl, and for X^- of $I^- > Br^- > Cl^-$.[391,394] Under catalytic conditions, the alkyl radicals thus produced then recombine in the usual manner (*i.e.* by H• abstraction from solvent or each other, by dimerization etc.), while for low substrate:Ni ratios the dominant pathway is quenching of the alkyl radicals by a second molecule of $[Ni(tmc)]^{+}$ to form detectable organonickel(II) species (reaction 26).[287,391,400] The resultant $[Ni(tmc)R]^{+}$ complexes are

$$[Ni^{I}(tmc)]^{+} + R{-}X \rightarrow [Ni^{II}(tmc)X]^{+} + R^{\bullet} \quad (24)$$

$$[Ni^{II}(tmc)X]^{+} \rightarrow [Ni^{II}(tmc)]^{2+} + X^{-} \quad (25)$$

$$[Ni^{I}(tmc)]^{+} + R^{\bullet} \rightarrow [Ni^{II}(tmc)R]^{+} \quad (26)$$

themselves unstable for most R, and decay by Ni–C bond hydrolysis (reaction 27), by reaction with excess alkyl halide (reaction 28) or by intramolecular cyclization or fragmentation, but not by Ni–C homolysis.[391,393,395-397] An early suggestion that the $[Ni(hmc)]^{+}$ (hmc = 5,7,7,12,14,14-hexamethylcyclam) and $[Ni(salen)]^{-}$ [salenH$_2$ = 1,2-bis[[(2-hydroxyphenyl)methylene]amino]ethane] catalyzed reactions in MeCN proceed via an oxidative addition step to give a *trans*-$[Ni^{III}L(R)(X)]$ species (reaction 29)[401-405] was erroneous, although this mechanism is operative for coupling reactions of aryl halides with Ni^0 catalysts.

$$[Ni^{II}(tmc)R]^{+} + H_2O \rightarrow [Ni^{II}(tmc)OH]^{+} + R{-}H \quad (27)$$

$$[Ni^{II}(tmc)R]^{+} + R{-}X \rightarrow [Ni^{II}(tmc)]^{2+} + X^{-} + 2R^{\bullet} \quad (28)$$

$$[Ni^{I}L]^{(n-1)+} \rightarrow [Ni^{III}L(R)(X)]^{(n+1)+} \rightarrow [Ni^{II}L]^{n+} + R^{\bullet} + X^{-} \ldots \quad (29)$$

In contrast to the above results, the $[Ni(OEiBC)]^{-}$ (OEiBCH$_2$ = 2,3,7,8,12,13,17,18-octaethylisobacteriochlorin, Figure 16) catalyzed reduction of alkyl halides to alkanes under chemical or electrochemical conditions shows the reactivity patterns for R and X^- of methyl > primary > secondary > tertiary and $I^- > Br^- > Cl^-$.[406-409] This is consistent with the rate-limiting step being S_N2-type nucleophilic attack at R–X by $[Ni(OEiBC)]^{-}$ to generate a (probably octahedral[410]) Ni^{III}–alkyl species (reaction 30).[406,407] The subsequent decay of $[Ni^{III}(OEiBC)R]$ is complex, and may involve elimination of R• (reaction 31), elimination of H• from the bound alkane to form an alkene and nickel hydride (reaction 32) and/or reduction to a Ni^{II}–alkyl (reactions 33 and 34) which would then decay as described above. No organo- or hydridonickel species were detected from this reaction, although their existence was inferred by the observation of alkene isomerization during the reduction of longer chain alkyl bromides.[408] Ni^{III}–C bond homolysis (reaction 31) has been observed for the decay of $[Ni^{III}(N_4)R]^{n+}$ (N_4 = porphyrin dianion,[411] cyclam,[410,412] *N*-cetylcyclam[413]) species generated by pulse radiolysis.

$$[Ni^{I}(OEiBC)]^{-} + R{-}X \rightarrow [Ni^{III}(OEiBC)R] + X^{-} \quad (30)$$

$$[Ni^{III}(OEiBC)R] \rightarrow [Ni^{II}(OEiBC)] + R^{\bullet} \quad (31)$$

$$[Ni^{III}(OEiBC)R] \rightarrow [Ni^{III}(OEiBC)H] + R_{-H} \quad (32)$$

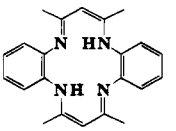
$$[Ni^{III}(OEiBC)R] + e^{-} \rightarrow [Ni^{II}(OEiBC)R]^{-} \quad (33)$$

$$[Ni^{III}(OEiBC)R] + [Ni^{I}(OEiBC)] \rightarrow [Ni^{II}(OEiBC)R]^{-} + [Ni^{II}(OEiBC)] \quad (34)$$

This mechanism is broadly similar to that observed for the reaction of cobalamin with C–X bonds; indeed, the second-order rate constants for the reduction of CH_3I (10^8 M^{-1} s^{-1}) and CH_3Cl (10^4 M^{-1} s^{-1}) by $[Ni(OEiBC)]^{-}$ are *ca.* 2000 times faster than those obtained for cobalamin.[409] An alternative mechanism for C–X activation by $[Ni(OEiBC)]^{-}$ that accounts for the nonobservation of $[Ni(OEiBC)R]^{n-}$ in the reaction mixtures has also been proposed, namely that $[Ni(OEiBC)]^{-}$ acts as a three-electron nucleophile in an unprecedented "S_N2 NBF" (no bond formed) reaction (reaction 35).[409] This implies that the subsequent formation of organic products arises purely from radical recombination processes, however, which is not consistent with the product distributions observed.[408]

$$[Ni^{I}(OEiBC)]^{-} + R_3C{-}X \rightarrow \{Ni^{I}(OEiBC){-}CR_3{-}X\}^{-} \rightarrow [Ni^{II}(OEiBC)] + R_3C^{\bullet} + X^{-} \quad (35)$$

The S_N2-type mechanism has also been proposed for the electroreductions of alkyl bromides or iodides by other Ni tetraazamacrocycles[414,415] such as $[Ni(Me_4bz_2[14]ineN_4)]^{-}$ ($Me_4bz_2[14]ineN_4H_2$ = 6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetraazacyclotetradecene, **36**)[414] and of CH_3I by a series of tetraazamacrocyclic Ni complexes.[416] The catalysis of anthracene anion reduction of 1,1-dichlorocyclopropane by Ni salts[417] and the reductions of several halogenated



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substrates by $[Ni^{I}(salen)]^{-}$ [401,403,418,419] have also been noted. Interestly, several reduced Ni porphyrins have also been reported to dehalogenate 1,2-dibromocyclohexane and CH_3I via a nucleophilic mechanism;[321,420,421] the active species here may be the $[Ni^{I}(porph)]^{-}$ resonance form known to be present at low temperatures (section V.A.i).[307] While reduced F_{430} itself was shown to reduce CH_3Cl to CH_4 50 times faster than cobalamin, no data were presented that distinguished between the above mechanisms.[303,304]

VI. Carbon Monoxide Dehydrogenase

A. Introduction

Carbon monoxide dehydrogenase (acetyl-CoA synthase, CODH), "nature's carbonylation catalyst",[451] is a component in the respiratory systems of methanogens and acetogenic and photosynthetic bacteria.[19,33-37] The enzymes from these classes of source differ in their tertiary structures and perform different functions within the respiratory cycles of these organisms. The enzyme catalyzes two reactions *in vivo*, namely the reversible oxidation of CO to CO_2 (reaction 37)[426] and the reversible assembly of CO, CH_3^+ [427] (from a corrinoid/iron-sulfur methyltransport protein), and coenzyme A (CoA) into acetyl-CoA (reaction 38), from which acetate is subsequently liberated. These two processes take place at different sites within the enzyme (Figure 20),[434,464] which are considered separately below. Isolated CODH also catalyzes the reduction of N_2O to N_2,[428] and acetyl-CoA/CO isotopic exchange (reaction 39). Several

$$CO + H_2O \rightleftharpoons CO_2 + 2H^+ + 2e^- \quad (37)$$

$$CO + CH_3^+ + CoA\text{-}S^- \rightleftharpoons CoA\text{-}SC(O)CH_3 \quad (38)$$

$$CoA\text{-}SC(O)CH_3 + {}^*CO \rightleftharpoons CoA\text{-}S{}^*C(O)CH_3 + CO \quad (39)$$

systems of nomenclature for the Ni centers in CODH have been employed in the literature, the acetyl-CoA synthesis site having been termed "center A", "the NiFe complex", or "the NiFeC species" by various authors; similarly, the CO oxidation site is known as "center C" or the "$g = 1.82$ cluster". For the purposes of this discussion, we shall refer to the acetyl-CoA synthase center as center A, and the CO oxidation site as center C.

CODH is a two-subunit enzyme, containing 1−2 Ni, 8−14 Fe, 1−3 Zn, and 13−14 acid-labile inorganic S^{2-} per $\alpha\beta$ dimer,[429-431,458] depending on source, which are organized into at least three distinct sites, including centers A and C, a typical $[Fe_4S_4]$ cluster ("center B") and a "ferrous component" whose nature is unclear. Metal analyses and other measurements are complicated by the presence of two distinct forms of the enzyme, only one of which appears to be catalytically competent.[432,434,435] A Ni-containing fraction of the enzyme is readily extracted, the resultant apoenzyme being inactive to both acetyl-CoA/CO isotopic exchange (reaction 39)[434,436] and CO oxidation.[429,462] The suggestion that a third, disulfide-reductase component may be required for acetyl-CoA synthesis by CODH has been discounted.[428]

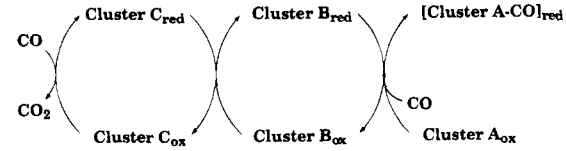


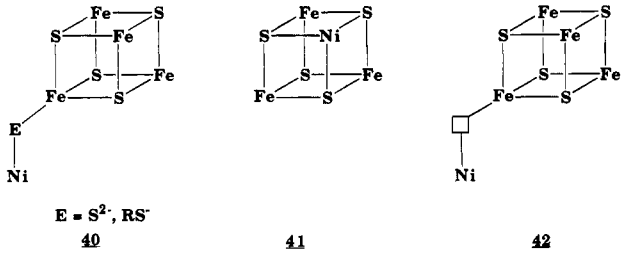
Figure 20. Proposed mechanism for the reductive activation of the [NiFe]C cluster of CODH by CO.

CODHs derived from acetogens or methanogens show both acetyl-CoA synthase and CO oxidation activity; despite only poor sequence homology between these two classes, the spectroscopic and redox properties of the A and C centers show very little variation between CODHs from different sources.[457] By far the best characterized of these enzymes is that from *Clostridium thermoacetium*, and data quoted for center A (section VI.B) derive from this source, unless otherwise stated. By contrast, photosynthetic CODHs catalyze CO oxidation only, and correspondingly lack center A; center C in these enzymes appears to be identical to those from other sources, however.[457] Data relating to center C (section VI.C) are quoted for the CODHs from both *C. thermoacetium* and the photosynthetic bacterium *Rhodospirillum rubrum*.

B. Acetyl-coenzyme A Synthesis and Center A

Acetyl-CoA synthesis by CODH almost certainly occurs at a Ni- and Fe-containing cluster (center A),[434,437,439-441] and much effort has been directed toward the derivation of the structure of this novel species. Mössbauer ($\delta = 0.44$ mm s^{-1}, $\Delta E_Q = 1.15$ mm s^{-1})[432] and Fe-EXAFS[443] measurements from as-isolated CODH are consistent with the presence of a $[Fe_4S_4]^{2+}$ moiety within the A-cluster, while Ni-EXAFS data from the as-isolated *C. thermoacetium* enzyme have been interpreted as showing four Ni−S vectors at 2.16 Å,[443] possibly in a square-planar geometry,[444] or a five-coordinate Ni center[434,445] with two Ni−S and three Ni−(N/O) distances at *ca.* 2.23 and 1.87 Å;[442] both these possibilities are consistent with a +2 oxidation state for the Ni ion.[438] No unambiguous Ni−Fe interaction was observed. The Ni absorption K-edge shows similar features to those shown by H_2-ase (section VIII.C), with the exception of an enhanced $1s \rightarrow 4p_z$ transition at 8338 eV[442] that appears to rule out tetrahedral coordination about the Ni ion(s);[61,445] little change in edge position was observed on incubation of the sample with CO, raising questions about the role of the Ni ion in the redox chemistry of CODH (*vide infra*).[442] The interpretation of these data did not take account of the possibility of the presence of more than one Ni environment within the enzyme, however. An ENDOR investigation of [center A-CO]$_{red}$ (*vide infra*) showed the presence of 3−4 Fe and 1 Ni atom.[441] Taken together, these results imply the presence of a cluster of stoichiometry $[NiFe_{3-4}S_{\geq 4}]$, possibly in the form of $[Fe_4S_4]$ and mononuclear Ni centers bridged by a cysteine thiolate or inorganic S^{2-} donor (**40**);[432] an analogous {[siroheme](μ-X)$[Fe_4S_4]$} (X = S^{2-}, SR^-)

motif is observed in assilimatory sulfite reductase.[448] The alternative structural models for center A of a [$NiFe_3S_4$] cubane (**41**),[441] and a nonbridged Ni-[Fe_4S_4] cluster which would coordinate CO in bridging fashion (**42**),[443] have been discounted (*vide infra*, section VII.A).[446,449]



40 **41** **42**

Center A in as-isolated, oxidized, and dithionite-reduced CODH is EPR silent. Incubation with CO affords a new reduced state "[center A-CO]$_{red}$", which typically shows two overlapping EPR signals that are sometimes collectively termed "spectrum C" or the "NiFeC spectrum" ("signal 1" $g_\perp = 2.08$, $g_\parallel = 2.03$; "signal 2" $g_1 = 2.06, g_2 = 2.05, g_3 = 2.03$);[439] treatment of [center A-CO]$_{red}$ with CoA converts signal 2 to signal 1.[439] Labeling studies employing ^{61}Ni, ^{57}Fe, and ^{13}CO all gave broadened [center A-CO]$_{red}$ spectra ($A_\perp\{^{13}C\} = A_\parallel\{^{13}C\} = 27$ MHz; $A_\perp\{^{57}Fe\} = 34.5$ and 28.7, $A_\parallel\{^{57}Fe\} = 29.5$ and 25.0 MHz assuming four Fe per center A, in two distinct doubly occupied sites; $A_\perp\{^{61}Ni\} = 24.3$, $A_\parallel\{^{61}Ni\} = 10.5$ MHz);[441] interestingly, the ^{61}Ni hyperfine coupling constants derived for the [center A-CO]$_{red}$ spectra are low for a Ni^I complex,[574,809,811] suggesting some form of electronic delocalization away from the Ni ion. Consistent with this, the lack of enhanced Fe–S vibrations in the resonance Raman spectrum of [center A-CO]$_{red}$ suggests the presence of a $[Fe_4S_4]^+$ moiety within the Ni/Fe cluster, and thus that the primary site of reduction is Fe- rather than Ni-based.[451] The Mössbauer spectrum of [center A-CO]$_{red}$ shows a paramagnetic species with $\delta_{av} = 0.42$ mm s^{-1} and $\Delta E_Q = 0.9–1.5$ mm s^{-1}, however (compared to the diamagnetic spectrum derived from the oxidized enzyme, *vide supra*), implying little change in average oxidation state of the Fe fraction of center A upon reduction and CO binding;[432] these resonance Raman and Mössbauer data have not yet been reconciled. The IR spectrum of CO-incubated CODH shows an absorption from the [center A-CO]$_{red}$ complex at 1995 cm^{-1}, consistent with a terminally coordinated CO ligand;[449] a very recent Raman study on ^{61}Ni- and ^{57}Fe-enriched enzyme showed that CO binds at an Fe ion of the Ni/Fe cluster in center A (Figure 21).[451] Generation of the [center A-CO]$_{red}$ state occurs in two stages: coordination of CO to the Ni/Fe center, followed by reduction of the resultant "[center A-CO]$_{ox}$" species, this reduction being necessary for catalysis.[450] The half potential of the [center A-CO]$_{ox/red}$ couple lies near $E_{1/2} = -541$ mV *vs* NHE.[37,437]

Isolated CODH catalyzes the synthesis of acetyl-CoA from CoA, CO, and a methyl source (either methyl cobalamin or MeI with the physiological corrinoid/iron–sulfur protein) in the presence of an electron acceptor. Center A is a competent intermediate in both acetyl-CoA synthesis (reaction 38) and

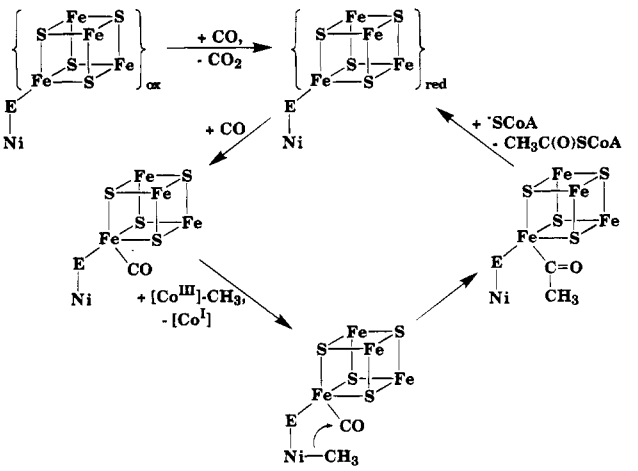


Figure 21. Proposed mechanism of acetyl-coenzyme A synthesis by carbon monoxide dehydrogenase. Adapted from ref 451.

acetyl-CoA/CO isotopic exchange (reaction 39),[437,464] implying that C–C bond formation and cleavage may occur at this site. In addition to center A–CO binding, a controlled potential enzymology study gave evidence in favor of initial methyl coordination to center A,[453] rather than to a cysteine residue as previously proposed;[454] binding of CO and CH_3^+ by center A probably occurs in a random order.[37,453] The acetyl-CoA/CO isotopic exchange (reaction 39)[455] and acetyl-CoA synthase[456] reactions employing labeled CoASC(O)CHDT were both shown to occur with overall retention of configuration at the methyl C-atom, consistent with CO insertion into a M–CH_3 bond (M = Ni or Fe) but not with an intermolecular M → substrate methyl-transfer step,[37] while CoA has been proposed to bind near, but not directly to, center A;[37,439,463] a proposed CoA binding domain was not located in the primary sequence of the polypeptide, however,[463] although at least one tryptophan residue in the polypeptide chain has been suggested to interact with enzyme-bound CoA.[463] In the absence of CoA, incubation of methylated CODH with CO generates acetate, presumably by hydrolysis of a Ni- or Fe-bound acyl ligand.[451]

The above data are consistent with the most recently proposed mechanism for acetyl-CoA synthesis by CODH, which is shown in Figure 21,[451] although of the postulated intermediates only the [center A-CO]$_{red}$ species has been observed directly. While it is now clear that the CO insertion chemistry probably occurs at Fe rather than Ni, several details of this scheme remain to be clarified. In particular, given that stereochemical data show that acetate assembly at center A almost certainly occurs via CO insertion into a M–CH_3 bond (M = Ni, Fe),[455,456] a bimetallic insertion reaction of the type proposed is unprecedented in organometallic chemistry without a preceding migration of either the CO or methyl groups such that both become bound to the same metal ion. This difficulty is avoided if the CO insertion step is proposed to occur at the Ni ion (preceded by CO migration from Fe to Ni, rather than methyl transfer from Ni to Fe as shown), or if the methyl binding site of the center A were also an Fe ion. In the latter regard, while the CH_3^+ substrate has been generally assumed to bind center A at Ni

(as until recently was the CO ligand), there is as yet no evidence to support this hypothesis. Indeed, given that the primary site of reduction of the center A is now believed to be Fe based,[451] it is possible that the function of Ni bridging to a $[Fe_4S_4]$ moiety in the CODH A-cluster may be purely to modulate the reduction potential of this site; this is one effect of the imidazolate-bridged Zn^{2+} ion on the Cu active site in mammalian superoxide dismutase (**6**),[110] for example.

C. Carbon Monoxide Oxidation and Center C

The mechanism of CO oxidation or CO_2 reduction by CODH has been little studied by comparison with acetyl-CoA synthesis. Incubation of CODH with CO_2 generates the [center A-CO]$_{red}$ EPR signals, at a potential ($E_{1/2} < -450$ mV *vs* NHE) suggestive of the involvement of a metal cluster in this process;[426] however, inhibition of acetyl-CoA synthesis in *C. thermoacetium* CODH has little effect on the rate of CO_2 reduction by this enzyme, suggesting that different active sites may be involved in these reactions.[433] The CO oxidation activity of CODH is inhibited by COS and CN^-, which compete with the CO binding site for this reaction.[447,458-460] Recent studies have shown that the cyanide inhibition is Ni specific,[447,458] involving CN^- binding to a separate redox-active cluster ("center C"; Figure 20) that shows an EPR spectrum in its reduced form distinct from the cluster A signals ($\langle g \rangle = 1.82$; $g_1 = 2.01$, $g_2 = 1.81$, $g_3 = 1.65$; $E_{1/2} = -220$ mV *vs* NHE[426,447,452,461,462]) and contains at least two Fe atoms[432,447] and Ni.[429,432,447,461] Further reduction of center C causes its conversion to a second EPR-active form ($\langle g \rangle = 1.86$; $g_1 = 1.97$, $g_2 = 1.87$, $g_3 = 1.75$; $E_{1/2} = -530$ mV *vs* NHE;[426] *cf.* $E_{1/2} = -517$ mV for the CO_2/CO couple[426,452]). It is unclear how the $g = 1.82$ and $g = 1.86$ states might differ from each other, although the latter has been suggested to contain bound CO,[464] or to correspond to a different conformational state of the protein.[457] The CN^--bound C-cluster also shows a $S = {}^1/_2$ EPR spectrum ($\langle g \rangle = 1.72$; $g_1 = 1.87$; $g_2 = 1.78$, $g_3 = 1.55$).[461] It is noteworthy that the observed pattern of g values for all these states (g_1, g_2, $g_3 < g_e$) is inconsistent with a Ni-centered radical, which should show g values greater than g_e.[8]

The Mössbauer spectrum of center C in the $g = 1.82$ state is similar to that of [center A-CO]$_{red}$, showing a paramagnetic species with $\delta \approx 0.4$ mm s^{-1} and $\Delta E_Q \approx 0.9$ mm s^{-1},[432] although unusually for a Fe/S cluster center C exhibits no strong absorptions in the visible region.[452] A Ni XAS study of a CODH from *R. rubrum* that exhibits CO oxidation activity only showed a Ni center bound by 2 S- and 2–3 N/O-donors, with preedge features consistent with a distorted tetrahedral or 5-coordinate ligand geometry[446] and an absorption edge similar to that shown by the *C. thermoacetium* enzyme;[442] a $[Ni(\mu\text{-}X)Fe_4S_4]$ (X = S^{2-}, RS^-; **40**) structure was proposed for center C on the basis of these data, an alternative $[NiFe_3S_4]$ cubane model (**41**)[447] for this cluster being ruled out by comparison with synthetic compounds. Given that this model is currently favored for both center A and center C in CODH, however, it is unclear how variations in the ligand environment about the metal ions might produce the different EPR properties of the two sites.

To summarize, CO oxidation activity appears to be associated with a second Ni/Fe center whose Ni structural environment is comparable to, but whose redox and spectroscopic properties are distinct from, center A. There is kinetic evidence that electrons generated by CO oxidation at center C in acetogenic and methanogenic CODHs are transferred directly to center A via cluster B, thus reductively activating the latter to CO binding (Figure 20).[464]

VII. Model Systems for Carbon Monoxide Dehydrogenase

In addition to the work described in this section, several of the compounds discussed in sections IX.A–C are also relevant to the chemistry of CODH.

A. Mixed Ni/Fe/S Clusters and Related Species

The early suggestion of a novel $[NiFe_3S_4]$ cluster (**41**) within the CODH active site sparked renewed interest in the synthesis of model complexes of this type. Reaction of the linear $[Fe_3Q_4(SR)_4]^{3-}$ (Q^{2-} = S^{2-}, Se^{2-}; R = Et, mes) with $[Ni(PPh_3)_4]$ affords, depending on work-up conditions, $[NiFe_3Q_4(SR)_4]^{3-}$ or $[NiFe_3Q_4(SR)_3(PPh_3)]^{2-}$.[465-467] Single-crystal structure determinations on these latter species (Q^{2-} = S^{2-}, Se^{2-}) show the expected $[NiFe_3Q_4]^+$ cubane core (Figure 22), with unremarkable Fe···Fe and Fe–Q distances, but an exceptionally short Ni–P bond of 2.18 Å. An EXAFS study of $[NiFe_3S_4(SEt)_4]^{3-}$ gave Ni–S = 2.26 and Ni–Fe = 2.74 Å, in good agreement with the X-ray results; the observed Ni K-edge implied the Ni atom to be present in the +2 oxidation state.[446] EPR ($g = 4.4$, 3.3, 1.9), magnetic, and Mössbauer data are consistent with an $S = {}^3/_2$ ground state for these species, presumably arising from antiparallel coupling of an $S = {}^5/_2$ $[Fe_3Q_4]^+$ fragment with an $S = 1$ Ni^{II} center ($J = -67$ cm^{-1} for $[NiFe_3Se_4(SEt)_3(PPh_3)]^{2-}$);[466] however, the observed isomer shift of 0.42 mm s^{-1} implies a significant charge delocalization onto the Ni site.[467,469] $[NiFe_3S_4(SR)_3(PPh_3)]^{2-}$ (R = Et, mes) can be reversibly

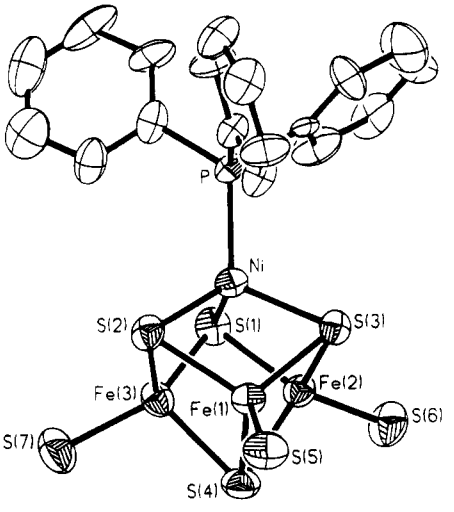


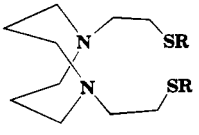
Figure 22. Structure of $[NiFe_3S_4(SEt)_3(PPh_3)]$. (Reprinted from ref 465. Copyright 1990 American Chemical Society.)

oxidized or reduced by cyclic voltammetry, at potentials more negative than those of the $[Fe_4S_4(SR)_4]^{2-}$ analogues, although it is unclear whether the Ni center is involved in these processes.[467] The Ni-bound PPh_3 ligand selectively exchanges with a variety of other phosphines, thiolates, or CN^-, the Ni ion being able to accommodate a chelating ligand without fragmentation of the cubane structure.[466]

Concurrently with the above synthetic studies, a $[NiFe_3S_4]^+$ cluster (**41**) in a protein environment was obtained by the insertion of Ni^{2+} into the $[Fe_3S_4]$ ferredoxins of *Pyrococcus furiosus*[468,469] and *Desulfovibrio gigas*.[470] The EPR and Mössbauer spectra from the resultant proteins are very similar to those described for the synthetic $[NiFe_3S_4]^+$ species,[467,469] confirming that the cubane cluster remains intact upon nickel insertion, although the nature of the terminal ligands about the Ni ion is unclear. The Ni-substituted *P. furiosus* protein was also shown to bind CN^-, an inhibitor of CODH, at the Ni site within the cluster.[468] However, while EPR and Mössbauer spectra from the synthetic and proteinaceous $[NiFe_3S_4]^+$ clusters do show similarities to those observed for CODH,[465,468] the most recent XAS data clearly preclude the presence of a similar cubane moiety at the CO oxidation site of this enzyme (section VI.C).[446]

No $[Ni_4S_4]$ clusters are known, although the synthesis of $[Ni_4Se_4(PPh_3)_4]$ has been alluded to;[478] intriguingly, the chalcogenide cubanes $[Ni_4Se_4(Se_3)_5(Se_4)]^{4-}$ [471] and $[Ni_4Te_4(Te_2)_2(Te_3)_4]^{4-}$ [472] containing octahedral Ni^{IV} centers have been described by Ibers and co-workers. Mixed-metal cubanes containing the $[NiMo_3S_4]^{4+}$ [473] and $[Ni_2Mo_2S_4]^{2+}$ [474] cores have also been characterized, although their electronic structures are not well defined. Incubation of $[NiMo_3S_4(OH_2)_{10}]^{4+}$ with CO affords $[NiMo_3S_4(CO)(OH_2)_9]^{4+}$, containing a Ni-bound carbonyl ligand (ν_{CO} = 2060 cm^{-1});[475] reactivity studies of this novel species were not reported.

Few other Ni/Fe/S heterometallic complexes have been structurally characterized. Reaction of [Ni(BME-DACO)] (BME-DACOH$_2$ = *N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane, **43**) with $FeCl_2$ affords



43

$R^1 = R^2 = H$; BME-DACOH$_2$
$R^1 = H$, $R^2 = Me$; MeBME-DACOH
$R^1 = R^2 = Me$; Me$_2$BME-DACO.

the tetranuclear $[\{Ni(BME\text{-}DACO)FeCl\}_2(\mu\text{-}Cl)_2]$, with square planar $[Ni^{II}(N_2S_2)]$ centers doubly thiolate bridged to square pyramidal Fe^{II} ions.[476] The related species $[\{Ni(dmpm)\}_3Fe]^{2+}$ (dmpmH$_2$ = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-diaminopropane; Figure 23) contains a five-coordinate Fe^{II} ion with two double and one single thiolate bridges to square planar Ni^{II} centers.[477] No electrochemical, Mössbauer or XAS studies have thus far been reported for these complexes. From these structures and those of related homometallic $[(L)_2Ni(\mu\text{-}SR)]_2$ and $[\{(L)_2Ni(\mu\text{-}SR)\}_2Ni]$ complexes (sections VIII.B,C; Table

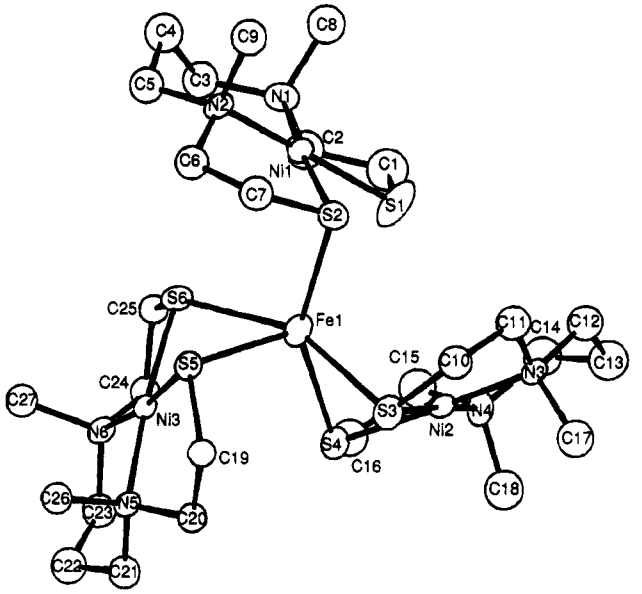


Figure 23. Structure of $[\{Ni(dmpn)\}_3Fe]^{2+}$ (dmpnH$_2$ = *N,N'*-dimethyl-*N,N'*-bis(2-mercaptoethyl)-1,3-propanediamine). (Reprinted from ref 477. Copyright 1992 American Chemical Society.)

4), it appears that the Ni···M (M = Ni, Fe) distance is relatively constant for single and double thiolate bridges between these metal atoms,[477] but varies drastically with Ni–S–M angle[476] (Table 4). For example, two different structural determinations of the $[Ni_3(edt)_4]^{2-}$ (edtH$_2$ = ethane-1,2-dithiol; Figure 32) anion afforded Ni···Ni distances of 2.830(1) and 2.856(1) Å, corresponding to Ni···(μ-S)···Ni angles of *ca.* 80.2 and 81.4°, respectively, little change in Ni-(μ-S) bond lengths being observed between the two structures.[669,674] Hence, a range of Ni···Fe distances between thiolate-bridged Ni and Fe centers appears to be possible, and the number of bridging thiolate ligands between these two metal centers cannot be reliably inferred from an observed Ni···Fe distance.

A variety of other high nuclearity nickel chalcogenide clusters have been synthesized, containing thiolate, phosphine, or organometallic coligands. These are not relevant to the discussion of bioinorganic nickel chemistry and have been reviewed elsewhere.[478,479,641,651]

B. Redox Reactions of Nickel Complexes with CO and CO_2

By far the best characterized example of CO_2 fixation by a nonorganometallic Ni complex is the aqueous electroreduction of CO_2 to CO at a Hg electrode by $[Ni(cyclam)]^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[488–497] A seminal kinetic study of this reaction by Sauvage and co-workers was consistent with η^1-coordination of CO_2 to reduced $[Ni^I(cyclam)]^+$, followed by sequential electron- and proton-transfer steps (Figure 24);[488–490] a recent theoretical investigation supported this mechanism.[493] The cyclam amine protons are believed to play an important role, stabilizing the initial Ni–CO_2 adduct by hydrogen bonding.[492] Detailed electrochemical studies, while broadly favoring the Sauvage mechanism, have shown that the active species for this reduction is

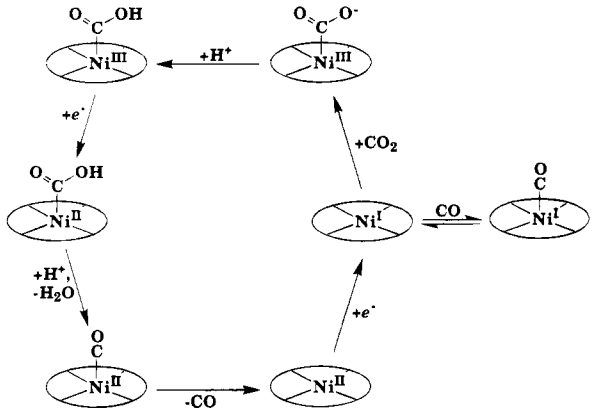


Figure 24. Proposed catalytic cycle for the electroreduction of CO_2 by $[Ni(cyclam)]^+$. Adapted from ref 488.

$[Ni^I(cyclam)]^+$ adsorbed onto the Hg electrode[488,494-497] and that this adsorption may be accompanied by a ligand conformational change;[497] unadsorbed $[Ni^I(cyclam)]^+$ coordinates CO, but not CO_2.[495,497] Such adsorption is believed to occur via formation of a covalent Ni–(surface) bond,[495,497,498] which should increase the nucleophilicity of the sixth, *trans*-Ni coordination site.[493] The $[Ni(cyclam)]^{2+}$-catalyzed electroreductions of NO_3^- to NO_2^-, of NO_2^- to NH_2OH, and of N_2O to N_2 are believed to occur via similar mechanisms.[499-501] Interestingly, reaction of $[Ni(cyclam)]^+$ with CO_2 in DMF affords formate as the major product.[490]

Several photocatalytic systems for aqueous CO_2 reduction containing $[Ni(cyclam)]^{2+}$, and GaAs or free or tethered $[Ru(bpy)_3]^{2+}$/ascorbate as photoelectron donor, have been described.[502-505] In the latter case, which is the only published example of this process believed to involve nonadsorbed $[Ni(cyclam)]^+$, it has been proposed that this reaction proceeds by CO_2 insertion into a Ni–H bond formed by protonation of the initial reduced species (reactions 44–46), by analogy with better-characterized cobalt-containing systems.[502,503] None of the postulated intermediates

$$[Ni^I(cyclam)]^+ + H^+ \rightarrow [Ni^{III}(cyclam)H]^{2+} \quad (44)$$

$$[Ni^{III}(cyclam)H]^{2+} + CO_2 \rightarrow [Ni^{III}(cyclam)(OCHO)]^{2+} \quad (45)$$

$$[Ni^{III}(cyclam)(OCHO)]^{2+} + H^+ \rightarrow [Ni^{III}(cyclam)]^{3+} + CO + H_2O \text{ etc.} \quad (46)$$

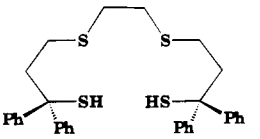
were detected; insertion of CO_2 into a Ni^{II}–H bond to give a *O,O'*-formate complex has been reported.[506]

The electrocatalytic reduction of CO_2 to CO and/or HCO_2^- by several other nickel complexes of saturated or unsaturated tetraazamacrocycles or polypyridyl ligands,[488,507-517] and by reduced Ni porphyrins (to MeOH)[518,519] and porphyrazines (to CO),[520] has been described, although few mechanistic details for these reactions are available. For saturated tetraazamacrocyclic complexes of Ni, a 14-membered macrocyclic frame with a 5,6,5,6 sequence of chelate rings appears to be essential for CO_2 reduction to take place.[517]

The reduction of Ni^0-bound CO_2 by H_2S or PhSH (reaction 47; R = H, Ph) has been communicated.[521]

$$3[(PCy_3)_2Ni^0(CO_2)] + 4RSH \rightarrow [(PCy_3)_2Ni^0(CO)_2] + 2[(PCy_3)_2Ni^{II}(SR)_2] + CO_2 + 2H_2O \quad (47)$$

The reducing agent here appears to be the thiol, since PhSSPh was observed during the course of the reaction; although Ni coordination of the CO_2 substrate is necessary for the reduction, the precise role of the Ni center is unclear. The authors related this result to the (since discredited[37]) suggestion that CODH activity for CO_2 reduction requires the presence of a disulfide reductase. The square-planar $[Ni^I(tpttd)]^-$ ($tpttdH_2$ = 2,2,11,11-tetraphenyl-1,5,8,-12-tetrathiadodecane, **48**) was shown by cyclic voltammetry to react with CO_2, although the products were not characterized.[522]



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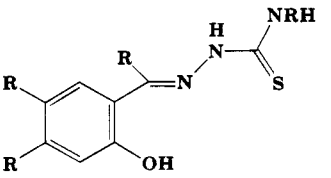
A large number of Ni^I and Ni^{II} complexes have been shown to bind CO (section VII.C). To date, however, only one example of the oxidation of CO to CO_2 by a Ni complex has been reported, namely the catalysis of reaction 49 (MV = methyl viologen) by $[Ni(tmtss)]_2$

$$CO + H_2O + 2MV^{2+} \rightarrow CO_2 + 2MV^{\bullet+} + 2H^+ \quad (49)$$

($tmtssH_2$ = 2′-hydroxy-4′,5′-dimethylacetophenone 4-methylthiosemicarbazone, **50**).[523] In the absence of MV^{2+}, incubation of $[Ni^{II}(tmtss)]_2$ with CO affords a reduced Ni^I adduct, no Ni^{II}–CO complex being observed.



50
R = H; $tssH_2$
R = Me; $tmtssH_2$

C. Thioester Formation Mediated by Nickel Centers

The currently accepted mechanism of thioester assembly by CODH involves several steps (Figure 21), namely coordination of CO and a methyl group to a reduced NiFe complex, CO insertion into a M–CH_3 (M = Ni, Fe) bond, and transfer of the resultant bound acyl moiety to a nearby thiolate center. Examples of each of these processes occurring about a Ni center are known, although all are rare.

Coordination of CO to a four-coordinate Ni^I complex, affording a five-coordinate adduct, is a well-known reaction, although few such species are isolable. The resultant carbonyl complexes may exhibit trigonal bipyramidal or square pyramidal geometries, depending on the supporting ligands. The reported

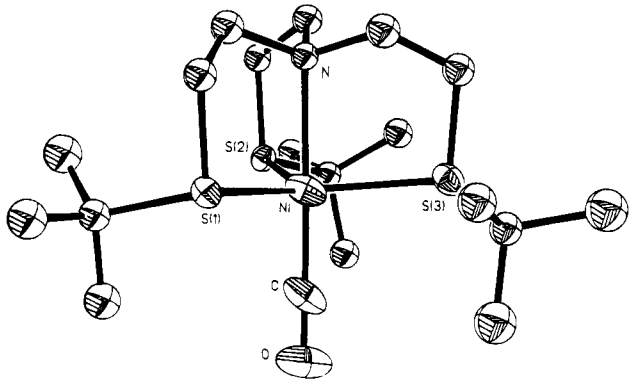


Figure 25. Structure of $[Ni^{I}(N\{C_2H_4SBu^t\}_3)(CO)]^+$. (Reprinted from ref 524. Copyright 1991 American Chemical Society.)

ν_{CO} IR stretching frequencies for Ni^I monocarbonyls[378,522,524-528] span a range from 2026 to 1940 cm^{-1}. A study of a series of Ni^I–tetraaza carbonyl adducts found no correlation between ν_{CO} and K_{CO}, suggesting only weak d-orbital participation in the Ni–CO bond.[527] Only one Ni^{II} complex has been reported to mirror the spontaneous $Ni^{II} \rightarrow Ni^I$ reduction exhibited by NiFe on exposure to CO (section VII.B).[523] The formation of octahedral $[Ni^I(L)(SR)_2(CO)]^-$ (L = terpy, DAPA; R = aryl) adducts has been reported, although only EPR data for these species are available (section IX.C).[529-531] No Ni–CO complex has yet been reported to reproduce the small $g_\perp > g_\parallel$ g-shifts observed in the NiFeC EPR signals (section VI; relevant examples are $[Ni(tmtss)(CO)]$ $g_\parallel = 2.29$, $g_\perp = 2.05$;[523] $[Ni(N\{C_2H_4SBu^t\}_3)(CO)]^+$ $g_\parallel = 2.119$, $g_\perp = 2.008$;[524] $[Ni(DAPA)(SPh)_2(CO)]^-$ $g_1 = 2.20$, $g_2 = 2.15$, $g_3 = 2.02$[531]). The single-crystal X-ray structure of $[Ni(N\{C_2H_4SBu^t\}_3)(CO)]^+$ shows a trigonal-bipyramidal cation with Ni–S = 2.353(2)–2.384(3) Å, Ni–N 2.208(6) Å, Ni–C = 1.85 Å, C–O = 1.15(1) Å (Figure 25).[524]

Most Ni–methyl complexes are unstable,[532] and few have been isolated: of relevance to this discussion are the trigonal-bipyramidal $[Ni(N\{C_2H_4PPh_2\}_3)(CH_3)]^+$ [525] and $[Ni(N\{C_2H_4SR\}_3)(CH_3)]^+$ (R = Pr^i, Bu^t),[524] and the square-planar $[Ni(Mebzdt)_2(CH_3)]^-$ (MebzdtH = 2-(methylthio)thiophenol),[533] which were synthesized by reaction of a Ni^{II} precursor with MeLi or MeMgCl. The first two of these react with CO to form isolable Ni^{II} acyls (reaction 51, E = SR, PPh_2), presumably via *cis*-$[Ni(N\{C_2H_4E\}_3)(CO)(CH_3)]^+$ intermediates.[524,526] In addition, the structurally characterized $[Ni(N\{C_2H_4SR\}_3)(C\{O\}CH_3)]^+$ were shown to react with thiols according to reaction 52 (R′ = Et, Ph, Bz), thus reproducing the acetyl-CoA synthesis reaction sequence.[524] Ni acyl and thioester products

$$[Ni^{II}(N\{C_2H_4E\}_3)(CH_3)]^+ + CO \rightarrow [Ni^{II}(N\{C_2H_4E\}_3)(C\{O\}CH_3)]^+ \quad (51)$$

$$[Ni^{II}(N\{C_2H_4SR\}_3)(C\{O\}CH_3)]^+ + R'SH \rightarrow R'S{-}C(O)CH_3 + [HN\{C_2H_4SR\}_3]^+ + Ni^0 \quad (52)$$

were also observed during the reactions of $[Ni(Mebzdt)_2(CH_3)]^-$ or $[Ni(L)(PMe_3)]$ (LH^- = 2-HS-C_6H_4-$SCH_2C(Me)_2CH_2^-$) with CO, which ultimately yield carbonyl-containing Ni species.[533,534] The Ni^I methyl adducts $[Ni(terpy)(SAr)_2(CH_3)]^{2-}$ (R = 2,6-Me_2-C_6H_3, 2,4,6-Pr^i_3-C_6H_2) have been detected by EPR spectroscopy (Table 6).[530]

The Na/Hg reduction of the square-planar $[Ni(PS)_2]^{2+}$ (PS = $Ph_2PC_2H_4SEt$, $^1/_2Ph_2PC_2H_4SC_3H_6SC_2H_4PPh_2$) generates $[Ni^0(PS)_2]$ *in situ*; reaction of the resultant solutions with CH_3I affords $[Ni(PS)_2(CH_3)]^+$ in good yield.[535] Both these Ni methyls form $[Ni(PS)_2(COCH_3)]^+$ with CO at −60 °C, but release the inserted CO on warming to −30 °C to reform the methyl derivatives. Attempts to insert CO into the Ni–methyl bond of $[Ni(S\text{-}2,6\text{-}Me_2\text{-}C_6H_3)_2(terpy)(CH_3)]^{2-}$ were unsuccessful, presumably because of the coordinative saturation at Ni in this complex.[530] The only well-characterized example of CH_3^+ addition to a Ni^I precursor occurs during the reaction of $[Ni(OEiBC)]^-$ with CH_3I (section V.B).

None of the above Ni acyls were shown to undergo CO-exchange reactions (reaction 41), although this process has been noted in other Ni^{II}–acyl complexes.[536]

VIII. Hydrogenase

A. Introduction

In contrast to MCR and CODH, which are components of the respiratory cycles of certain relatively specialized organisms, hydrogenases (H_2-ases) are ubiquitous among several classes of anaerobic, and occasionally aerobic, bacteria. These enzymes catalyze the reversible oxidation of H_2 (reaction 53), allowing the cell to generate or dispose of reducing equivalents during respiration. The protons gener-

$$H_2 \rightleftharpoons 2H^+ + 2e^- \quad (53)$$

ated by H_2 reduction may take part in the maintenance of trans-membrane proton gradients, while the electrons thus produced are employed in the reduction of electron carriers such as NAD^+, flavins, or cytochromes, or fed into one of several possible respiratory chains, depending on the bacterium; a particular cell may contain several distinct H_2-ases, each tailored to provide energy for a specific process.[19] *In vitro*, H_2-ases also catalyze H^+/D_2 exchange (reaction 54).

$$H_2O + D_2 \rightleftharpoons HDO + HD \quad (54)$$

The majority of known H_2-ases contain 1 mol of Ni and varying amounts of Fe and acid-labile S^{2-} per catalytic unit, and hence are known as [NiFe] H_2-ases.[19,38] A subset of this class has been discovered to contain selenium; these [NiFeSe] H_2-ases are discussed separately in section VIII.E. While H_2 oxidation (reaction 53) is thermodynamically reversible, most [NiFe] H_2-ases show a preference for H_2 consumption rather than production, and so are classed as "uptake" H_2-ases. A small number of Fe-only H_2-ases are also known, which contain Fe/S clusters as their only transition metal component and appear to operate by a different mechanism to the Ni-containing enzymes.[537] The preliminary charac-

terization of a H_2-ase that appears to have no metal content has been described.[538]

In contrast to the other three known Ni enzymes, Ni-containing H_2-ases show wide variations in the number and types of Fe/S cluster present, in the cofactor requirement for activity, and in tertiary structure.[19,38] Importantly, however, although the optimum conditions for activity and the redox potentials of the various oxidation states of different H_2-ases can differ between enzymes, the EPR and catalytic properties of all known [NiFe] H_2-ases are sufficiently similar to lead to the belief that an identical Ni site exists in all of them. Extensive characterizations of several H_2-ases have been described, most notably those from *Desulfovibrio gigas*, *Thiocapsa roseopersicina*, *Methanobacterium thermoautotrophicum*, and *Clostridium vinosum*, and data on enzymes from all these sources are discussed below.

The [NiFe] H_2-ases are by far the most studied, and at the same time probably the least understood, of all the Ni enzymes described in this review.[38-44] While the Ni center in Ni-containing H_2-ases is thought to be the catalytic site of these enzymes, the structure of this novel Ni coordination complex, its relation to the Fe/S clusters present in all H_2-ases, the nature of any Ni oxidation state changes during redox cycling of the enzyme, and the mechanism of action of the catalytic site, are all unclear, if not somewhat controversial. Detailed discussions of the differences between individual H_2-ases, and of all the models put forward for the H_2-ase Ni site, are beyond the scope of this article, and we will restrict ourselves to summarizing experimental data relevant to the Ni center, together with those inferences of relevance to the inorganic chemist that can be derived from these studies: it should be emphasized that the arguments presented are far from conclusive. The interested reader is referred to refs 15, 19, and 44 for more in-depth discussions.

B. Redox Chemistry of [NiFe] Hydrogenases

The following redox states are shown by the Ni center in [NiFe] H_2-ase (Figure 26). Aerobically purified [NiFe] H_2-ase is obtained in either one, or a mixture of both, of two oxidized forms, distinguishable by their EPR spectra and termed the Ni-A, "unready" or Ni^{III}_u ($g_1 = 2.31$, $g_2 = 2.23$, $g_3 = 2.02$) and Ni-B, "ready" or Ni^{III}_r ($g_1 = 2.33$, $g_2 = 2.16$, $g_3 = 2.02$) states. Neither of these forms of the enzyme reacts catalytically with H_2, and both must be reductively activated by incubation with H_2 or dithionite; the Ni-B state is rapidly reduced to one or more of a number of active species, depending on the duration of the activation process, whereas Ni-A shows a significant lag time before full activity is reached, reduction from this state sometimes requiring mild heating.[539,540] Brief exposure of Ni-B to H_2 affords an active state showing no EPR signal from the Ni center (the "silent intermediate", "SI", "EPR-silent", or Ni^{II} state). Anaerobic oxidation of the silent intermediate with $[Fe(CN)_6]^{3-}$ or flushing the sample with He regenerates exclusively Ni-B, while incubation with O_2 gives a mixture of Ni-A and Ni-B. Upon further exposure to H_2 the EPR-silent state is converted to a new EPR signal called the Ni-C or Ni^I state ($g_1 = 2.20$, $g_2 = 2.15$, $g_3 = 2.01$). This form of the enzyme is thermally stable in the strict absence of H_2[571] but is photosensitive, irradiation at below 100 K causing its quantitative conversion to a new EPR-active species known as Ni-C* or Ni-L ($g_1 = 2.3$, $g_2 = 2.14$, $g_3 = 2.04$);[541,542,544,545,576,577] warming this photoproduct above 100 K regenerates the Ni-C signal. Further incubation of Ni-C with H_2 affords a fully reduced state, Ni-R or "Ni^0", in which the Ni center is again EPR silent. The Ni-R state is unstable in the absence of H_2, exposure of Ni-R to He or Ar regenerating the Ni-C spectrum. The Ni-C, Ni-R, and (in the presence of redox mediators)[539] silent intermediate states exist in redox equilibrium with H_2.[546] These redox reactions are discussed more fully in the following paragraphs. It should be noted that despite the labels often attached to these redox states, the oxidation state of the Ni center in some of these forms is far from clear. We will not consider in this article the redox changes associated with Fe/S clusters, although these play important roles in shuttling electrons to and from the Ni center, and in the interaction of H_2-ase with external electron donors and acceptors.[19]

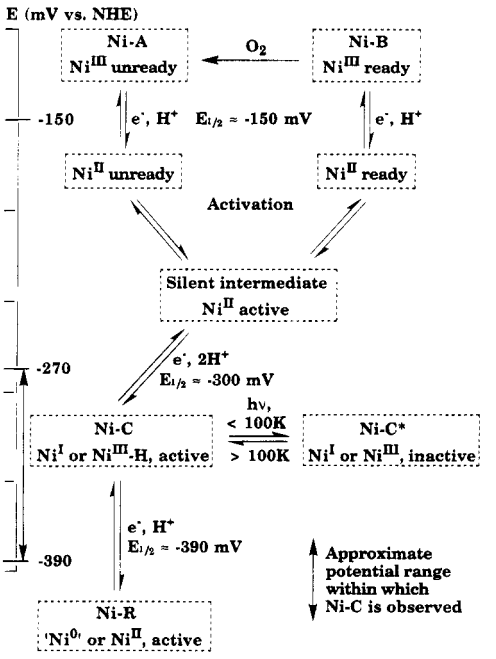


Figure 26. Redox states shown by [NiFe] hydrogenases, showing the approximate potentials at which they are observed.

In most [NiFe] H_2-ases, both the Ni-A and Ni-B states are reversibly reduced at similar potentials to Ni^{II} by one-electron processes: the potential for this reductive activation is variable, but most often occurs at $E_{1/2} \approx -150$ mV *vs* NHE at pH 7.0[539,547-549,557,572] (examples with $E_{1/2}\{Ni^{III/II}\} = -310$ mV at pH 7.7,[551] and $E_{1/2} = -410$ mV at pH 8.0,[552] have been reported). Hence, Ni-A and Ni-B are both thought to contain Ni^{III} centers, the differences in their EPR spectra most likely corresponding to different conformational states of the protein rather than changes in Ni primary coordination sphere.[553-555] Interestingly in the light of this hypothesis, it has been demonstrated that the Ni site in Ni-A, but not in Ni-B, is inacces-

sible to solvent (section VIII.C). In most cases[551] Ni-B shows a slightly more negative reduction potential than Ni-A,[549,556] consistent with the possibility that reduction of Ni-B may involve a smaller protein conformational change than Ni-A.[555] Both these reductive processes are pH dependent ($\Delta(E_{1/2}) = -60$ mV per unit increase in pH),[548,557] indicating that the $Ni^{III/II}$ reduction is accompanied by a protonation step. The EPR spectra shown by both states are consistent with low-spin d^7 ions and have been interpreted in terms of $(d_{z^2})^1$ radicals with octahedral or square pyramidal geometries. The Ni-A spectrum shows hyperfine coupling in enriched samples to ^{61}Ni ($A_1\{^{61}Ni\} = 7.5$, $A_2 = 15$, $A_3 = 27$ G[544,558-561]) but not to ^{57}Fe,[559] while the Ni-B signal exhibits coupling to one ^{33}S nucleus ($A_1\{^{33}S\} = 9.5$, $A_2 = 13.9$ G, A_3 not observed);[562] both these signals show splittings and relaxation properties consistent with weak coupling to a nearby paramagnet (*cf.* Ni-C, *vide infra*).[543] While the magnitude of the observed hyperfine coupling constants to these nuclei imply significant Ni^{III} character for these radical centers,[563-565,685,686,711] the paucity of ^{61}Ni hyperfine coupling data reported for Ni^{III} model complexes with innocent ligands and the lack of detailed structural or electronic spectral information about the Ni site prevent a definitive assignment of the ground state of the Ni-A complex.[566] A ^{61}Ni-enrichment study of a Ni^{III} tetrathiolate such as $[Ni(ndt)_2]^-$ (section IX.B) would be of use here, for comparison with data derived from oxidized Ni dithiolene complexes which typically show $A_{||}(^{61}Ni) \leq 15$ G. The MCD spectrum of Ni-A shows the presence of d−d and S → Ni charge transfer transitions, at $\lambda_{max} = 530-670$ and 300−460 nm, respectively.[567]

The Ni-B state is only stable with respect to Ni-A over a narrow pH range centered near pH 7.8, the exposure of Ni-B to O_2 or an oxidizing dye outside this range rapidly affording Ni-A;[555] in at least one enzyme, the Ni-B state is not stable under any conditions.[539] Incubation of reduced H_2-ase with labeled $^{17}O_2$ gave both broadened Ni-A *and* Ni-B spectra but did not affect EPR signals arising from Fe/S clusters,[568] showing that O_2 interacts with the enzyme in the vicinity of the Ni site, although since Ni-B can also be generated by anaerobic oxidation it seems unlikely that any [O] content incorporated into the protein upon aerial oxidation is directly bound to Ni in this state. A suggestion that O_2 may function as a ligand to Ni^{III} in the Ni-A state has also been discounted.[568] It has been proposed that the ^{17}O-broadened Ni-A and Ni-B EPR spectra may reflect oxidation of a Ni-bound thiolate to a sulfinate center.[646] The possibilities that the oxidative deactivation process may involve depletion of the enzymic metal content, or the formation of cysteinyl disulfide bridges, have been ruled out.[540]

The silent intermediate state is now agreed to contain a Ni^{II} ion. The previous suggestion that this state may correspond to antiferromagnetically coupled Ni^{III} and $S = {}^1/_2$ Fe/S cluster centers[549] was disproved by the demonstration that all the $[Fe_4S_4]$ clusters in the EPR-silent state of the *D. gigas* enzyme are in their oxidized $S = 0$ forms.[569] There is some evidence for the presence of "unready" and "ready" EPR-silent states as intermediates in the reductive activation of H_2-ase from Ni-A and Ni-B, respectively, although it is not known how these may differ from the active silent intermediate form (Figure 26).[539]

The reduction of the silent intermediate to Ni-C, while not a simple Nernstian process, occurs as a one-electron transformation at approximately $E_{1/2} = -300$ mV *vs* NHE at pH 7;[539,544,546,549,556,569,617] this transition becomes irreversible in the absence of a redox-mediating dye.[546] Since this potential is very close to that demonstrated for H_2-ase activity ($E_{1/2} = -310$ mV *vs* NHE at pH 7 for the *D. gigas* H_2-ase[570]), and as the Ni-C signal is also observed during H_2-ase catalysis *in vivo*,[280,546] Ni-C is believed to be an intermediate in the catalytic cycle. The reductive generation of Ni-C is pH dependent ($\Delta E_{1/2} = -120$ mV per unit increase in pH),[544] implying that this reduction is coupled to a double protonation. The Ni-C EPR spectrum shows hyperfine coupling to ^{61}Ni ($A_1\{^{61}Ni\} \approx A_2 = 2-6$ G,[544,561] $A_3 = 27$ G[558]) and is broadened in the presence of enriched ^{33}S,[562] but becomes slightly sharper in D_2O.[541,556] Unusually, at temperatures below 10 K the Ni-C signal shows additional fast-relaxing components at $g = 2.21-2.11$ (the "$g = 2.21$ *or* "split Ni-C" signal)[542,544,546,549,569,572] which are slightly broadened in ^{61}Ni-enriched enzyme samples[544] and appear to arise from coupled paramagnetic centers.[542] It has been suggested that this low-temperature behavior may reflect splitting of the Ni-C signal by weak dipolar coupling to an adjacent $S = {}^1/_2$ $[Fe_4S_4]$ cluster[542,543,569] (see also section VIII.C) and that the two signals interconvert with variation of temperature.[544,555] The latter conclusion has been questioned by more recent data,[569] which shows that the Ni-C and $g = 2.21$ spectra exhibit different redox profiles and hence that they correspond to different oxidation states of the enzyme, implying that the observation of the $g = 2.21$ signal is in fact dependent upon the oxidation state of the interacting Fe/S cluster (reaction 55). Such an interaction does not

$$\underset{\substack{S = {}^1/_2 \\ \text{Ni-C}}}{[Ni]-[Fe_4S_4]_{ox}} \xrightarrow{+e^-} \underset{\substack{S = {}^1/_2 \\ g = 2.21}}{[Ni]-[Fe_4S_4]_{red}} \qquad (55)$$

require that the $S = {}^1/_2$ Ni and $[Fe_4S_4]$ centers be in close proximity, however, a similar effect having been noted in xanthine oxidase between a Mo^V ion and a $[Fe_4S_4]$ cluster that lie 11 ± 3 Å apart.[573]

The Ni−C EPR signal has been proposed by different authors to correspond to a Ni^{III} or a Ni^I species, the frozen glass EPR spectra from these ions being almost indistinguishable in the absence of corroborating redox or structural data. The observation of g_3 in the Ni−C EPR spectrum at a value close to the free electron value suggests a $(d_{z^2})^1$ ground state for this species,[569] which could correspond to a square pyramidal or tetragonally elongated octahedral d^7 center, or to a trigonal bipyramidal, tetragonally compressed octahedral or three-coordinate d^9 complex.[556] The assignment of Ni-C as a Ni^{III}-containing species is favored by the similarity of the ^{61}Ni hyperfine coupling constants derived from the Ni-C and Ni-A spectra (Ni^I complexes of S-donor ligands

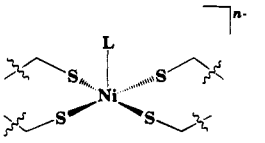
generally show 50 < $A_{||}\{^{61}Ni\}$ < 70 G,[342,574,809] although almost all published data are derived from complexes with $\{d_{x^2-y^2}\}^1$ ground states), and by the fact that Ni-C is itself further reduced by H_2 to Ni-R. This reduction seems more likely to correspond to a $Ni^{III/II}$ transition,[549,569] since a $Ni^{I/0}$ reduction for a thiolate/histidine-ligated complex should occur at too low a potential for a physiological process (typically $E_{1/2}\{Ni^{I/0}\}$ = −2.5 V *vs* NHE for S-rich Ni complexes[535,785,806,808,809]). The proposition that Ni-C may contain a Ni^I center is based on the observations that this state is generated by a one-electron reduction from a Ni^{II} precursor, and that the initial species generated upon incubation of Ni-C with CO shows very similar EPR and photolysis properties to that of Ni-C itself (section VIII.D);[577] the binding of carbonyl ligands to Ni centers in oxidation states greater than +2 is unknown.

Irradiation of Ni-C causes its quantitative conversion to Ni-C*,[541,576,577] whose EPR spectrum shows pronounced rhombicity with no *g* value near 2.0 and has been suggested to arise from a $(d_{x^2-y^2})^1$ ion. The reversibility of this process, together with the XAS and ENDOR results described in section VIII.C, suggest that the conversion of Ni-C to Ni-C* corresponds to the elimination of H_2 from the Ni center. The photolysis reaction was shown to occur 6 times more slowly in D_2O compared to H_2O,[541,577] suggesting that the [Ni-C]-bound hydrogen ligand that is eliminated during photolysis is hydridic in character and that the proton source for H_2 elimination is exchangeable with solvent. The ENDOR and ESEEM data that suggest that the Ni−H site may itself be solvent-exchangeable do not necessarily support this interpretation, however. While the quantitative reversibility of the Ni-C → Ni-C* transformation suggests that the H_2 produced by the photolysis reaction remains in close proximity in the Ni site, either as a free H_2 molecule or by hydrogenation of a neighboring amino acid residue or Fe/S cluster, it is not known how Ni-C* differs structurally from Ni-B or Ni-A.

The final reduction of Ni-C to Ni-R shows $E_{1/2}$ = −390 mV *vs* NHE at pH 7, and is again coupled to a protonation ($\Delta\{E_{1/2}\}$ = −60 mV per pH unit).[544,546] This reduction has been described as a reversible one-[539,544,556] or two-electron[546] process in the presence or absence of an external redox mediator, respectively; in the latter case, the expected one-electron reduction of Ni-C was assumed to be coupled to the reduction of another redox center, possibly a low potential $[Fe_4S_4]$ cluster.

C. Structural Properties of [NiFe] Hydrogenases

Independent Ni K-edge XAS studies of the Ni-A states of the *M. thermoautotrophicum*[578] and *D. gigas*[579] [NiFe] H_2-ases were communicated in 1984. Both analyses were consistent with sulfur ligation to Ni; Fe EXAFS data on the former enzyme also demonstrated the presence of Fe/S clusters, while XAS data on the H_2-reduced silent intermediate form of the *D. gigas* enzyme showed a shift to lower energy of the Ni K-edge by *ca.* 2 eV compared to Ni-A, suggesting that reduction of the Ni center had taken place. Similar models for the Ni coordination sphere in the two enzymes were proposed, both groups suggesting the presence of a Ni ion bound to four sulfur donors, at Ni−S distances of 2.25 and 2.20 Å, respectively, possibly lying in an equatorial plane (**56**);[444,578] neither analysis was able to unambiguously detect the presence of N/O scatterers. It has been suggested that these early investigations may have employed heterogeneous enzyme samples, however, in mixtures of redox states.[581] ESEEM experiments of the Ni-A and Ni-C signals of several [NiFe] H_2-ases have shown the presence of (at least) one N-donor ligand to Ni,[583−585] although such an interaction appeared to be absent in one case,[583] while a comparison of the EPR spectra of Ni-A and Ni-B with Ni^{III} model complexes of sulfhydryl peptides suggested that the number of S-donors to Ni is equal to or smaller than four.[624]



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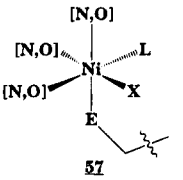
L = N/O donor, vacant coordination site.
***n* = 2, 3.**

More recently, a comprehensive structural study of the different redox states of the *T. roseopersicina* [NiFe] H_2-ase has been carried out by Bagyinka, Maroney, and co-workers.[545,580−582] Ni XAS spectra obtained from all redox states of the enzyme (*i.e.* Ni-A, Ni-B, silent intermediate, Ni-C, Ni-C*, and Ni-R) were fitted to 2 ± 1 S scatterers at Ni−S = 2.23(3) Å and 3 ± 1 N/O scatterers at Ni−(N/O) = 2.00(6) Å (**57**),[581,582] values consistent with a Ni^{II} center.[438]



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E = S, Se

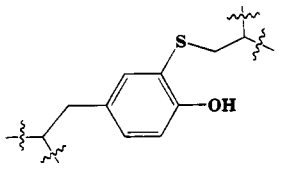
X = SCys⁻, (μ-S)[Fe_yS_y] (y = 1, 4)

L = N/O donor, vacant coordination site.

Some evidence was obtained for the presence of additional S and Fe scatterers approximately 4.2 and 6.2 Å from the Ni site, respectively, suggesting the presence of a Fe/S cluster adjacent to the Ni ion.[581] This observation led the authors to propose that the Ni ion may be covalently bridged to a $[Fe_4S_4]$ cluster, possibly via a μ-S^{2-} ion (**40**, **57**);[581] this seems unlikely, however, given the absence of ^{57}Fe hyperfine broadening to Ni-A[559] (*cf.* centers A and C of CODH, section VI[439,441]), and the weakness of the coupling observed between Ni-C and the $[Fe_4S_4]$ cluster[542,543,569] (section VIII.B; *cf.* 2-ME-inhibited urease, section II[54,55]). It has also been suggested from Mössbauer data that the Fe moiety adjacent to the Ni ion may be a mononuclear Fe center, which might mediate dipolar interactions between Ni and a more distant $[Fe_4S_4]$ cluster.[575] The similarity in structural parameters for the different redox states in this enzyme is mirrored in their Ni K-absorption edges, which are

distinct from those reported in the earlier studies[444] and show minimal changes in energy or preedge features between states.[582] All samples (except the Ni-B state) show no resolvable 1s → $4p_z$ transition and only a weak 1s → 3d feature at 8332 eV, which implies octahedral or trigonal-bipyramidal coordination at Ni;[582] the former possibility is ruled out for the silent intermediate state by the demonstration that the Ni^{II} ion in this form is low spin (section VIII.E).[616]

The above results are difficult to reconcile with the earlier data and throw doubt on the role of Ni as a redox center in this enzyme; the authors noted the presence of a thioether residue, which may be redox active, derived from tyrosine and cysteine (**58**) in the Cu enzyme galactose oxidase.[586] The Mo pterin cofactor (**59**), found in several oxidases,[573] also provides precedent for non-innocent sulfur-donor ligands to metallobiosites. It is unclear, however, whether



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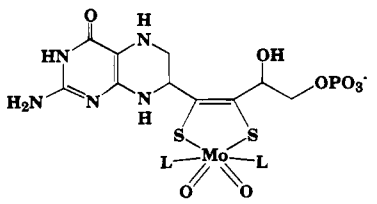

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this study implies ligand-based redox chemistry for H_2-ase, or simply that Ni K-edge XANES is insufficiently sensitive to detect any structural changes at Ni during redox cycling; a comprehensive study of model compounds showed only small changes in Ni K-edge spectra for different coordination geometries, and between the +3 and +2 oxidation states, in sulfur-ligated Ni complexes (section IX.C).[804] It may be that a more sensitive structural technique, such as Ni L-edge XAS,[623] is required to detect subtle changes in coordination geometry about Ni between redox states in H_2-ase.

The observations of ^{61}Ni and ^{33}S hyperfine coupling to [NiFe] H_2-ase and of ^{77}Se hyperfine coupling to the Ni-C state of [NiFeSe] H_2-ases (section VIII.E), which contain Ni-bound selenocysteine as the only proteinaceous Se component, argue for at least one axial cysteine or selenocysteine ligand to Ni (**57**) and clearly demonstrate the role of the Ni ion itself, or of a Ni-coordinated chalcogen-donor which remains Ni-bound upon oxidation, in the redox chemistry of these enzymes. In the latter case, the above XAS results suggest that the redox-active ligand should contain a π-system adjacent to the Ni-coordinated S-donor to allow delocalization of the ligand unpaired electron (*cf.* the pterin cofactor, **59**), since the formation of a Ni^{II}-bound oxidized cysteinyl or methionyl radical would be expected to significantly lengthen the corresponding Ni−S bond, because of the positive increment in charge at, and reduced π-donation from, an oxidized thiolate or thioether radical.[711] Additionally, model studies have shown that oxidation of a Ni-bound thiolate, and oxidation or reduction of a nonconjugated thioether (*e.g.* methionine) ligand, may result in ligand degradation by disulfide formation[642-645] and C−S bond cleavage (section V.B),[384,385] respectively. Clearly, there remain several questions to be answered regarding the electron-transfer chemistry of Ni-containing H_2-ases.

Protein sequences for several [NiFe] H_2-ases have been published,[19,44,587] all examples showing a conserved pair of cysteine residues at both the *N*- and *C*-termini of the peptide chain of the Ni-binding subunit (*cf.* rubredoxin, section IX.A), each pair of cysteines also being associated with a neighboring histidine residue. The sequence of a [NiFeSe] H_2-ase (section VIII.E) shows that one of these *C*-terminus cysteine residues is replaced by a selenocysteine in this enzyme;[615] since this selenolate donor is known to coordinate to the Ni ion, it is likely that the corresponding cysteine residue in the [NiFe] enzymes, and possibly the neighboring cysteine and histidine donors, also bind the Ni center. Mutagenesis studies support this view, and further implicate both *N*-terminus cysteines as ligands to Ni.[44] The authors also suggest that an *N*-terminus arginine residue may bind the Ni ion, although no example of a metallobiosite containing this function as a ligand has yet been published.

The possibility of Ni as the H_2 activation site has been established by ENDOR and ESEEM spectroscopic investigations of several redox states of the *D. gigas* and *T. roseopersicina* H_2-ases.[545,584,588] Both studies demonstrated the presence of a proton environment at the Ni-C center that is exchanged by D_2O and interacts strongly with the Ni center ($\langle A\{^1H\}\rangle$ = 17−20 MHz), and is derived from H_2; this proton environment is not present in the Ni-A, Ni-B, or Ni-C* forms. The magnitude of this coupling, while small compared to that observed for other Ni^I hydrides,[589] was thought to be too large to arise from Ni-bound solvent or protonated thiolate ligand and was proposed to correspond to either an equatorial hydride bound to a $\{d_{z^2}\}^1$ Ni^{III} center, or to an acidic proton interacting with the Ni ion in an agostic fashion;[588] such an agostic interaction could derive from a (possibly Ni-coordinated) alcohol or thiol protein residue, or an adjacent protonated Fe/S cluster. A third possible structural assignment, of a η^2-H_2 ligand bound to Ni^I,[588] seems unlikely since the high kinetic acidity of dihydrogen complexes of odd-electron metal ions[590,873] should lead to the rapid deprotonation of such a species, which would not be expected to be observable on the timescale of these experiments. Assuming the validity of this assignment, it is noteworthy that the solvent exchangeability observed for this proton would imply either a protic character for the Ni-bound H-ligand, or that the H−H cleavage reaction is reversible under thermal, as well as photochemical, conditions (reaction 60, B = base: section VIII.B). This latter interpretation seems reasonable, given that the reduced states of [NiFe] H_2-ase exist in redox equilibrium with H_2. In addition to the Ni−H coupling, a nonexchangeable

$$[\text{Ni-H}] + \text{B-H}^+ \overset{+D_2O,\ -HDO}{\rightleftharpoons}$$
$$[\text{Ni-H}] + \text{B-D}^+ \rightleftharpoons \text{H-D} + [\text{Ni}] + \text{B}$$
$$\rightleftharpoons [\text{Ni-D}] + \text{B-H}^+ \quad (60)$$

proton environment with an isotropic hyperfine interaction of 12 MHz assigned to cysteine β-CH_2 hydrogen atoms[545] and a weaker exchangeable proton site ($\langle A\{^1H\}\rangle \approx 4$ MHz) which may derive from Ni-bound H_2O or OH^-,[584,588] were observed in Ni-C; the latter coupling was also shown by Ni-A and Ni-B, but was no longer solvent exchangeable for the former state.

D. The Mechanism of H_2 Oxidation and H^+/D_2 Exchange by Hydrogenase

The question of whether H−H bond cleavage by H_2-ase occurs via a homolytic (oxidative addition) or heterolytic (deprotonation) pathway has been addressed in two ways. Firstly, it was demonstrated that ortho/para H_2 conversion is effected by H_2-ase upon incubation with H_2 in H_2O, but not with H_2 in D_2O;[591] this is rationalized by proposing that at least one H atom derived from the substrate molecule is readily solvent exchangeable, thus producing HD rather than H_2 upon back-reaction (reaction 61; B = base). This is consistent with heterolytic cleavage

$$H_2 + [\text{Ni}] + \text{B} \rightleftharpoons$$
$$[\text{Ni-H}] + \text{B-H}^+ \overset{+D_2O,\ -HDO}{\rightleftharpoons} [\text{Ni-H}] + \text{B-D}^+$$
$$\rightleftharpoons \text{HD} + [\text{Ni}] + \text{B} \quad (61)$$

of H_2 to generate a (presumably Ni-bound) hydride and an exchangeable proton. Secondly, the initial product ratios for H^+/D_2 exchange catalysis (reaction 54) can be used to distinguish between homolytic and heterolytic mechanisms. Several measurements of this type have shown that catalysis of this reaction by [NiFe] H_2-ase yields initial H_2:(H_2 + HD) ratios of 0.2−0.3,[591−595] close to those shown by other catalysts known to cleave H_2 heterolytically; homolytic H−H scission would generate a ratio of ≥ 1.[625] Hence, while some authors have proposed mechanisms for H_2 oxidation by H_2-ase involving homolytic H−H cleavage,[40] it seems more likely that a heterolytic mechanism is in fact operative.

The nature of the proton acceptor site at the Ni center is unknown, the most common suggestions being a Ni-bound thiolate donor (Figure 27),[19,39,42,569] a noncoordinated basic amino acid residue adjacent to the Ni ion,[569] a flavin cofactor,[40] or a neighboring [Fe/S] cluster.[42,550,569] This type of heterolytic H−H bond cleavage or formation assisted by a thiolate ligand has been proposed to play a role in H^+/D_2 exchange catalysis by Rh^{III} and Ir^{III} thiolate complexes[596] and in proton reduction by reduced Ni dithiolene complexes.[880] In addition, CH_3^+ transfer from a methyl phosphate triester to a Zn^{2+}-coordinated cysteine S-donor has been demonstrated in a bacterial DNA repair enzyme,[597] showing that a metal-bound cysteine residue can act as a nucleophile in the manner proposed for H_2-ase (CH_3^+ and H^+ are isolobal). No proton environment assignable to a coordinated thiol in Ni-C was detected by ENDOR or ESEEM spectroscopies, however (section VIII.C). Heterolytic H−H cleavage at bridging sulfide ligands is also well known,[598] H_2 activation by Fe-only H_2-ases probably occurring by this method.[537]

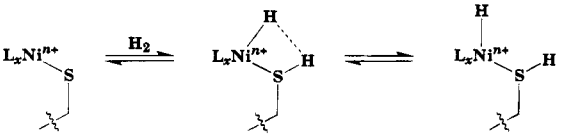


Figure 27. Possible role of a Ni-bound cysteinyl thiolate donor as a proton acceptor during H−H bond cleavage by hydrogenase.

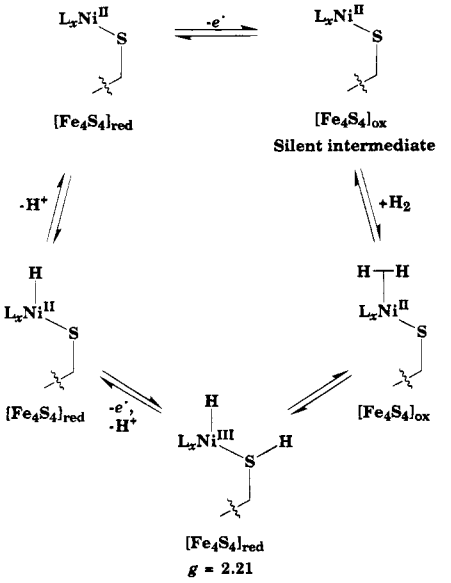


Figure 28. Proposed mechanism of H_2 oxidation by hydrogenase, involving cycling between the +3 and +2 Ni oxidation states.

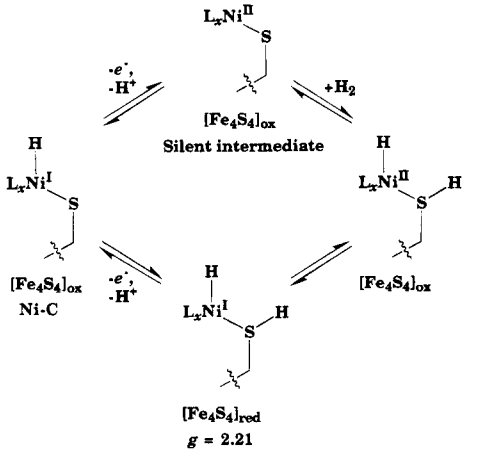


Figure 29. Proposed mechanism of H_2 oxidation by hydrogenase, involving cycling between the +2 and +1 Ni oxidation states.

Given the above conclusion, any more detailed mechanism for H_2 oxidation by H_2-ase is dependent on the uncertain assignment of Ni oxidation states in the Ni-C and Ni-R forms of the enzyme. Two plausible schemes involving heterolytic cleavage and cycling between the +2 and +3,[19,39,42,549,569] and +2 and +1,[38,544] Ni oxidation states are shown in Figures 28 and 29. These mechanisms differ only in the order of oxidation of the adjacent Ni and $[Fe_4S_4]$ centers, and in the formal description of the paramagnetic Ni

hydrido intermediate as $Ni^{III}-H^-$, or Ni^I-H^+; they also have the merit of avoiding Ni^{IV} or Ni^0 species as intermediates, which would be very difficult to generate in a cysteine-rich ligand environment.[39,44] Note that while we have shown a coordinated thiolate residue acting as a base in these figures, a proposition which is favored by several authors,[19,39,42] the nature of the participating base within the H_2-ase catalytic cycle is unclear. It has been proposed that H_2 may form an η^2-complex with the Ni center prior to the H−H cleavage step (*cf.* Figure 28);[19,541,542,599] although no evidence for such a precoordination step has been reported, any [Ni(H_2)] species formed might be expected to be short-lived. Finally, it should be stressed that these and other proposed schemes are purely speculative, and that the role of Ni in the redox cycle of the enzyme is still uncertain (section VIII.C).[582] In particular, a very recent redox titration study has suggested that Ni-R rather than Ni-C may in fact be the active proton reductant state of the enzyme (reaction 62).[571] It has been suggested that Ni in one

$$2H^+ + \text{Ni-R} + [Fe_4S_4]^+ \rightleftharpoons H_2 + \text{Ni-C} + [Fe_4S_4]^{2+} \quad (62)$$

H_2-ase may play a purely structural role, H_2 activation occurring at Fe/S clusters by an analogous mechanism to that shown by Fe-only H_2-ases.[550]

Indirect evidence for η^2-H_2 binding to Ni in H_2-ase is provided by the strong, reversible inhibition of the enzyme by CO.[600,617] The reaction of Ni-C with CO at 4 °C affords rapid conversion to a new rhombic EPR signal which shows coupling to ^{13}C in the presence of ^{13}CO and exhibits additional fast relaxing components on cooling to 4 K ($g_1 = 2.12$, $g_2 = 2.07$, $g_3 = 2.02$; $A_1\{^{13}C\} = 28.8$, $A_2 = 30.4$, $A_3 = 32$ G), together with a weak axial signal that is also split by ^{13}CO ($g_{\parallel} = 2.02$, $g_{\perp} = 2.11$).[568,577] Further incubation with CO leads to the disappearance of the rhombic signal to afford a nonoxidizable Ni^{II}−CO center (Figure 30),[575,577] but not the axial one. Importantly, flushing of the initial CO-inhibited products with H_2 rapidly regenerates Ni-C, while photolysis of CO-inhibited H_2-ase causes the quantitative conversion of the major rhombic signal to the Ni-C* spectrum, presumably by loss of CO;[577] the rate of this photolysis reaction was identical in H_2O and D_2O. These results have led to the proposition that CO inhibition of H_2-ase occurs by simple substitution of H_2 by CO at the Ni-C center.[568,577] The almost isotropic ^{13}C hyperfine coupling constants observed for the rhombic spectrum suggest that CO binds at an axial site to the $(d_{z^2})^1$ Ni ion, which is almost certainly in the +1 oxidation state; to account for the lack of an equivalent coupling to ^1H in the Ni-C spectrum, it has recently been proposed that the orbital axes about the Ni ion flip on binding of CO, so that the d_{z^2} orbital lies along the Ni−CO bond in the CO-inhibited enzyme, but perpendicular to the Ni−H bond in Ni-C (Figure 30).[601] No reaction was observed between CO and Ni-A. H_2-ases are reversibly inhibited to a lesser extent by acetylene,[617] NO, and NO_2^- [603,614] and are irreversibly deactivated by CN^-,[604] although it is unknown whether these inhibitors also bind to the Ni ion.

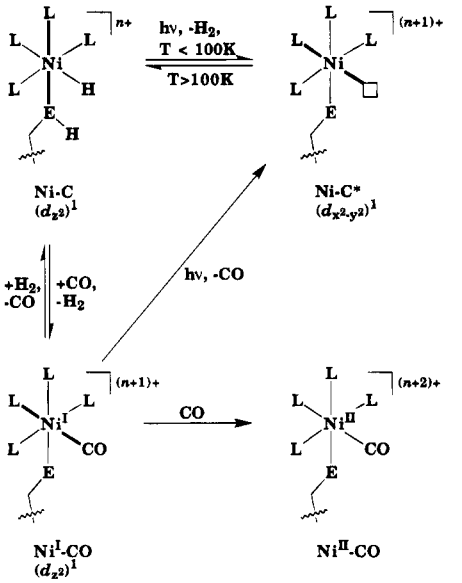


Figure 30. Changes in coordination and electronic structure at Ni proposed to occur upon inhibition of Ni−C by CO and upon generation of Ni−C* from Ni−C or the CO-inhibited Ni center (E = S, Se). The bold line corresponds to the molecular *z* axis. Ni oxidation states for Ni−C and Ni−C* are unclear. Adapted from ref 601.

E. [NiFeSe] Hydrogenase

Nickel−selenium hydrogenase is a member of the relatively small class of Se-containing enzymes.[605] Examples of [NiFeSe] H_2-ases have been isolated from several bacteria of the *Desulfovibrio* and *Methanococcus* geni,[41,606-610] the chemical data quoted here having been obtained from the soluble *D. bacalatus* enzyme unless otherwise stated. All characterized [NiFeSe] H_2-ases contain 1 mol of Se per mole of Ni,[607-610] in the form of selenocysteine,[602,606,611] together with varying numbers of $[Fe_4S_4]$ clusters.[612]

The Ni center in aerobically purified [NiFeSe] H_2-ase is generally almost EPR silent,[594,607,608] although under certain conditions EPR spectra corresponding to the Ni-A and Ni-B states are observed ($g_1 = 2.33$, $g_2 = 2.24$, $g_3 = 2.0$ and $g_1 = 2.34$, $g_2 = 2.16$, $g_3 = 2.0$).[594] No preactivation of the EPR-silent samples is required for proton reduction to take place.[608] Upon reduction with H_2,[594,612] or in anaerobically purified enzyme,[601] an EPR signal strongly reminiscent of the Ni-C state in [NiFe] H_2-ase is obtained ($g_1 = 2.23$, $g_2 = 2.17$, $g_3 = 2.01$ with associated fast-relaxing components at $g = 2.25-2.10$), which is broadened in enzyme samples obtained from bacteria grown on a ^{77}Se-enriched medium ($A_1\{^{77}Se\} = 53.2$, $A_2 = 15.5$, $A_3 = 9.6$ G)[601,613] and disappears upon further incubation with H_2.[594,608] Illumination of this Ni-C signal in the *M. voltae* [NiFeSe] H_2-ase causes its conversion to a Ni-C* state ($g_1 = 2.285$, $g_2 = 2.107$, $g_3 = 2.049$; $A_1\{^{77}Se\} = 43.3$, $A_2 = 46.7$, $A_3 = 38.1$ G).[601] Interestingly, the ^{77}Se hyperfine constants in the Ni-C* signal are almost isotropic, which contrasts with the distinctly anisotropic ^{77}Se hyperfine interactions shown by the Ni-C state. These data, together with the absence of broadening of the Ni-C spectrum after incubation of the sample with D_2O, were rationalized by the suggestion that the Ni−Se bond lies in a cis position to the hydride ligand of the Ni-C state, and that loss of H_2 from Ni-C to form Ni-C* causes a flip

in electronic axes at the Ni ion, with a concomitant change in electronic ground state from $(d_{z^2})^1$ to $(d_{x^2-y^2})^1$ (Figure 30).[601]

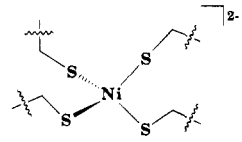
The similarity of the Ni-C EPR spectra and the midpoint reduction potential ($E_{1/2}$ = −0.32 V *vs* NHE)[594] derived from [NiFeSe] and [NiFe] H_2-ases imply a close structural homology for the Ni sites in the two classes of enzyme. In contrast to most other Ni-containing H_2-ases,[41] however, the [NiFeSe] enzymes show greater activity toward H_2 production rather than uptake *in vitro*,[595] while H^+/D_2 exchange by [NiFeSe] H_2-ase shows an initial H_2:(H_2 + HD) product ratio of 0.5−0.6[594,608] at optimal pHs (*ca.* pH 4[595]). This latter result, and the pH profile of the product ratios for the H^+/D_2 exchange reaction (reaction 54),[594,595] still favor a heterolytic H−H cleavage mechanism for [NiFeSe] H_2-ase,[625] but suggest that the (presumably Ni-containing) hydride intermediate in the catalytic cycle is significantly destabilized in the Se-containing enzyme compared to the [NiFe] protein. Such a destabilization is not reflected in the properties of the (probably hydride containing) Ni-C states in the two classes of enzyme, however. The role of the selenocysteine ligation to Ni in producing this effect is unclear, although the increased basicity of a selenolate over a thiolate donor to the Ni site might be expected to increase the hydridic character of any Ni−hydride species formed during catalysis. The [NiFeSe] H_2-ases are markedly more sensitive to inhibition by CO, NO or NO_2^- than are the [NiFe] enzymes.[614]

Ni and Se EXAFS measurements of a [NiFeSe] H_2-ase showed the presence of a Ni-coordinated selenocysteine ligand, together with one Ni−S and two or three Ni−(N/O) vectors at Ni−Se = 2.44 Å, Ni−S = 2.17 Å, and Ni−(N/O) = 2.06 Å (**57**);[602] the amino acid sequence of this enzyme shows the selenocysteine residue to lie near the C-terminus of the peptide chain, in a position occupied by a strongly conserved cysteine residue in other [NiFe] H_2-ases (section VIII.C).[615] The Ni K-edges shown by the [NiFeSe] enzyme and the *D. gigas* and *T. roseopersicina* [NiFe] H_2-ases show broadly similar features, the small differences observed being taken to indicate a difference in ligation or symmetry between the two sites rather than a major stereochemical change.[602] Importantly, saturation magnetization measurements of as-isolated, non-EPR-active [NiFeSe] H_2-ase showed the Ni^{II} center to be diamagnetic, which in combination with the above EXAFS results argues strongly for five coordination at the Ni^{II} ion in this state.[616] Given the similarity in redox and EPR behavior between this enzyme and the non-Se-containing [NiFe] H_2-ases, this result can probably be generalized to other Ni-containing H_2-ases.

IX. Structural and Functional Models for Nickel Hydrogenases

A. Nickel-Substituted Proteins as Models for Hydrogenase

Incubation of $NiCl_2$ with aporubredoxin (Rd) from *P. furiosus*, *C. pasteurianum*, or *D. vulgaris* affords a Ni-substituted protein, containing 0.95 ± 0.2 Ni/molecule. UV/visible, MCD, ^1H NMR, resonance Raman, and Ni L-edge XANES studies indicate that the Ni centers in Ni−Rd retain the distorted tetrahedral $[Ni(cys)_4]^{2-}$ coordination sphere observed for the native Fe proteins (**63**) although EXAFS or crystallographic data on Ni−Rd is yet to be published.[618−623] Treatment of Ni−Rd with ferricyanide



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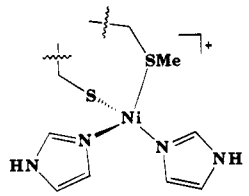
affords oxidized species whose EPR spectrum (g_1 = 2.29, g_2 = 2.11, g_3 = 2.04) is very similar to both the Ni-A/B and Ni-C* signals obtained from H_2-ase and is consistent with a Ni^{III} center in a highly distorted environment.[619,621] Importantly, this supports the assignment of the Ni^{III} oxidation state to the Ni-C* photolysis product and hence favors the formulation of Ni-C as a Ni^{III} hydride. Oxidation of Ni−Rd in the presence of CN^- affords a new EPR signal ($g_\perp$ = 2.16, $g_\parallel$ = 2.02; $A_\perp\{^{61}Ni\} \approx 2$, $A_\parallel$ = 22 G; $A_\perp\{^{13}C\} \approx A_\parallel \approx 4$ G) that is reminiscent of the Ni-C H_2-ase signal and was taken to support the hypothesis that CN^- inhibition of H_2-ase involves CN^- coordination at the H^- binding site of the enzyme, which lies at an equatorial coordination site of a $(d_{z^2})^1$ Ni ion.[621] Interestingly, the cysteinyl residues known to coordinate Fe^{2+} in native Rd are also present and strongly conserved in H_2-ase, implying that all four of these residues may be involved in Ni-binding.[619,621] The Ni L-edge XAS spectrum of Ni-Rd shows several changes upon partial ferricyanide oxidation, although these were not analyzed in detail.[623] EPR spectra comparable to those of oxidized Ni−Rd were observed on Ir^{IV} oxidation of several Ni^{II} complexes of monosulfhydryl (g_1 = 2.27, g_2 = 2.20, g_3 = 2.02) and disulfhydryl ($g_\perp$ = 2.163, $g_\parallel$ = 2.015) peptides, which were assumed to adopt tetragonal stereochemistries with $[N_3S]$ and $[S_4]$ donor sets, respectively.[624]

Remarkably, the *D. gigas* Ni−Rd catalyzes the H^+/D_2 exchange and proton reduction reactions (reactions 53 and 54), albeit at much lower rates than H_2-ase, this activity being efficiently inhibited by CO.[625] The initial H_2:(H_2 + HD) ratio of 0.45−0.60 determined for Ni−Rd-catalyzed H^+/D_2 exchange is of the same order as that observed for [NiFeSe] H_2-ase,[594] and implies similar heterolytic H−H cleavage steps for these reactions.

In contrast to the above results, similar studies for Ni-substituted *D. gigas* desulferodoxin were consistent with a square-pyramidal $[Ni(cys)_4L]^{2-}$ coordination sphere with basal thiolate donors (**56**; L = OH_2, histidine residue, n = 2; L = carboxylate donor, n = 3);[620,622] this Ni protein catalyzes H^+/D_2 exchange (reaction 56) at rates similar to Ni−Rd, but does not reduce protons.[625] In addition, horse liver alcohol dehydrogenase (LADH) substituted with Ni^{2+} at the noncatalytic metal site is diamagnetic; MCD data imply that the Ni^{2+} ion here may adopt a square-planar $[Ni(cys)_4]^{2-}$ geometry (**56**, L = vacant coordination site, n = 2), in contrast to the tetrahedral $[Zn(cys)_4]^{2-}$ center observed in the native enzyme.[626] Detailed structural or redox studies for these two

intriguing enzymes have yet to be reported, however. Proteinaceous $[Ni(cys)_4]^{2-}$ sites have also been obtained by substitution of Ni^{2+} into metallothionein[627] and aspartate transcarbamoylase.[628]

Nickel has also been employed as a structural probe in several mixed histidine/cysteine protein metal sites. Ni azurin has been particularly well studied, and is believed to contain a $[Ni(his)_2(cys)(met)]^+$ center in a relatively undistorted (compared to the native Cu^{2+} site) tetrahedral geometry (**64**).[629-633] Ni stellacyanin has also been synthesized,[634,635] while similar tetrahedral ligand environments have been obtained by substitution of Ni^{2+} into the catalytic site of horse LADH and other alcohol dehydrogenases ($[Ni(his)(cys)_2(OH_2)]$ centers)[101,636-639] and a zinc finger protein ($[Ni(his)_x(cys)_{4-x}]$, $x = 2$, 3).[640] Again, however, no structural or redox data relating these Ni protein environments to that in H_2-ase have been described.



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B. Nickel Complexes Containing Thiolate and Thioether Donor Ligands Only

The early EXAFS results for hydrogenase[578,579] and CODH,[443] which suggested a tetragonal $[Ni(SR)_4]^{2-}$ geometry about the Ni center in these enzymes, sparked a renewed interest in nickel thiolate chemistry. The aim of these studies, to synthesize a discrete mononuclear $[Ni(SR)_4]^{2-}$ complex capable of reversibly generating an oxidized $[Ni^{III}(SR)_4]^-$ species, was nontrivial for two reasons. First, thiolate complexes in general, and Ni thiolates in particular, show a marked tendancy to aggregate to polynuclear species *via* thiolate bridge formation, with complex ligand dissociation/aggregation equilibria often being observed in solution (*vide infra*). Second, Ni-coordinated thiolate ligands often oxidize irreversibly under electrochemical or chemical conditions to form disulfide[642-645] or sulfoxo[646-648] products. Taken together, these factors strongly mitigate against the observation of reversible metal-centered redox behavior for Ni thiolates.

Two general classes of mononuclear $[Ni(SR)_4]^{2-}$ complexes are known.[641,649,650] Complexes containing monodentate thiolates (R = Ph, *p*-Tol, *m*-Tol, *p*-Cl-C_6H_4, *m*-Cl-C_6H_4, *p*-NO_2-C_6H_4, Bu^t),[649,650,652-657] together with $[Ni(NMTP)_4]^{2+}$ (NMTP = *N*-methyl-2-thioxopyrrolidine),[658] adopt flattened tetrahedral geometries in the solid state, typically with Ni–S bonds of 2.26–2.33 Å and S–Ni–S angles in the range 88–125° (Table V; Figure 31). These distortions from local T_d symmetry appear to be maintained in solution[622] and have been ascribed to both steric[656,659] and electronic[658] effects. The dinuclear complex $[Ni_2(SR)_2(\mu\text{-}SR)_3]^-$ (R = 2,4,5-Pr$^i_3$$C_6H_2$) containing two tetrahedral Ni^{II} centers has recently been

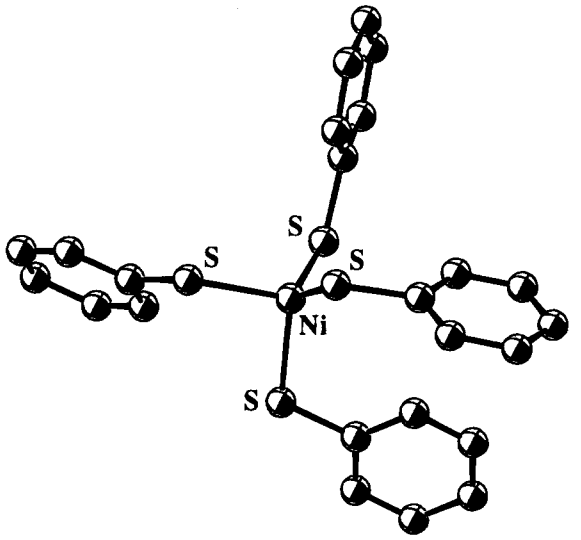


Figure 31. Structure of $[Ni(SPh)_4]^{2-}$. Atomic coordinates were taken from ref 657.

structurally characterized, and exhibits similar distortions.[660] Tetrahedral $[Ni(SR)_4]^{2-}$ complexes exhibit complex, irreversible electrochemical oxidations, reflecting partial dissociation (reaction 65) and/or

$$[Ni(SR)_4]^{2-} \rightleftharpoons [Ni(SR)_3(solv)]^- + RS^- \quad (65)$$

ligand oxidation in solution or at the electrode;[653,654] a DPV study in DMSO yielded anodic peak potentials of $Ep_a = -0.1$ to -0.6 V *vs* SCE for a series of these compounds, and allowed an estimation of the oxidation potential for the (hypothetical) tetrahedral species $[Ni(cys)_4]^{2-}$ of $Ep_a = -0.5$ to -0.6 V.[654] The NMR spectra, electronic spectra, and solution effective magnetic moments of $[Ni(SR)_4]^{2-}$ (R = aryl, ^{t}Bu) are temperature and concentration dependent,[655,656] which also presumably reflects these dissociation/aggregation equilibria.[655]

In contrast, mononuclear $[Ni(SS)]^{2-}$ complexes of chelating thiolates (SS^{2-} = ethane-1,2-dithiolate {edt^{2-}}, butane-2,3-dithiolate {bdt^{2-}}, *cis*-norbornane-2,3-dithiolate {ndt^{2-}}, *trans*-cyclohexane-1,2-dithiolate {cdt}$^{2-}$}),[649,650,661-664] as well as $[Ni(SC_6F_5)_4]^{2-}$,[649] $[Ni(S_4)_2]^{2-}$,[665,666] $[Ni(CS_4)_2]^{2-}$,[666] and $[Ni(MImt)_4]^{2+}$ (MImt = *N*-methylimidazoline-2(3*H*)-thione),[667,668] are diamagnetic and show square planar geometries by X-ray crystallography and EXAFS,[661,664] with Ni–S relatively invariant at 2.18–2.20 Å (Table 5; Figures 32 and 33). The nuclearities of these, and analogous complexes of simple alkyl thiolates, are highly dependent on the solvent, the identity of the thiolate ligand, and metal:ligand ratios employed in their syntheses;[649] linear $[Ni_x(SR)_{2x+2}]^{2-}$ ($x = 2$; RS^- = EtS^-, *p*-Cl-$C_6H_4S^-$, $^1/_2${edt^{2-}}, $^1/_2${1,3-pdt^{2-}}; $x = 3$, RS^- = EtS^-, $^1/_2${edt^{2-}}, $^1/_2${xdt^{2-}}, $^1/_2${1,2-pdt^{2-}}; $x = 6$, RS^- = $^1/_2${1,3-pdt^{2-}}; 1,2-pdtH_2 = propane-1,2-dithiol; 1,3-pdtH_2 = propane-1,3-dithiol; xdtH_2 = *o*-xylene-α,α′-dithiol; Figure 32)[649-651,669-675] and toroidal $[Ni_x(\mu\text{-}SR)_{2x}]$ ($x = 4$, R = Et, Pr^i, cyclohexyl, C_5H_9NMe; $x = 5$, R = Et; $x = 6$, R = Me, Et, C_2H_4-OH, $C_3H_6NHMe_2^+$; $x = 8$, R = $C_2H_4CO_2Et$)[649-651,676,677] species containing square-planar Ni^{II} centers linked by two thiolate bridges have been structurally characterized. A related cyclic structure containing singly

Table 5. Structural Data for Selected Nickel Complexes Containing Thiolate and Thioether Donors Only[c]

complexes[b]	coordination geometry[a]	d(Ni···S{thiolate}), Å	d(Ni···S{thioether}), Å	ref
		Ni^{II}		
$[Ni(SPh)_4]^{2-}$	Tet	2.272(4), 2.287(4), 2.289(5), 2.303(4)	–	652
	Tet	2.279(2), 2.287(3), 2.296(3), 2.306(3)	–	653
	Tet	2.258(2), 2.293(2), 2.302(2), 2.331(2)	–	657
$[Ni(S\text{-}4\text{-}Cl\text{-}C_6H_4)_4]^{2-}$	Tet	2.269(1), 2.279(1), 2.281(1), 2.293(1)	–	656
$[Ni(NMTP)_4]^{2+}$	Tet	2.282(2), 2.286(2), 2.286(3), 2.294(2)	–	658
$[Ni(bzdt)_2]^{2-}$	SqPl	2.168(4), 2.172(4), 2.174(4), 2.181(4)	–	383
$[Ni(edt)_2]^{2-}$	SqPl	2.191(1), 2.198(1)	–	661
	SqPl	2.188(1), 2.201(1)	–	662
$[Ni(ndt)_2]^{2-}$	SqPl	2.182(2), 2.186(2)	–	663
$[Ni(cdt)_2]^{2-}$	SqPl	2.187(3), 2.196(3)	–	664
$[Ni(S_4)_2]^{2-}$	SqPl	2.185(2)	–	665
	SqPl	2.146(7), 2.179(3)	–	666
$[Ni(CS_4)_2]^{2-}$	SqPl	2.165(2), 2.174(2)	–	666
$[Ni(MImt)_4]^{2+}$	SqPl	2.207(2), 2.212(2), 2.215(2), 2.217(2)	–	667
	SqPl	2.199(2), 2.232(1)	–	668
[Ni(ttu)]	SqPl	2.177(2), 2.179(2)	2.166(2), 2.173(1)	696
$[Ni(tbmpte)]_3$	SqPl	2.137(3), 2.161(3), 2.167(3)	2.134(5), 2.153(3), 2.178(3)	699
[Ni(tpttd)]	SqPl	2.199(3), 2.207(3)	2.156(3), 2.159(3)	522
$[Ni(Mebzdt)_2]$	SqPl	2.169(2)	2.169(2)	533
[Ni(bmptp)]	SqPl	2.166(2), 2.175(2)	2.162(2), 2.175(2)	697
[Ni(bmpee)]	SqPl	2.184(1), 2.187(1)	2.164(1), 2.173(1)	697
$[Ni(bmpte)]_2$	SqPl	2.178(3), 2.180(3)	2.178(3), 2.178(3)	697
$[Ni(bmptt)]_2$	SqPl	2.177(2), 2.182(2)	2.165(2), 2.177(2)	697
$[Ni([14]aneS_4)]^{2+}$	SqPl	–	2.175(1), 2.177(1)	707
$[Ni(Me_2[14]aneS_4)]^{2+}$	SqPl	–	2.172(4), 2.179(4), 2.179(4), 2.182(4)	708
$[Ni(Me_4[14]aneS_4)]^{2+}$	SqPl	–	2.176(2), 2.184(2)	708
[Ni(mptds)]	SqPy	2.176(3), 2.197(4)	2.204(3), 2.223(3), 2.741(3)	697
	SqPy	2.176(2), 2.201(2)	2.204(2), 2.219(2), 2.747(2)	698
$[Ni([15]aneS_5)]^{2+}$	SqPy	–	2.146(7), 2.169(6), 2.177(6), 2.198(6), 2.413(6)	694
$[Ni(metme)]^{2+}$	Oct	–	2.397(2)–2.436(2)	693
$[Ni(keto\text{-}[10]aneS_3]_2)^{2+}$	Oct	–	2.381(3), 2.422(3), 2.424(3)	702
$[Ni(bzo_2\text{-}[18]aneS_6)]^{2+}$	Oct	–	2.375(2), 2.391(2), 2.401(2)	704
$[Ni(bzo\text{-}[11]aneS_3)_2]^{2+}$	Oct	–	2.387(2), 2.434(2), 2.452(2)	705
$[Ni([10]aneS_3)_2]^{2+}$	Oct	–	2.386(2), 2.396(2), 2.403(2)	710
$[Ni([9]aneS_3)_2]^{2+}$	Oct	–	2.377(1), 2.380(1), 2.400(1)	712
$[Ni([12]aneS_3)_2]^{2+}$	Oct	–	2.409(1), 2.421(2), 2.435(1)	713
$[Ni([18]aneS_6)]^{2+}$	Oct	–	2.377(1), 2.389(1), 2.397(1)	713
$[Ni([24]aneS_6)]^{2+}$	Oct	–	2.413(1), 2.437(1), 2.443(1)	713
		Ni^{III}		
$[Ni([9]aneS_3)_2]^{3+}$	Oct	–	2.313(3)	711

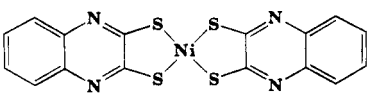
[a] Tet = tetrahedral; SqPl = square planar; SqPy = square pyramidal; Oct = octahedral. [b] $bmpeeH_2$ = 1,2-bis[[2-[(2-mercaptophenyl)thio]ethyl]thio]ethane; $bmpteH_2$ = bis[2-[(2-mercaptophenyl)thio]ethyl]ether; $bmptpH_2$ = 1,3-bis[(2-mercaptophenyl)thio]propane; $bmpttH_2$ = 1,5-bis[(2-mercaptophenyl)thio]pentane; $bzdtH_2$ = benzene-1,2-dithiol; bzo-[11]$aneS_3$ = 2,5,8-trithia[9]-*o*-benzophane; bzo_2-[18]$aneS_6$ = 2,3,11,12-dibenzo-1,4,7,10,13,16-hexathiacyclooctadeca-2,11-diene; $cdtH_2$ = 1,2-*trans*-cyclohexanedithiol; $edtH_2$ = ethane-1,2-dithiol; keto-[10]$aneS_3$ = 1,4,7-trithiacyclodecan-9-one; MebzdtH = 2-(methylthio)thiophenol; metme = 1,1,1-tris-[[[(2-(methylthio)ethyl]thio]methyl]ethane; Me_2[14]$aneS_4$ = 6,6-dimethyl-1,4,8,11-tetrathiacyclotetradecane; Me_4[14]$aneS_4$ = 6,6,13,13-tetramethyl-1,4,8,11-tetrathiacyclotetradecane; MImt = 1-methylimidazoline-2(3*H*)-thione; $mptdsH_2$ = bis[2-[(2-mercaptophenyl)thio]ethyl]sulfide; NMTP = *N*-methyl-2-thioxopyrrolidine; $ndtH_2$ = norbornane-2,3-*exo*-*cis*-dithiol; $tbmpteH_2$ = 1,2-bis[3,5-di-*tert*-butyl-2-mercaptophenyl)thio]ethane; $tpttdH_2$ = 3,3,10,10-tetraphenyl-1,5,8,12-tetrathiadodecane; $ttuH_2$ = 1,4,8,11-tetrathiaundecane; [9]$aneS_3$ = 1,4,7-trithiacyclononane; [10]$aneS_3$ = 1,4,7-trithiacyclodecane; [12]$aneS_3$ = 1,5,9-trithiacyclododecane; [14]$aneS_4$ = 1,4,8,11-tetrathiacyclotetradecane; [15]$aneS_5$ = 1,4,7,10,13-pentathiacyclopentadecane; [18]$aneS_6$ = 1,4,7,10,13,16-hexathiacyclooctadecane; [24]$aneS_6$ = 1,5,9,13,17,21-hexathiacyclotetracosane. [c] Complexes of noninnocent unsaturated dithiolate ligands have not been included.

thiolate-bridged Ni ions is shown by $[Ni(mpg)]_3$ ($mpgH_2$ = 2-mercaptopropionylglycine).[678] In the toroidal complexes, the Ni atoms protrude from their S_4 square plane by 0.1–0.3 Å; a theoretical study has attributed this deviation to repulsive Ni···Ni interactions.[679] The Ni···Ni distance in $[\{L_2Ni\}_2(\mu\text{-}SR)_2]^{n-}$ structures depends markedly on the dihedral angle between $NiL_2(\mu\text{-}S)_2$ square planes, examples with $2.64 \leq d(Ni\cdots Ni) \leq 3.36$ Å having been reported (Table 4).[672] Choudhury and Chakravorty have demonstrated a linear relationship (equation 66) for

$$d(Ni\cdots Ni) = 2[d(Ni\cdots\mu\text{-}S)]\cos(\theta/2)\sin(\alpha/2) \quad (66)$$

doubly thiolate-bridged dimers of square planar Ni^{II} ions (θ = {μ-S}–Ni–{μ-S} angle; α = dihedral angle between the NiL_4 square planes).[673]

To date, four square-planar Ni^{II} tetrathiolates have been shown to form observable oxidized $[Ni^{III}(SR)_4]^-$ species: $[Ni(ndt)_2]^{2-}$ (Figure 33),[663] $[Ni(bdt)_2]^{2-}$,[662] $[Ni(cdt)_2]^{2-}$,[664] and $[Ni(qdt)_2]^{2-}$ ($qdtH_2$ = quinoxalinedithiol, **67**).[680,681] The $Ni^{II/III}$ oxidation half-potentials in DMF solution for all these complexes except the latter lie within the range –0.69 to –0.76 V *vs*



67

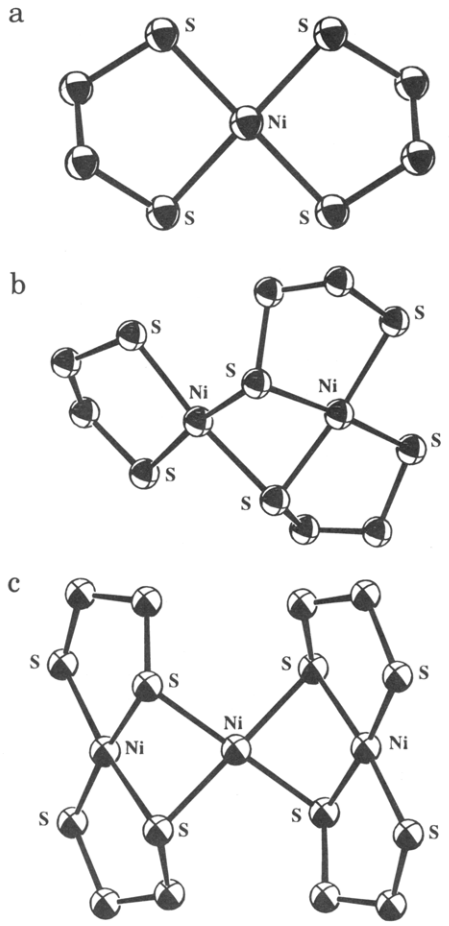


Figure 32. Structures of (a) $[Ni(edt)_2]^{2-}$, (b) $[Ni_2(edt)_3]^{2-}$, and (c) $[Ni_3(edt)_4]^{2-}$ ($edtH_2$ = ethane-1,2-dithiol). Atomic coordinates were taken from refs 662 and 669.

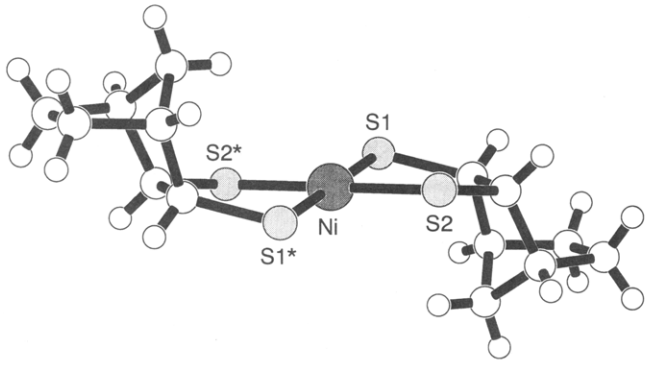


Figure 33. Structure of $[Ni(ndt)_2]^{2-}$ ($ndtH_2$ = *cis*-norbornane-2,3-dithiol). (Reprinted from ref 663. Copyright 1990 American Chemical Society.)

SCE. While no oxidized species has been structurally characterized, EPR data in frozen DMF solutions show the $g_{\|} > g_{\perp}$ pattern consistent with the retention of their square-planar geometries (for $[Ni(ndt)_2]^-$ $g_{\|} = 2.14, g_{\perp} = 2.05$; for $[Ni(bdt)_2]^-$ $g_{\|} = 2.19, g_{\perp} = 2.04$; for $[Ni(qdt)_2]^-$ $g_1 = 2.30$, $g_2 = 2.05$, $g_3 = 2.03$). Consistent with these spectra, a Fenske–Hall calculation on $[Ni(ndt)_2]^-$ implied a $(d_{xy})^1$ π^* ground state for this complex.[717] This contrasts with the rhombic $g_{\perp} > g_{\|}$ pattern shown by the H_2-ase Ni-A and Ni-B signals, and appears to rule out a square-planar $[Ni(cys)_4]^{2-}$ geometry for the active site of this enzyme.

A large number of square-planar $[Ni^{II}(SS)_2]^{n-}$ (n = 0, 2) complexes containing unsaturated 1,1-, 1,2-, and 1,3-dithiolate ligands are known:[682] examples include, but are not limited to, SS = S_2CE^- (E = CR_3, NR_2, OR), $S_2PE_2^-$ (E = R, OR), 1,3-dithioketonates, MS_4^{2-} (M = Mo, W), and a variety of 1,1- and 1,2-dithiolenes. These are of limited value as models for Ni biosites, owing to their short Ni–S bonds (*ca.* 2.20 Å) and because they generally exhibit complex redox behavior which can (for dithiocarbamate[683] and xanthate[684] ligands) involve ligand association or dissociation equilibria, and often afford redox products that show extensive ligand radical character. It is noteworthy that such "ligand"- and metal-centered redox activity in Ni dithiolenes cannot be readily distinguished by EPR spectroscopy in the absence of ^{61}Ni- or ^{33}S-enrichment studies,[685,686] since Ni^{II}-stabilized dithiolene ligand radicals exhibit anisotropic g shifts similar to those observed for the Ni^{III} tetrathiolates discussed in the previous paragraph (*e.g.* for $[Ni(mnt)_2]^-$ $g_1 = 2.160$, $g_2 = 2.042$ and $g_3 = 1.998$; $mntH_2$ = 1,2-dimercaptomaleonitrile).[686] There is a voluminous literature concerned with the structural, electronic, redox, and solid state properties of Ni complexes of these and other unsaturated S-donor ligands, and the reader is directed to refs 641, 682–684, and 687–690 for more complete discussions.

Thioethers are relatively poor ligands for Ni^{II}, and with the exception of macrocyclic complexes (*vide infra*) few homoleptic Ni thioether species are known.[691] Thioethers are rather weak field ligands, so that thioether complexes of Ni^{II} salts generally exhibit high-spin octahedral structures with coordinated halide or solvent.[691–694,823] In contrast, linear-chain ligands containing both thiolate and thioether donors afford low-spin Ni^{II} complexes. The dimeric species $[Ni(SC_2H_4SC_2H_4S)]_2$[695] has been structurally characterized as containing square-planar Ni^{2+} ions doubly bridged by thiolate donors, while both mononuclear $[Ni(ttu)]$[696] and $[Ni(tpttd)]$[522] (**48**) and trinuclear $[Ni_3(ttu)_2]^{2+}$ [691] ($ttuH_2$ = 1,4,8,11-tetrathiaundecane) complexes have been isolated. In particular, [Ni(tpttd)] is the only homoleptic Ni/S complex to show a chemically reversible reduction process by cyclic voltammetry, at $E_{1/2} = -1.34$ V *vs* Ag/AgCl, although the reduction product $[Ni(tpttd)]^-$ is not stable in chemically reduced solutions. The observed Ni–S(thiolate) and Ni–S(thioether) distances are indistinguishable in all the above complexes, although the latter may be artificially shortened by ring strain within the chelate backbone (see for example ref 693). A structural study of Ni^{II} complexes with ligands of type **22** (x = 1, 2) showed that square-planar complexes were observed for all bridge lengths;[697,698] the complex with $mptds^{2-}$ (**22**, x = 1), as well as some trimethylphosphine adducts of similar tetrathia ligands (**22**, x = 0 and alkylated derivatives), show quasi-square-pyramidal geometries with long apical Ni–S interactions of 2.61–2.75 Å.[383,697–699] These complexes only exhibit irreversible redox processes by cyclic voltammetry, electrochemical reduction resulting in radical-induced C–S(thioether) bond cleavage (section V.B).[383,384,698] The square-planar complex $[Ni(\{PhS\}_2BH_2)_2]$ has been synthesized.[700]

Several Ni^{II} complexes of tri-, tetra-, penta- and hexadentate homoleptic thioether macrocycles have

Table 6. Redox Behavior of Selected Ni-S- and Mixed −N/S-Donor Complexes Affording Observable Redox Products[s]

complexes[r]	coordination geometry and donor set[a]	$E_{1/2}$(V)[b] *vs* SCE	g_1	A_1, G[c]	g_2 $g_{\parallel}$	A_2, G[c] $A_{\parallel}$, G[c]	g_3 $g_{\perp}$	A_3, G[c] $A_{\perp}$, G[c]	ref
			$Ni^{II/III}$ Oxidations						
$[Ni(ndt)_2]^-$	SqPl S_4	−0.76[d]			2.14	–	2.05	–	663
$[Ni(bdt)_2]^-$	SqPl S_4	−0.75[d]			2.187	–	2.042	–	662
D. gigas H_2-ase Ni-C	6? $S_2(N/O)_3$(H?)	−0.60[e,f]	2.02	27[g]	2.14	2−6[g]	2.19	2−6[g]	544, 558, 561
D. gigas H_2-ase Ni-C*	5? $S_2(N/O)_3$	–[e]	2.04	–	2.14	–	2.3	–	544
C. vinosum CO-H_2-ase	6? $S_2(N/O)_3C$	–[e]	2.02	32[h]	2.07	30.4[h]	2.12	28.8[h]	568
M. voltae H_2-ase Ni-C	6? $SeS(N/O)_3$(H?)	−0.56[e,f,i]	2.009	53.2[j]	2.150	15.5[j]	2.209	9.6[j]	601
M. voltae H_2-ase Ni-C*	5? $SeS(N/O)_3$	–[e]	2.049	43.3[j]	2.107	46.7[j]	2.285	38.1[j]	601
$[Ni(emi)]^-$	5−6? $S_2N_2(X)_{1-2}$	−0.42[d]	1.96	–	2.27	–	2.44	–	717
$[Ni(emi)(py)]^-$	SqPy S_2N_3	–			2.00	23	2.30	–	717
$[Ni(emi)(CN)]^{2-}$	SqPy S_2N_2C	–	2.02	–	2.17	–	2.21	–	717
D. gigas H_2-ase Ni-B	5? $S_2(N/O)_3$?	−0.39[e]	2.02	–	2.16	13.9[k]	2.33	9.5[k]	547, 562
D. gigas H_2-ase Ni-A	5? $S_2(N/O)_3$?	−0.39[e]	2.02	27[g]	2.23	15[g]	2.31	7.5[g]	547, 558, 560
$[Ni(ema)]^-$	5−6? $S_2N_2(X)_{1-2}$	−0.34[d]	2.01	–	2.18	–	2.23	–	717
$[Ni(phma)]^-$	5−6? $S_2N_2(X)_{1-2}$	−0.24[d]	2.01	–	2.17	–	2.20	–	717
$[Ni(pdtc)_2]^-$	Oct S_4N_2	−0.09[d]			2.038[l]	21.1	2.137	16.2	798
$[Ni(emb)]^-$	5−6? $S_2N_2(X)_{1-2}$	−0.04[d]	2.04	–	2.11	–	2.29	–	724, 797
$[Ni(emb)(py)]^-$	SqPy S_2N_3	–	2.01	21.0	2.27	–	2.34	–	797
$[Ni(memta)]_2^+$	SqPl S_3N	+0.05[m]	2.17	–	2.11	–	2.07	–	643
$[Ni(SPh)_2(DAPA)]^+$	5−6 $S_2N_3(X?)$	–[n]			2.032	14.5	2.214	–	531
$[Ni(SPh)_2(DAPA)(CN)]$	Oct S_2N_3C	–	2.043	–	2.206	–	2.263	–	531
$[Ni(S\text{-}2,6\text{-}Me_2\text{-}C_6H_3)_2(terpy)]^+$	Oct? $S_2N_3(X)$?	–[n]			2.049	16.5	2.243	–	531
$[Ni(qdt)_2]^-$	SqPl S_4	+0.12[d]	2.299	–	2.054	–	2.036	–	680
$[Ni(qdtH_2)_2]^{3+}$	SqPl S_4	+0.32[d]	2.295	–	2.050	–	2.031	–	680
$[Ni(dadtdo)]^{3+}$	Oct S_2N_4	+0.33[e]			2.046	–	2.112	–	758
$[Ni(dadtpo)]^{3+}$	Oct S_2N_4	+0.37[e]	2.039	–	2.112	–	2.168	–	758
$[Ni(MC1)(S_2CNEt_2)]^{2+}$	SqPy S_2N_3	+0.46			2.03	19.2	2.20	–	810
P. furiosus Ni-Rd	Tet S_4	–[e,n]	2.04	–	2.11	–	2.29	–	619, 621
P. furiosus Ni-Rd-CN	6? $S_4C(X?)$	–			2.02	20,[g] 4[h]	2.16	2,[g] 4[h]	621
$[Ni(bhpte)]^{3+}$	Oct $S_2N_2O_2$	+0.71[m]			2.183	–	2.063	–	759
$[Ni(bbmtp)]^+$	Oct $S_2N_2O_2$	+0.74[m]	2.038	–	2.145	–	2.195	–	756
$[Ni(bc\text{-}[19]aneSN_4)(OH_2)]^{3+}$	Oct SN_5O	+0.76			2.025	–	2.169	–	783
$[Ni(bc\text{-}[19]aneSN_4)(F)]^{2+}$	Oct SN_5F	–			2.028	210[p]	2.163	48[p]	783
$[Ni(Prtto)_2]^+$	Oct $S_2N_2O_2$	+0.76[m]	2.221	–	2.083	–	2.078	–	757
$[Ni(Cl\text{-}bhptp)]^{3+}$	Oct $S_2N_2O_2$	+0.82[m]			2.180	–	2.064	–	759
$[Ni(DACO\text{-}DTP)]^+$	Oct $S_2N_2O_2$	+0.97	2.026	–	2.170	–	2.190	–	795
$[Ni([10]aneSN_2)_2]^{3+}$	Oct S_2N_4	+0.97[e]			2.046	–	2.236	–	789
$[Ni([9]aneSN_2)_2]^{3+}$	Oct S_2N_4	+1.19			2.02	–	2.11	–	807
$[Ni([10]aneS_2N)_2]^{3+}$	Oct S_4N_2	+1.26			2.127	–	2.061	–	788
$[Ni([9]aneS_2N)_2]^{3+}$	Oct S_4N_2	+1.28			2.019	20	2.121	–	784
$[Ni(bis\text{-}[10]aneS_2N)]^{3+}$	Oct S_4N_2	+1.30			2.148	–	2.063	–	788
$[Ni([10]aneS_3)_2]^{3+}$	Oct S_6	+1.30	2.091	–	2.041	–	2.022	–	710
$[Ni([18]aneS_4N_2)]^{3+}$	Oct S_4N_2	+1.38	2.027	–	2.104	–	2.129	–	779
$[Ni([9]aneS_3)_2]^{3+}$	Oct S_6	+1.38	2.027	7[g]	2.075	–	2.093	28[g]	711
			2.016	–	2.054	–	2.076	–	710
			$Ni^{II/I}$ Reductions						
$[Ni(N\{C_2H_4SPr^i\}_3)(CO)]^+$	TBP S_3NC	–			2.008	9.9	2.119	–	524
[Ni(tmtss)(CO)]	SqPl SNOC	–			2.29	–	2.05	–	523
$[Ni(TPyO)_2]^-$	SqPl S_2O_2	–	2.257	61[g]	2.086	15[g]	2.066	15.8[g]	811
[Ni(STPP)]	SqPl SN_3	−0.23	2.109	6.4[g,o]	2.039	30.7[g,o]	2.031	3.0[g,o]	340, 342

[Ni(STPP)(1,2-Me_2Im)]	SqPy SN_4	–	2.417	7.8[g,o]	2.246	4.8[g,o]	2.142	16.0[g,o]	342
[Ni(STPP)(1,2-Me_2Im)$_2$]	Oct SN_5	–	2.238	–	2.198	–	2.136	–	340
[Ni(Me_2BME-DACO)]$^+$	SqPl S_2N_2	−0.48			2.24	–	2.066	–	796
[Ni(OCBME-DACO)]$^+$	SqPy? S_2N_2(O?)	−0.66			2.24	–	2.06	–	794
[Ni(CyBME-DACO)]$^+$	SqPl S_2N_2	−0.73			2.20	–	2.06	–	794
C. thermoacetium CODH [A-CO]$_{red}$	6? $S_2(N/O)_3C$?	−0.78[e]			2.03	10.5,[g] 27[h]	2.08	24.3,[g] 27[h]	426, 441, 452
		–	2.03	–	2.05	–	2.06	–	439
[Ni($tssH_2$)$_2$]$^+$	SqPl S_2N_2	−1.05[d]	2.25	–	2.12	–	2.06	–	870
[Ni(pdmt)]$_2^-$	SqPl S_3N	−1.21[d]			2.196	–	2.058	–	642
[Ni(MeBME-DACO)]	SqPl S_2N_2	−1.23			2.25	–	2.071	–	796
[Ni(S-2,4,6-Pr^i_3-C_6H_2)$_2$(terpy)]$^-$	5 S_2N_3	−[q]			2.247	–	2.123	–	529, 530
[Ni(S-2,4,6-Pr^i_3-C_6H_2)$_2$(terpy)(CO)]$^-$	Oct S_2N_3C	–	2.247	–	2.128	–	2.025	13	529, 530
[Ni(S-2,4,6-Pr^i_3-C_6H_2)$_2$(terpy)(H)]$^{2-}$	Oct S_2N_3H	–	2.238	–	2.191	–	2.045	–	529, 530
[Ni(S-2,4,6-Pr^i_3-C_6H_2)$_2$(terpy)(CH_3)]$^{2-}$	Oct S_2N_3C	–	2.240	–	2.192	–	2.047	–	530
[Ni($SPh)_2$(DAPA)]$^-$	5 S_2N_3	−[q]	2.263	–	2.138	–	2.095	–	531
[Ni($SPh)_2$DAPA)(CO)]$^-$	Oct S_2N_3C	–	2.198	–	2.145	–	2.023	–	531
[Ni($SPh)_2$(DAPA)(CN)]$^{2-}$	Oct S_2N_3C	–	2.235	–	2.164	–	2.013	–	531

[a] Tet = tetrahedral; SqPl = square planar; SqPy = square pyramidal; TBP = trigonal bipyramidal; Oct = octahedral; 5 = 5-coordinate; 6 = 6-coordinate. [b] Potentials quoted from MeCN unless otherwise stated. Where necessary, potential conversions have been made according to the reference standard couples reported by the original authors, or by employing the standard potentials $E_{1/2}(Fc/Fc^+) = +0.40V$ *vs* SCE; $E_{1/2}(Ag/AgCl) = -0.02V$ *vs* SCE; $E_{1/2}(Ag/Ag^+) = +0.24V$ *vs* SCE; $E^0(NHE) = -0.24V$ *vs* SCE. [c] Hyperfine coupling to ^{14}N, unless otherwise stated. [d] In DMF. [e] In H_2O. [f] The electrochemical reductions generating the Ni−C state are not simple $n = 1$ processes. The oxidation state of the Ni center in the Ni−C state is unclear. [g] Hyperfine coupling to ^{61}Ni. [h] Hyperfine coupling to ^{13}C. [i] Midpoint potential quoted is from the *D. bacalatus* [NiFeSe] H_2-ase. [j] Hyperfine coupling to ^{77}Se. [k] Hyperfine coupling to ^{33}S. [l] $\langle A(^{61}Ni)\rangle = 22$ G. [m] In CH_2Cl_2. [n] Complex is oxidized by $[Fe(CN)_6]^{3-}$, $E^0 = +0.36$ V *vs* NHE. [o] Hyperfine constant converted from cm^{-1}: conversion factor A (G) = A (cm^{-1}) × $g\beta/hc$. [p] Hyperfine coupling to ^{19}F. [q] Complex is reduced by $S_2O_4^{2-}$, $E^0 = -1.12$ V *vs* NHE. [r] bbmtpH_2 = 1,3-bis[[2-(1-methyl-7-oxidotriazen-3-yl)phenyl]thio]propane; bc-[19]aneSN_4 = 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane; bdtH_2 = butane-2,3-dithiol; bhpte = 1,2-bis[[*o*-[(4-hydroxy-5-methylphenyl)azo]phenyl]thio]ethane; bis-[10]aneS_2N = 1,2-bis(8-aza-1,5-dithiacyclodecanyl)ethane; Cl-bhptp = 1,2-bis[(*o*-[(4-hydroxy-5-chlorophenyl)azo]phenyl]thio)propane; CyBME-DACO = 4,8-dithia-1,11-diazabicyclo[9.3.3]heptadecane; DACO-DTPH_2 = Λ-1,5-diazacyclooctane-1,5-diylbis(3-thiapentanoic acid); dadtdo = 3,14-dimethyl-4,13-diaza-7,10-dithiahexadeca-3,13-diene-2,15-dione dioxime; dadtpo = 3,15-dimethyl-4,14-diaza-7,11-dithiaheptadeca-3,14-diene-2,16-dione dioxime; DAPA = 2,6-bis[1-(phenylimino)ethyl]pyridine; emaH_4 = *N,N′*-ethylenebis[2-(acetylthio)acetamide]; embH_4 = *N,N′*-bis(*o*-mercaptobenzoyl)ethylenediamide; emiH_4 = *N,N′*-ethylenebis[2-(acetylthio)isobutyramide]; MC1 = 2,4,4-trimethyl-1,5,9-triazacyclododec-1-ene; MeBME-DACOH = *N*-(2-mercaptoethyl)-*N′*-(3-thiabutyl)-1,5-diazacyclooctane; Me_2BME-DACO = *N,N′*-bis(3-thiabutyl)-1,5-diazacyclooctane; 1,2-Me_2Im = 1,2-dimethylimidazole; memtaH_2 = bis(2-mercaptoethyl)[2-(methylthio)ethyl]amine; ndtH_2 = norbornane-2,3-*exo*-*cis*-dithiol; OCBME-DACO = 7-oxa-4,10-dithia-1,13-diazabicyclo[11.3.3]nonadecane; pdmtH_2 = 2,6-bis(mercaptomethyl)pyridine; pdtcH_2 = pyridine-2,6-bis(thiocarboxylic acid); phmaH_4 = *N,N′*-phenylenebis[2-(acetylthio)acetamide]; PrttoH = 1-propyl-3-[2-(methylthio)phenyl]triazene 1-oxide; qdtH_2 = quinoxalinedithiol; STPPH = 5,10,15,20-tetraphenyl-21-thiaporphyrin; terpy = 2,2′,6′,2″-terpyridine; tmtssH_2 = 2′-hydroxy-4′,5′-dimethylacetophenone 4-methylthiosemicarbazone; TPyOH = 2-mercaptopyridine *N*-oxide; tssH_2 = salicylaldehyde thiosemicarbazone; [9]aneS_3 = 1,4,7-trithiacyclononane; [9]aneS_2N = 1-aza-4,7-dithiacyclononane; [9]aneSN_2 = 1,4-diaza-7-thiacyclononane; [10]aneS_3 = 1,4,7-trithiacyclododecane; [10]aneS_2N = 1-aza-5,8-dithiacyclodecane; [10]aneSN_2 = 1-thia-4,8-diazacyclodecane; [18]aneS_4N_2 = 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane. [s] Complexes containing abiological halide or phosphine ligands have not been included. Compounds are ranked in order of increasing oxidation potential, and decreasing reduction potential.

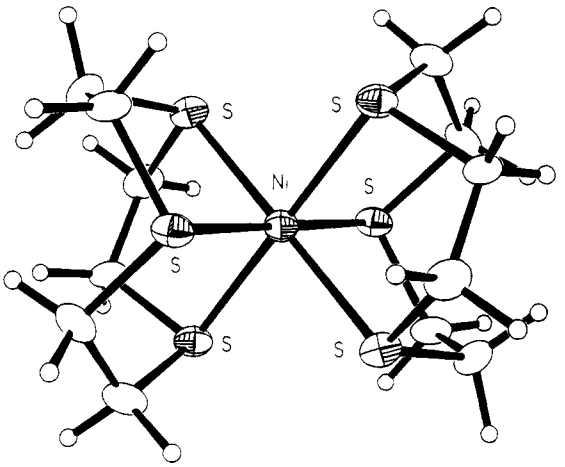
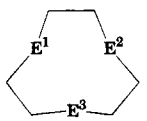


Figure 34. Structure of $[Ni^{III}([9]aneS_3)_2]^{3+}$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane). $[Ni^{II}([9]aneS_3)_2]^{2+}$ shows an identical coordination geometry. (Reprinted from ref 711. Copyright 1992 the Royal Society of Chemistry.)

been structurally characterized.[701] These generally exhibit high-spin square-pyramidal or octahedral coordination, often containing coordinated anion or solvent, with variable Ni–S distances of between 2.38–2.44 Å depending on ligand ring size;[694,701–705,709,712,713] the exception is square-planar $[Ni(14)aneS_4)]^{2+}$ ([14]aneS$_4$ = 1,4,8,11-tetrathiacyclotetradecane and methylated derivatives) which can be crystallized from nondonor solvents and exhibits considerably shorter Ni–S bonds of 2.18 Å (Table 5).[701,706–708] The only Ni^{II} crown thioether complexes for which reversible electrochemical behavior has been reported are the octahedral derivatives $[Ni([9]aneS_3)_2]^{2+}$ and $[Ni([10]aneS_3)_2]^{2+}$ ([9]aneS$_3$ = 1,4,7-trithiacyclononane, **68**; [10]aneS$_3$ = 1,4,7-



68

$E^1 = E^2 = E^3$ = NH; [9]aneN$_3$
$E^1 = E^2 = E^3$ = NMe; Me$_3$[9]aneN$_3$
$E^1 = E^2$ = NH, E^3 = S; [9]aneN$_2$S
E^1 = NH, $E^2 = E^3$ = S; [9]aneNS$_2$
$E^1 = E^2 = E^3$ = S; [9]aneS$_3$

trithiacyclodecane) which show chemically reversible oxidations in MeCN at $E_{1/2}$ = +0.98 and +0.90 V *vs* Fc/Fc^+, respectively.[701,709–711] The oxidized $[Ni(S_3)_2]^{3+}$ (S_3 = [9]aneS$_3$, [10]aneS$_3$) species give rhombic EPR spectra with relatively small g shifts (Table 6),[710,711] while the single-crystal X-ray structure of $[Ni([9]aneS_3)_2]^{3+}$ shows an octahedral Ni^{III} center, with considerably shortened Ni–S distances [Ni–S_{av} = 2.313(3) Å; Figure 34][711] compared to its Ni^{II} congener [Ni–S = 2.377(1), 2.380(1), 2.400(1) Å].[712] This is thus far the only homoleptic Ni–S system in which direct structural comparisons between Ni^{II} and Ni^{III}, as opposed to $Ni^{II}(L^{\bullet+})$, derivatives can unambiguously be made. Electrochemical reductions of $[Ni(S_3)_2]^{2+}$ are only quasireversible, possibly because of dissociation of one macrocycle from the reduced $[Ni(S_3)_2]^+$ complex and the resultant formation in the presence of added ligand of tetrahedral $[Ni(S_3)(L)]^+$ (reaction 69; X = S; L = solvent, etc.).[710,784]

$$[Ni([9]aneS_2X)_2]^{2+} \xrightarrow{+e^-} \text{“}[Ni([9]aneS_2X)_2]^{+}\text{”} \xrightarrow{-[9]aneS_2X,\ +L} [Ni([9]aneS_2X)(L)]^{+} \quad (69)$$

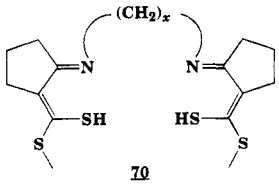
XAS studies of Ni thiolate and thioether complexes are discussed in the following section.

C. Nickel Complexes of Mixed S/N/O Donor Ligands

i. Structural Studies

A very large number of Ni complexes of mixed S-, N-, and/or O-donor polychelate ligands have been characterized by X-ray crystallography, some of which are summarized in Table 7. While every effort has been made to compile a comprehensive list of structurally characterized mixed-donor Ni thiolate and thioether complexes in Table 7 and the list of references, the breadth of literature available on these compounds requires that only those examples most relevant to the discussion of the Ni sites in H_2-ase and CODH will be discussed in detail.

The coordination chemistry of simple mixed amine/thiolate and pyridyl/thiolate chelates with Ni^{II} is similar to that of the all-sulfur chelates described in section IX.B, in that most such ligands afford square planar Ni^{II} complexes showing structural parameters similar to those in analogous homoleptic Ni^{II} thiolate derivatives,[672,717,719–724,726,727,729,730] with a tendency toward aggregation to di- or trinuclear species by thiolate bridge formation (Table 4).[672,728,731–733,736–741] Crabtree and co-workers have suggested that utilization of deprotonated thioamide, rather than thiolate, donors in a mixed S/N/O-donor thiosemicarbazone ligand (**50**)[734] greatly reduces the ability of the sulfur centers to bridge between Ni^{II} ions.[735] The structural characterization of a series of pseudo-square-planar *cis*-S_2N_2 bis(imino thiocarboxylate ester) (**70**) Ni^{II}



70

x = 1-3

complexes by Bereman and Martin has shown that introduction of a tetrahedral distortion of up to 38.6° into the Ni coordination sphere results in only a small shortening of the Ni–S bonds and lengthening of the Ni–N distances, each by *ca.* 0.01 Å,[824] suggesting that such a distortion about a protein-bound Ni ion might be difficult to detect by Ni XAS.

Different approaches have been taken toward the synthesis of mononuclear five- or six-coordinate Ni^{II} thiolate complexes in mixed-donor environments. Reaction of $[Ni(terpy)Cl_2]$ (terpy = 2,2′,6′,2″-terpyridine) with 2 equiv of Et_4NSR affords, depending on the aromatic thiolate employed, $[Ni(SR^1)(\mu\text{-}SR^1)(terpy)]_2$ (R^1 = Ph, *p*-Tol), $[Ni(SC_6F_5)_2(terpy)(NCMe)]$, or $[Ni(SR^2)_2(terpy)]$ (R^2 = 2,6-Me_2-C_6H_3, 2,4,6-Pr^i_3-C_6H_2), all of which form six-coordinate adducts $[Ni(SR)_2(terpy)(solv)]$ in DMSO solution;[529,530] with 2,6-

Table 7. Structural Data for Selected Nickel Complexes Containing S-, N-, and O-Donor Ligands[c]

complexes[c]	coordination geometry[a]	donor set[b]	d(Ni···S), Å	d(Ni···N), Å	d(Ni···X), Å (X = C, O)	ref
			Ni^{I}			
[Ni(SDPDTP)]	SqPl	SN_3	2.143(6)	1.91(1), 2.01(1), 2.02(1)	–	341
[Ni(N{$C_2H_4SBu^t$}$_3$)(CO)]$^+$	TBP	S_3NC	2.351(3), 2.353(2), 2.384(3)	2.208(6)	1.85(1)	524
			Ni^{II}			
[Ni(imaptMe)]	Tet	S_2N_2	2.237(2)	1.975(7)	–	812
[Ni(imaptPh)]	Tet	S_2N_2	2.229(1)	1.984(3)	–	812
[Ni(imaptBu)]	"Tet"	S_2N_2	2.253(1), 2.254(1)	1.984(4), 1.995(4)	–	812
[Ni(tmpdta)]	"Tet"	S_2N_2	2.161(1), 2.162(1)	1.919(4), 1.923(3)	–	824
[Ni(tsdbth)(py)]	SqPl	SN_3	2.137(1)	1.873(3), 1.915(3), 1.920(3)	–	813
[Ni(memta)(CN)]$^-$	SqPl	S_2NC	2.180(3), 2.175(3)	1.940(8)	1.82(1)	647
[Ni(tmtssA)]$_2$	SqPl	c-SNO_2	2.129(1)	1.855(5)	1.851(3), 1.912(4)	735
[Ni(SMPD)(py)]$^+$	SqPl	t-SN_2O	2.140(2)	1.845(4), 1.912(4)	1.843(4)	814
[Ni(SMPD)(ImH)]$^+$	SqPl	t-SN_2O	2.143(1)	1.840(4), 1.888(4)	1.860(3)	815
[Ni(saptz)(NH_3)]	SqPl	t-SN_2O	2.166(2)	1.844(7), 1.921(7)	1.858(6)	825
[Ni(tsdnPh)(tsdhd)]	SqPl	c-S_2NO	2.149(2), 2.154(2)	1.931(5)	1.869(4)	813
[Ni(MSA)(SPh)]$^-$	SqPl	c-S_2NO	2.144(1), 2.212(1)	1.917(2)	1.865(2)	645
[Ni(dmpdta)]	SqPl	c-S_2N_2	2.170(2), 2.174(4)	1.893(6), 1.90(1)	–	824
[Ni(bzdt)(py)$_2$]	SqPl	c-S_2N_2	2.139(2), 2.148(2)	1.930(4), 1.940(5)	–	741
[Ni(ema)]	SqPl	c-S_2N_2	2.179(1)	1.857(3)	–	717
[Ni(emb)]$^{2-}$	SqPl	c-S_2N_2	2.149(7), 2.161(7)	1.89(2), 1.90(2)	–	719
[Ni(tsalen)]	SqPl	c-S_2N_2	2.139(5), 2.174(5)	1.85(1), 1.86(1)	–	721, 724
[Ni(ebmba)]	SqPl	c-S_2N_2	2.1639(6), 2.170(1)	1.941(2), 1.949(2)	–	722, 724
[Ni(pmbt)$_2$]	SqPl	c-S_2N_2	2.180(1)	1.926(2)	–	726
[Ni(dmpn)]	SqPl	c-S_2N_2	2.174(1), 2.176(1)	1.999(3), 2.006(3)	–	672
[Ni(BME-DACO)]	SqPl	c-S_2N_2	2.159(2)	1.985(6)	–	716
[Ni(MeBME-DACO)]$^+$	SqPl	c-S_2N_2	2.155(3), 2.173(2)	1.935(5), 1.982(6)	–	794
[Ni(Me_2BME-DACO)]$^{2+}$	SqPl	c-S_2N_2	2.104(3), 2.211(3)	1.972(7), 1.974(7)	–	716
[Ni(CyBME-DACO)]$^{2+}$	SqPl	c-S_2N_2	2.188(3), 2.201(3)	1.983(8), 1.990(7)	–	794
[Ni(Dtdo)]$^+$	SqPl	c-S_2N_2	2.145(1), 2.163(1)	1.900(4), 1.903(3)	–	793
[Ni(SC{NH}N=$NCMe_2$)$_2$]	SqPl	c-S_2N_2	2.162(2), 2.166(2)	1.921(6), 1.934(5)	–	826
[Ni(pen)$_2$]$^{2-}$	SqPl	t-S_2N_2	2.147(3), 2.155(3)	1.949(9), 1.956(9)	–	827
[Ni($SC_2H_4NH_2$)$_2$]	SqPl	t-S_2N_2	2.159(1)	1.868(3)	–	727
	SqPl	t-S_2N_2	2.193(2)	1.904(7)	–	729
[Ni($SC_2H_4NMe_2$)$_2$]	SqPl	t-S_2N_2	2.198(3)	1.97(1)	–	730
[Ni(cys)$_2$]$^{2-}$	SqPl	t-S_2N_2	2.199(3), 2.209(4)	1.906(9), 1.928(9)	–	828
[Ni(mp)$_2$]$^{2-}$	SqPl	c-S_2O_2	2.153(2), 2.153(2)	–	1.865(3), 1.885(4)	799
[Ni(TPyO)$_2$]	SqPl	c-S_2O_2	2.129(1), 2.136(1)	–	1.864(3), 1.868(3)	816
[Ni_2(embH$_2$)$_2$]	SqPl	c-S_2O_2	2.125(1), 2.126(1)	–	1.877(3), 1.889(3)	720
[Ni(hdptp)$_2$]	SqPl	c-S_2O_2	2.117(3), 2.135(3)	–	1.847(6), 1.864(6)	817
[Ni(tetptu)]$_3$	SqPl	c-S_2O_2	2.131	–	1.830	818
[Ni(pdmt)(SPh)]$^-$	SqPl	S_3N	2.167(1), 2.171(2), 2.173(2)	1.901(4)	–	642
[Ni(pdmt)(SEt)]$^-$	SqPl	S_3N	2.165(1), 2.183(1), 2.183(1)	1.910(3)	–	642
[Ni({SC_2H_4}$_2$S)(CN)]$^-$	SqPl	S_3C	2.175(3), 2.156(3), 2.162(4)	–	1.859(8)	647
[Ni(Mebzdt)$_2$(CH_3)]$^-$	SqPl	S_3C	2.150(4), 2.205(3), 2.206(4)	–	1.954(7)	533
[Ni(S-2,4,5-Pr^i_3-C_6H_2)$_2$(terpy)]	TBP	S_2N_3	2.274(3), 2.332(2)	1.974(9), 2.086(7), 2.113(7)	–	529
[Ni(S-2,6-Me_2-C_6H_3)$_2$(terpy)]	TBP	S_2N_3	2.311(1)	1.975(4), 2.112(3)	–	530
[Ni(SPh)$_2$(DAPA)]	TBP	S_2N_3	2.263(2), 2.351(2)	1.936(5), 2.110(7), 2.131(6)	–	531
[Ni({$SCH_2C(Me)$=NC_3H_6}$_2$NH)]	TBP	S_2N_3	2.306(2), 2.359(2)	2.048(4), 2.065(4), 2.068(4)	–	742
[Ni(N{$C_2H_4SPr^i$}$_3$)(CH_3)]$^+$	TBP	S_3NC	2.228(4), 2.231(4), 2.335(4)	2.06(1)	1.94(2)	524
[Ni(N{$C_2H_4SPr^i$}$_3$)(C{O}CH_3)]$^+$	TBP	S_3NC	2.274(4), 2.286(4), 2.317(4)	2.10(1)	1.90(2)	524

Table 7 (Continued)

complexes[c]	coordination geometry[a]	donor set[b]	d(Ni···S), Å	d(Ni···N), Å	d(Ni···X), Å (X = C, O)	ref
			Ni^{II}			
$[Ni(N\{C_2H_4SBu^t\}_3)(H)]^+$	TBP	S_3NH	2.218(6), 2.227(7), 2.234(6)	2.02(1)	–	524
$[Ni(TIM)(SPh)]^+$	SqPy	SN_4	2.452(4)	1.87(1), 1.88(1), 1.88(1), 1.89(1)	–	802
$[Ni(OCBME\text{-}DACO)]^{2+}$	SqPy	S_2N_2O	2.362(2), 2.405(2)	2.101(5), 2.116(5)	2.387(5)	794
$[Ni(bc\text{-}[19]aneSN_4)(OClO_3)]^+$	Oct	t-SN_4O	2.385(2)	2.055(5), 2.065(5), 2.072(5), 2.087(5)	2.563(6)	783
$[Ni(mda)(OH_2)_3]^-$	Oct	SO_5	2.439(2)	–	1.998(7), 2.010(7), 2.05(1), 2.063(7), 2.065(6)	770
[Ni(DACO-DTP)]	Oct	c,c,t-$S_2N_2O_2$	2.435(2)	2.094(4)	2.067(3)	795
$[Ni(bhpte)]^{2+}$	Oct	c,t,c-$S_2N_2O_2$	2.418(2), 2.436(2)	2.027(4), 2.031(4)	1.972(4), 1.986(4)	759
$[Ni(Cl\text{-}bhptp)]^{2+}$	Oct	c,t,c-$S_2N_2O_2$	2.396(2)	2.038(3)	1.973(4)	759
$[Ni(tssH)_2]^{2+}$	Oct	c,t,c-$S_2N_2O_2$	2.36, 2.39	2.01, 2.02	2.09, 2.14	870
$[Ni(biimdt)(OH_2)_2]^{2+}$	Oct	c,t,c-$S_2N_2O_2$	2.448(1), 2.453(1)	2.027(3), 2.050(3)	2.077(2), 2.084(3)	749
$[Ni(bzimdt)(O_2CMe)]^+$	Oct	c,t,c-$S_2N_2O_2$	2.414(2), 2.415(2)	2.025(5), 2.048(5)	2.109(4), 2.137(4)	750
$[Ni(bzimdt)(OH_2)_2]^{2+}$	Oct	c,t,c-$S_2N_2O_2$	2.437(2)	2.078(4)	2.054(4)	752
	Oct	c,t,c-$S_2N_2O_2$	2.421(2), 2.466(3)	2.063(3), 2.074(4)	2.050(4), 2.088(6)	753
$[Ni(pyimdt)(OH_2)(ONO_2)]^+$	Oct	c,t,c-$S_2N_2O_2$	2.411(1), 2.453(1)	2.119(4), 2.139(4)	2.035(3), 2.099(3)	755
[Ni(bbmtp)]	Oct	c,t,c-$S_2N_2O_2$	2.494(4), 2.526(3)	1.984(8), 1.993(8)	2.060(7), 2.075(8)	756
$[Ni(Prtto)_2]$	Oct	c,t,c-$S_2N_2O_2$	2.519(2), 2.549(2)	1.970(4), 1.972(4)	2.048(4), 2.051(4)	757
$[Ni(Me_2ottht)_2(OH_2)_2]^{2+}$	Oct	t,t,t,-$S_2N_2O_2$	2.377(3)	2.079(9)	2.135(9)	819
$[Ni(aetpa)(OClO_3)]^+$	Oct	f-S_2N_3O	2.363(3), 2.393(3)	2.081(6), 2.081(7), 2.167(6)	2.249(7)	774
$[Ni(bzo_2\text{-}[17]aneS_2N_3)(OH_2)]^{2+}$	Oct	f-S_2N_3O	2.396(5), 2.428(5)	2.07(1), 2.08(1), 2.09(1)	2.23(1)	786
$[Ni(SC_6F_5)_2(terpy)(NCMe)]$	Oct	c-S_2N_4	2.482(4), 2.499(4)	1.987(9), 2.047(8), 2.080(7), 2.085(7)	–	529
$[Ni(SPh)_2(bpy)_2]$	Oct	c-S_2N_4	2.444(2), 2.445(2)	2.086(4), 2.086(4), 2.088(4), 2.104(4)	–	745
$[Ni(dadtdo)]^{2+}$	Oct	c-S_2N_4	2.408(2), 2.418(2)	2.017(6), 2.031(6), 2.069(6), 2.077(6)	–	758
$[Ni(dadtpo)]^{2+}$	Oct	c-S_2N_4	2.410(7), 2.419(7)	2.02(1), 2.03(1), 2.06(2), 2.09(2)	–	758
$[Ni(dato)_2]^{2+}$	Oct	c-S_2N_4	2.473(1)	2.101(3), 2.129(3)	–	760
$[Ni(dsdb)]^{2+}$	Oct	c-S_2N_4	2.434(2), 2.435(2)	2.099(4), 2.111(5), 2.117(4), 2.125(5)	–	761
$[Ni(MeIm_2SPr)_2]^{2+}$	Oct	c-S_2N_4	2.496(2), 2.513(2)	2.040(6), 2.041(5), 2.044(6), 2.068(6)	–	762
$[Ni(Py_2S_2)(NCMe)_2]^{2+}$	Oct	c-S_2N_4	2.411(3), 2.421(3)	2.042(7), 2.078(7), 2.104(6), 2.105(6)	–	768
$[Ni(AMS_2N_4sar)]^{2+}$	Oct	c-S_2N_4	2.397(5), 2.399(5)	2.09(1), 2.10(1), 2.11(1), 2.11(1)	–	790
$[Ni(Py_2bzo_2\text{-}[14]ineS_2N_2)]^{2+}$	Oct	c-S_2N_4	2.417(2), 2.439(2)	2.092(5), 2.098(6), 2.124(4), 2.151(4)	–	791
$[Ni(Pz4DM)_2]$	Oct	c-S_2N_4	2.380(1), 2.409(1)	2.014(3), 2.017(4), 2.096(4), 2.110(6)	–	763
$[Ni(pymt)_2(bpy)]$	Oct	t-S_2N_4	2.480(3), 2.523(2)	2.036(5), 2.041(5), 2.072(4), 2.078(5)	–	820
$[Ni(pyt)_2(bpy)]$	Oct	t-S_2N_4	2.475(2), 2.495(1)	2.053(3), 2.067(3), 2.068(2), 2.074(2)	–	821
$[Ni([9]aneSN_2)_2]^{2+}$	Oct	t-S_2N_4	2.418(1)	2.108(2), 2.122(2)	–	781
$[Ni([10]aneSN_2)_2]^{2+}$	Oct	t-S_2N_4	2.395(1)	2.141(5), 2.143(4)	–	789
$[Ni(mda)_2]^{2-}$	Oct	c-S_2O_4	2.396(5), 2.406(5)	–	1.99(2), 2.01(1), 2.01(2), 2.03(2)	769
$[Ni(dtda)(OH_2)_2]$	Oct	c-S_2O_4	2.443(2)	–	2.014(7), 2.036(7)	771
	Oct	c-S_2O_4	2.449(1)	–	2.025(3), 2.039(2)	772
$[Ni(Py_2S_3)(OH_2)]^{2+}$	Oct	f-S_3N_2O	2.392(2), 2.426(2), 2.460(2)	2.058(5), 2.084(5)	2.100(4)	768
$[Ni(\{H_2NC_2H_4SC_2H_4\}_2S)(py)]^{2+}$	Oct	f-S_3N_3	2.428(6), 2.457(6), 2.459(6)	2.05(2), 2.09(2), 2.12(1)	–	698
$[Ni(aetea)]^{2+}$	Oct	f-S_3N_3	2.461(1), 2.478(1), 2.490(1)	2.102(3), 2.120(3), 2.132(3)	–	774
$[Ni(pymt)_3]^-$	Oct	m-S_3N_3	2.460(3), 2.480(3), 2.545(2)	2.025(5), 2.051(5), 2.053(5)	–	822
$[Ni(pyt)_3]^-$	Oct	m-S_3N_3	2.518(1), 2.526(1), 2.541(1)	2.034(4), 2.041(4), 2.081(4)	–	822
$[Ni(tbmpte)(py)_2]$	Oct	c-S_4N_2	2.409(1), 2.412(1), 2.413(1), 2.424(1)	2.130(3), 2.132(4)	–	699
$[Ni(Py_2S_4)]^{2+}$	Oct	c-S_4N_2	2.425(2), 2.434(2)	2.091(5)	–	768
$[Ni([18]aneS_4N_2)]^{2+}$	Oct	t-S_4N_2	2.403(6), 2.407(6), 2.416(7), 2.430(5)	2.07(1), 2.13(1)	–	779
$[Ni([9]aneS_2N)_2]^{2+}$	Oct	t-S_4N_2	2.408(1), 2.415(1)	2.104(4)	–	784
$[Ni(bzo_2\text{-}[18]aneS_4N_2)]^{2+}$	Oct	t-S_4N_2	2.398(2), 2.440(2)	2.082(4)	–	785
$[Ni([10]aneS_2N)_2]^{2+}$	Oct	t-S_4N_2	2.407(2), 2.408(2), 2.410(2), 2.411(2)	2.124(6), 2.125(5)	–	788

$[Ni(bis\text{-}[10]aneS_2N)]^{2+}$	Oct	$t\text{-}S_4N_2$	2.389(2), 2.415(2)	2.112(5)	–	788
$[Ni(pdtc)_2]^{2-}$	Oct	$t\text{-}S_4N_2$	2.4079(9), 2.4290(8)	2.047(2)	–	798
$[Ni([16]aneS_4)(OH_2)_2]^{2+}$	Oct	$t\text{-}S_4O_2$	2.429(1), 2.423(1)	–	2.083(3)	694
$[Ni(pth)(OH_2)]^{2+}$	Oct	S_5O	2.388(2), 2.403(2), 2.404(2), 2.404(2), 2.425(2)	–	2.153(4)	692
$[Ni(bta)(OClO_3)]^{+}$	Oct	S_5O	2.36–2.42	–	2.227(5)	823
$[Ni(btpa)(OH_2)]^{2+}$	Oct	S_5O	2.38–2.43	–	2.092(5)	823
			Ni^{III}			
$[Ni(mp)_2]^{-}$	SqPl	$c\text{-}S_2O_2$	2.117(2), 2.119(2)	–	1.849(4), 2.851(4)	799
$[Ni(pdtc)_2]^{-}$	Oct	$t\text{-}S_4N_2$	2.267(1), 2.271(1), 2.288(1), 2.289(1)	2.033(3), 2.040(4)	–	798

[a] Tet = tetrahedral; SqPl = square planar; TBP = trigonal bipyramidal; SqPy = square pyramidal; Oct = octahedral. [b] *c* = *cis*, *t* = *trans*, *f* = *fac*, *m* = *mer*. [c] aetea = tris({2-[2-aminoethyl]thio}ethyl)amine; aetpa = tris[2-[(2-aminophenyl)thio]ethyl]amine; AMS_2N_4sar = 1-methyl-8-amino-3,13-dithia-6,10,16,19-tetraazabicyclo[6.6.6]icosane; $bbmtpH_2$ = 1,3-bis[[2-(1-methyl-1-oxidotriazen-3-yl)phenyl]thio]propane; bc-[19]aneSN$_4$ = 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]nonadecane; bhpte = 1,2-bis[[*o*-[(4-hydroxy-5-methylphenyl)azo]phenyl]thio]ethane; biimdt = 1,6-bis(4-imidazolyl)-2,5-dithiahexane; bis-[10]aneS$_2$N = 1,2-bis(8-aza-1,5-dithiacyclodecanyl)ethane; H_2BME-DACO = *N*,*N*′-bis(2-mercaptoethyl)-1,5-diazacyclooctane; bta = 1,3-bis(3-thia-4-sulfidobutyl)-5-thiane; btpa = 1,4-bis{3-thia-4-sulfidobutyl)-6-thiepane; $bzdtH_2$ = benzene-1,2-dithiol; bzimdt = 1,6-bis(2-benzimidazolyl)-2,5-dithiahexane; bzo_2-[17]aneS$_2$N$_3$ = 1,12,15-triaza-5,8-dithia-3,4:9,10-dibenzocycloheptadecane; bzo_2-[18]aneS$_4$N$_2$ = 1,10-diaza-4,7,13,16-tetrathia-5,6:14,15-dibenzocyclooctadecane; Cl-bhptp = 1,2-bis[[*o*-[(4-hydroxy-5-chlorophenyl)azo]phenyl]thio]propane; CyBME-DACO = 4,8-dithia-1,11-diazabicyclo[9.3.3]heptadecane; $cysH_2$ = (*R*)-cysteine; H_2DACO-DTP = 1,5-diazacyclooctane-1,5-diylbis(3-thiapentanoic acid); dadtdo = 3,14-dimethyl-4,13-diaza-7,10-dithiahexadeca-3,13-diene-2,15-dione dioxime; dadtpo = 3,15-dimethyl-4,14-diaza-7,11-dithiaheptadeca-3,14-diene-2,16-dione dioxime; DAPA = 2,6-bis[1-(phenylimino)ethyl]pyridine; dato = 1,8-diaza-4-thiaoctane; $dmpdtaH_2$ = *N*,*N*′-dimethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylic acid); H_2dmpn = *N*,*N*′-dimethyl-*N*,*N*′-bis(2-mercaptoethyl)-1,3-propanediamine; dsdb = 1,12-bis(3,5-dimethylpyrazol-1-yl)-2,11-diaza-5,8-dithiadodecane; $dtdaH_2$ = 2,5-dithiahexane-1,6-dicarboxylic acid; Dtdo = 2,3,9,10-tetramethyl-4,8-dithiaundecane-1,11-dione dioxime; $ebmbaH_2$ = *N*,*N*′-bis(*o*-mercaptobenzyl)ethylenediamine; $emaH_2$ = *N*,*N*′-ethylenebis(2-{acetylthio}acetamide); $embH_4$ = *N*,*N*′-bis(*o*-thiobenzoyl)ethylenediamide; hdptpH = 2-hydroxy-4,6-diphenyl-thiobenzophenone; imaptBuH = 1-isopropyl-3-methyl-4-*tert*-butylaldiminopyrazole-5-thione; imaptMeH = 1-isopropyl-3,4-dimethylaldiminopyrazole-5-thione; imaptPhH = 1-isopropyl-3-methyl-4-phenylaldiminopyrazole-5-thione; mdaH = mercaptodiacetic acid; MeBME-DACO = *N*-(2-mercaptoethyl)-*N*′-(3-thiabutyl)-1,5-diazacyclooctane; Me_2BME-DACO = *N*,*N*′-bis(3-thiabutyl)-1,5-diazacyclooctane; MebzdtH = 2-(methylthio)thiophenol; MeIm$_2$SPr = 1,3-bis(5-methyl-4-imidazolyl)-2-thiapropane; $memtaH_2$ = bis(2-mercaptoethyl)[2-(methylthio)ethyl]amine; Me_2ottht = 2,6-dimethyl-5-oxo-3-thioxo-2,3,4,5-tetrahydro-1,2,4-triazine; mpH_2 = *o*-mercaptophenol; $MSAH_2$ = 2-(2-mercaptophenyl)salicylaldimine; OCBME-DACO = 7-oxa-4,10-dithia-1,13-diazabicyclo[11.3.3]nonadecane; $pdmtH_2$ = pyridine-2,6-dimethanethiol; $pdtcH_2$ = pyridine-2,6-bis(thiocarboxylic acid); $penH_2$ = (*S*)-penicillamine; pmbtH = 2-*N*-(phenylmethylide)benzenethiol; PrttoH = 1-propyl-3-(2-methylthiophenyl)triazene 1-oxide; pth = 3,6,9,12,15-pentathiaheptadecane; Py$_2$bzo$_2$-[14]ineS$_2$N$_2$ = 8,17-bis(2-pyridylmethyl)-6,7,8,9,15,16,17,18-octahydrodibenzo[*f*,*m*]dithiadiazacyclotetradecine; pyimdt = 1,8-bis(2-pyridyl)-3,6-dithiaoctane; pymtH = pyrimidine-2-thione; Py$_2$S$_2$ = 1,6-bis(2-pyridyl)-2,5,8-dithiahexane; Py$_2$S$_3$ = 1,9-bis(2-pyridyl)-2,5,8-trithianonane; Py$_2$S$_4$ = 1,12-bis(2-pyridyl)-2,5,8,11-tetrathiadodecane; pytH = pyridine-2-thione; Pz4DMH = acetylpyrazine 4,4-dimethylthiosemicarbazone; $saptzH_2$ = salicylaldehyde 4-phenylthiosemicarbazone; SDPDTPH = 5,20-diphenyl-10,15-di-*p*-tolyl-21-thiaporphyrin; SMPDH = *S*-methyl *β*-*N*-(*N*-oxido-pyridin-2-ylmethylidene)dithiocarbazate; $tbmpteH_2$ = 1,2-bis[(3,5-di-*tert*-butyl-2-mercaptophenyl)thio]ethane; terpy = 2,2′,6′,2″-terpyridine; $tetptuH_2$ = 1,1,1′,1′-tetraethyl-3,3′-terephthaloylbis(thiourea); TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraaza-1,3,8,10-tetraene; $tmpdtaH_2$ = *N*,*N*′-tetramethylenebis(methyl-2-amino-1-cyclopentenedithiocarboxylic acid); tmtssH = 2′-hydroxy-4′,5′-dimethylacetophenone 4-methylthiosemicarbazone; $tmtssAH_2$ = 2-hydroxy-5-methylacetophenone *N*,*N*-dimethylthiosemicarbazone; TPyOH = 2-mercaptopyridine *N*-oxide; $tsalenH_2$ = *N*,*N*′-bis(*o*-mercaptobenzylidene)ethylenediamine; tsdhdH = thiosalicylaldehyde; $tsdbthH_2$ = *N*-(thiosalicyl)-*N*′-(2-benzthiazolyl)hydrazone; tsdnPhH = *N*,*N*-diphenyl-*N*′-thiosalicylhydrazone; $tssH_2$ = salicylaldehyde thiosemicarbazone; [9]aneS$_2$N = 1-aza-4,7-dithiacyclononane; [9]aneSN$_2$ = 1,4-diaza-7-thiacyclononane; [10]aneS$_2$N = 1-aza-5,8-dithiacyclodecane; [10]aneSN$_2$ = 1-thia-4,8-diazacyclodecane; [16]aneS$_4$ = 1,5,9,13-tetrathiacyclohexadecane; [18]aneS$_4$N$_2$ = 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane. [d] Structures containing abiological halide or phosphorus donors or oxidized sulfur donors, and of complexes of delocalized noninnocent ligands, are not included.

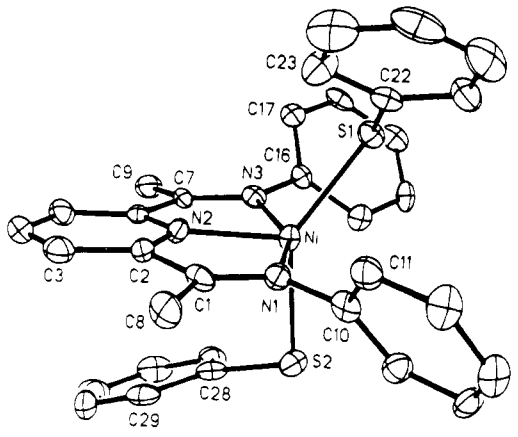
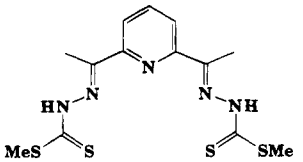


Figure 35. Structure of $[Ni^{II}(SPh)_2(DAPA)]$ (DAPA = 2,6-bis[1-(phenylimino)ethyl]pyridine). (Reprinted from ref 531. Copyright 1992 American Chemical Society.)

bis[1-(phenylimino)ethyl]pyridine (DAPA) as the tridentate ligand, the mononuclear five-coordinate complex $[Ni(SPh)_2(DAPA)]$ was obtained (Figures 35 and 36).[531] The $[Ni(SR)_2(L)]$ complexes exhibit high-spin, distorted trigonal-bipyramidal structures with two equatorial thiolate donors in the solid state, showing Ni–S distances up to 0.15 Å shorter than those of the corresponding octahedral derivatives, at 2.26–2.35 Å compared to *ca.* 2.43 Å in the latter species.[529–531] The synthesis and structure of the high-spin trigonal-bipyramidal complex $[Ni(L_{S2\{Me\}N3\{Pr\}})]$ ($L_{S2\{Me\}N3\{Pr\}}H_2$ = $\{HSCH_2C(Me)=NC_3H_6\}_2NH$), also containing two equatorial thiolate donors, has very recently been communicated (Figure 37).[742] The S → Ni charge-transfer absorptions in the UV/visible spectrum of this complex occur 30 nm (5.8 kcal mol^{-1}) higher in energy in H_2O as opposed to nonprotic solvents, which is strongly suggestive of solvent hydrogen bonding to the Ni-bound thiolate donors and implies a high proton affinity for these S-centers. Interestingly, the Ni–S distances in the solid state structure of $[Ni(L_{S2\{Me\}N3\{Pr\}})]$ are significantly different [Ni–S = 2.306(2), 2.359(2) Å], possibly because of hydrogen bonding between the more distant thiolate donor and a lattice solvent molecule.[742] No trigonal-bipyramidal Ni^{II} complex containing an axial thiolate ligand has yet been reported, although there is some EPR evidence that such a geometry may be present in some states of the H_2-ase Ni site.[601] Both the oxidation of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) by diaryl disulfides in the presence of 2,2′-bipyridine (bpy),[743] and the electrochemical oxidation of a Ni anode in the presence of aryl thiol and bpy,[744] afford the octahedral species *cis*-$[Ni(SR)_2(bpy)_2]$, one of which (R = Ph) has been structurally characterized (Figure 38);[745] the low-spin, five-coordinate Ni^{II} complex of ligand **71** has also been synthesized.[746]



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A large number of Ni^{II} complexes of mixed thioether/nitrogen/oxygen donor linear[747–762,764–773] and tripodal[524,774] polychelate, and macrocyclic,[775–793] ligands have been reported. These adopt almost exclusively octahedral stereochemistries in the solid state and solution, with solvent or anion ligands completing the Ni coordination sphere if required (Table 7); exceptions are the trigonal-bipyramidal derivatives $[Ni(N\{C_2H_4SR\}_3)X]^+$ (R = Pr^i, Bu^t; X^- =

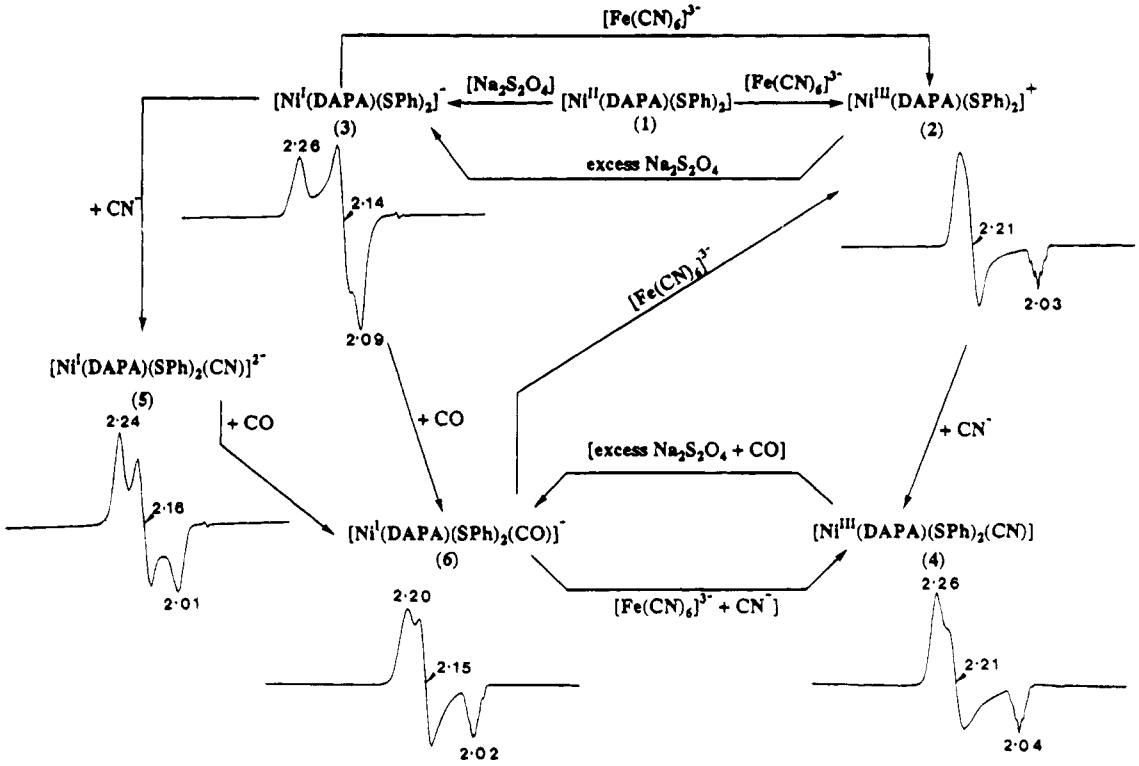


Figure 36. Scheme showing the redox and adduct formation reactions exhibited by $[Ni(SPh)_2(DAPA)]$ (DAPA = 2,6-bis-[1-(phenylimino)ethyl]pyridine). (Reprinted from ref 531. Copyright 1992 American Chemical Society.)

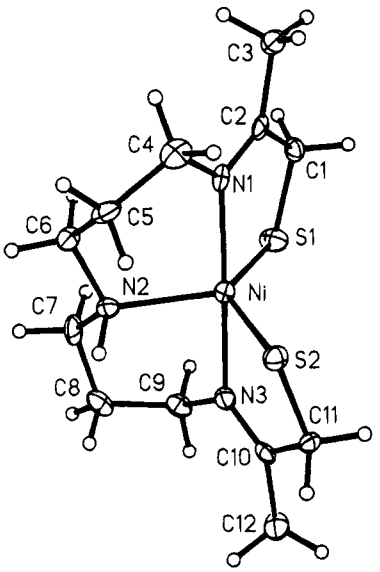


Figure 37. Structure of $[Ni(L_{S2\{Me\}N3\{Pr\}})]$ ($L_{S2\{Me\}N3\{Pr\}}H_2$ = $\{HSCH_2C(Me)=NC_3H_6\}_2NH$). (Reprinted from ref 742. Copyright 1994 American Chemical Society.)

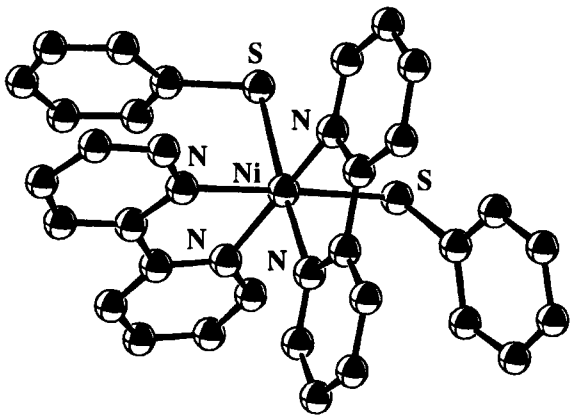


Figure 38. Structure of $[Ni(SPh)_2(bpy)_2]$. Atomic coordinates were taken from ref 745.

Cl^-, CH_3^-, $C(O)CH_3^-$),[524] pseudo-square-planar diaza dithioether complexes based on the BME-DACO ligand (**43**) which form five- or six-coordinate halide or solvent adducts in solution,[716,794,796] and some macrocyclic complexes where a low-spin configuration is favored by hole–size considerations.[793]

A systematic study by Darensbourg and co-workers of the effects of derivatization of thiolate centers in a series of square-planar *cis*-N_2S_2 complexes of BME-DACO-based ligands (**43**) showed that oxidation of a Ni-bound thiolate to a sulfinate center results in a shortening of the Ni–S bond by *ca.* 0.025 Å, while alkylation of the same S-donor leads to a lengthening of this bond by up to 0.05 Å, with concomitant weak axial coordination of halide anions in the solid state to form pseudo-five- or pseudo-six-coordinate Ni centers (Ni···X = 2.8–3.6 Å; X^- = Br^-, I^-);[716,794,796] the former result has been confirmed by other groups,[646,647] while examination of Tables 5 and 7 shows that the latter trend also appears to be general for low-spin Ni^{II} complexes with similar ligand geometries and donor sets. In contrast, although the available database for octahedral Ni^{II} thiolates is small, for comparable octahedral species Ni–S(thioether) distances appear to be similar to or shorter than Ni–S(thiolate) bond lengths. It should be noted,

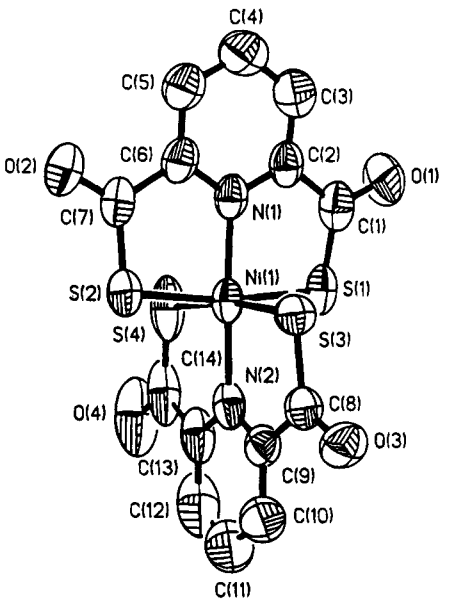
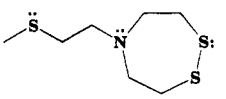


Figure 39. Structure of $[Ni^{III}(pdtc)_2]^-$ ($pdtcH_2$ = pyridine-2,6-bis(thiocarboxylic acid)). $[Ni^{II}(pdtc)_2]^{2-}$ shows an identical coordination geometry. (Reprinted from ref 798. Copyright 1990 American Chemical Society.)

however, that most structurally characterized Ni^{II} thioether complexes involve polychelate or macrocyclic ligands, where the observed Ni–S bonds may be significantly shortened by ring strain effects (Table 5). Two Ni^{II} complexes of disulfides (RSSR′) have been structurally characterized: [Ni(tbadh)I_2] (tbadh = 1-(3-thia-1-butyl)-1-aza-4,5-dithia-heptane, **72**)[643]



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and $[Ni_2(\mu\text{-pmads})(\mu\text{-}O_2CMe_2)]^{2+}$ (pmads = bis[2-[bis(2-pyridylmethyl)amino]ethyl] disulfide),[644] both of which show Ni–S distances similar to those found in comparable thiolate-containing species.

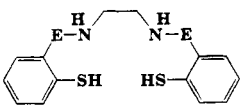
Only two Ni^{III} complexes of mixed S/N/O-donor ligands have been characterized by X-ray crystallography. One-electron oxidation of the octahedral $[Ni(pdtc)_2]^{2-}$ ($pdtcH_2$ = pyridine-2,6-bis(thiocarboxylic acid))[798] results in contraction of the Ni–S and Ni–N distances by approximately 0.14 and 0.02 Å, respectively, with little other detectable change in geometry [Figure 39, for $[Ni(pdtc)_2]^{2-}$ Ni–S = 2.408(1), 2.429(1) Å, Ni–N = 2.047(2) Å; for $[Ni(pdtc)_2]^-$ Ni–S = 2.267(1), 2.271(1), 2.288(1), 2.289(1) Å, Ni–N = 2.033(3), 2.040(4) Å].[581,798] The crystal structure of $[Ni(mp)_2]^-$ (mpH_2 = *o*-mercaptophenol) has also been described;[799] while the square-planar oxidized complex shows significantly shortened Ni–S and Ni–O bond lengths compared to $[Ni^{II}(mp)_2]^{2-}$, consistent with the authors' description of $[Ni(mp)_2]^-$ as a Ni^{III} complex as opposed to a Ni^{II}-stabilized ligand radical cation,[682,689,800] there is still some ambiguity concerning the electronic character of the oxidized product.[801] The single-crystal X-ray structures of two Ni^{I} complexes containing S-donor ligands have also been reported. The equatorial Ni–S distances of [Ni(N{$C_2H_4SBu^t$}$_3$)(CO)]$^+$ (Figure 25) are little changed from those of the analogous Ni^{II} complex [Ni(N{C_2H_4-

$SBu^t\}_3)Cl]^+$, both showing an average Ni–S bond length of 2.36 Å, although the axial Ni–N distance in the former complex is 0.03 Å longer than in the Ni^{II} structure, consistent with the expected $(d_{z^2})^1$ configuration at the trigonal-bipyramidal Ni^I center.[524] In contrast, both Ni–S and Ni–N distances in the square-planar [Ni^I(SDPDTP)] [SDPDTPH = 5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin; Figure 17, Ni–S = 2.143(6) Å, Ni–N = 1.91(1), 2.01(1), 2.02(1) Å] are significantly shorter than in the square-pyramidal complex [Ni^{II}(STTP)Cl] (STTPH = 5,10,15,20-tetraphenyl-21-thiaporphyrin), reflecting the π-acceptor capabilities of the thiaporphyrin macrocycle,[341] although detailed structural comparisons between these two compounds cannot be made because of the different coordination geometries present.

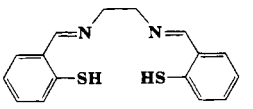
A variety of homoleptic and mixed-donor Ni thiolate and thioether complexes have been characterized by XAS.[61,444,446,530,578,579,581,661,664,696,723,803–805] With one exception,[803] EXAFS data from Ni thiolate and thioether complexes have been modeled using previously published structural parameters for these compounds obtained by X-ray crystallography, the EXAFS analyses satisfactorily reproducing the crystallographic results.[530,578,579,581,661,723,803,804] An investigation of Ni K-edge XANES data from structurally characterized model complexes,[804] including some $Ni^{II/III}$ structural pairs, concluded that the +2 and +3 Ni oxidation states could not be reliably distinguished from XAS near-edge features alone for complexes with sulfur-rich coordination spheres, because of the small shifts in K-edge energy observed between complexes in these two oxidation states and broadening of the absorption edges by the polarizable S ligand donors. However, with corroborating EXAFS or X-ray crystallographic data useful structural information regarding the coordination geometry about a Ni center could be deduced by this method.[739,804] XPS data on the same set of sample compounds show an increasing trend toward ligand- rather than metal-centered oxidation in Ni^{II} complexes with increasing numbers of S-donors, consistent with the similar Ni K-edge energies observed for the Ni^{II} and Ni^{III} complexes examined and suggesting that thiolate donors might play a role in the redox chemistry of the Ni center in H_2-ase.[804] Reduction of a Ni^{II} complex to Ni^I generally results in a larger shift in K-edge energy,[61,378] although no S-ligated Ni^I complexes have been examined by this technique. It is noteworthy that no synthetic Ni *thiolate* complex in an oxidation state other than +2 has been characterized by EXAFS or X-ray diffraction, making it difficult to draw conclusions about the structural properties of the Ni centers in H_2-ase or CODH from the XAS data obtained from the different oxidation states of these enzymes.

ii. Redox Studies

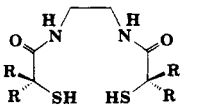
The groups of Holm and Yamamura have studied the structural and redox chemistry of Ni complexes of several S_2N_2 chelates of type **73–75**. These form (with one exception[720]) square planar Ni^{II} complexes,[717,719,721–724] which exhibit chemically reversible oxidations at $E_{1/2} = -0.04$ to -0.42 V *vs* SCE (Table 6).[717,723,797] The resultant oxidized Ni^{III} species



73
E = C(O), $embH_4$
E = CH_2, $ebmbaH_2$



74
$tsalenH_2$



75
R = H, $emaH_4$
R = Me, $emiH_4$

exhibit EPR spectra with $g_\perp > g_\parallel$,[717,797] consistent with a $(d_{z^2})^1$ ground state and similar to those shown by H_2-ase, but contrasting with the $g_\parallel > g_\perp$ pattern and $(d_{xy})^1$ ground state shown by square-planar Ni^{III} tetrathiolates[662,663] (section IX.B); this difference in electronic configuration may reflect solvent coordination to $[Ni^{III}(L)]^{n-}$ [725] (L = emb^{2-}, $ebmba^{2-}$, ema^{2-}, emi^{2-}; **73**, **75**). Addition of excess pyridine to the oxidized species affords five-coordinate monoadducts, whose EPR spectra show the $g_\perp > g_\parallel$ pattern and $(d_{z^2})^1$ ground state expected for a square-pyramidal Ni^{III} center, and superhyperfine coupling to one ^{14}N nucleus (*e.g.* for [Ni^{III}(emb)(py)]$^-$; $g_1 = 2.34$, $g_2 = 2.27$, $g_3 = 2.01$, $A_3\{^{14}N\} = 21.0$ G).[717,797]

Krüger and Holm have also investigated the redox chemistry of 2,6-di(mercaptomethyl)pyridine ($pdmtH_2$) and pyridine-2,6-bis(thiocarboxylic acid) ($pdtcH_2$) derivatives of Ni^{II}. The former ligand affords the square-planar $Ni^{II/II}$ dimer $[Ni(pdmt)]_2$ (*vide infra*), which is readily cleaved by thiolates to give [Ni(pdmt)(SR)]$^-$ (R = Et, Ph); the mononuclear species show ligand-centered oxidative processes, affording $[Ni(pdmt)]_2$ and RSSR on coulometric oxidation (reaction 76).[642] In contrast, reaction of $[Ni(OAc)_2]\cdot 4H_2O$ with $pdtcH^-$ affords the octahedral *trans*-S_4N_2 complex $[Ni(pdtc)_2]^{2-}$ (Figure 39), which shows a chemically reversible oxidation at $E_{1/2} = -0.085$ V *vs* SCE.[798] Together with the square-planar Ni^{II} tetrathiolates described in section IX.B, $[Ni(pdtc)_2]^{2-}$, and the compounds $[Ni(emb)]^{2-}$, $[Ni(ebmba)]^{2-}$, $[Ni(ema)]^{2-}$, and $[Ni(emi)]^{2-}$ (**73** and **75**) form the small class of "low-potential" Ni S-donor complexes, whose $Ni^{II/III}$ oxidation potentials approach that shown by H_2-ase (Table 6).[717] Low-potential $Ni^{II/III}$ couples have also been reported for Ni^{II} complexes of ligands related to $pdtc^{2-}$ containing oximate rather than thiolate donors,[718,798] although these have limited biological relevance.

$$[Ni^{II}(pdmt)(SR)]^- \xrightarrow{-e^-} [Ni^{II}(pdmt)]_2 + {}^1/_2RSSR \quad (76)$$

Mascharak and co-workers have shown that the trigonal-bipyramidal complexes [Ni^{II}(SR)$_2$(L)] (R = aryl; L = terpy, DAPA; Figure 35, *vide supra*) are reduced by dithionite to form moderately stable [Ni^I(SR)$_2$(L)]$^-$ species, which give EPR spectra consistent with five-coordinate d^9 ions with a $(d_{x^2-y^2})^1$ ground state ($g_\parallel = 2.25$, $g_\perp = 2.13$).[529–531] Interestingly, incubation of the reduced solutions with CO reversibly affords adducts assigned as the unusual octahe-

dral Ni^{I} derivatives $[Ni(SR)_2(L)(CO)]^-$ ($g_1 = 2.24$, $g_2 = 2.13$, $g_3 \approx 2.03$). Similar Ni^{I} adducts with H^-, CN^-, and CH_3^- were also reported; importantly, the EPR spectra of $[Ni(SR)_2(terpy)(CO)]^-$ and $[Ni(SR)_2(terpy)(H)]^{2-}$ (R = 2,4,6-Pr^i_3-C_6H_2) are very similar (Table 6), suggesting that the latter is best formulated as a Ni^{I} complex bearing a hydrido ligand and mimicing the small changes in EPR spectra observed upon CO inhibition of the Ni-C state of H_2-ase (section VII-I.D).[530] The complex $[Ni(SPh)_2(DAPA)]$ is also oxidized by $[Fe(CN)_6]^{3-}$ to a species whose EPR spectrum in DMF ($g_\perp = 2.21$, $g_\parallel = 2.03$) is suggestive of an octahedral species $[Ni^{III}(SPh)_2(DAPA)(solv)]^+$, and which itself forms a Ni^{III} cyanide adduct;[531] $[Ni(SPh)_2(DAPA)]^-$ and $[Ni(SPh)_2(DAPA)]^+$ can be directly interconverted in solution with the appropriate redox agent (Figure 36). This is the only Ni thiolate or thioether complex yet reported to afford observable and interchangeable Ni^{III} *and* Ni^{I} derivatives, which is particularly noteworthy given the similarity of the XAS spectra obtained from $[Ni(SR)_2(terpy)]$ to those reported for H_2-ase in the Ni-C oxidation state.[530] Electrochemical half-potentials for these redox processes were not quoted.

The thiolate-bridged dimer of square-planar Ni^{II} centers $[Ni(memta)]_2$ ($memtaH_2 = \{HSC_2H_4\}_2NC_2H_4SMe$) shows a quasireversible one-electron oxidation by cyclic voltammetry in CH_2Cl_2, with $E_{1/2} = -0.35$ V *vs* Fc/Fc^+.[643] Controlled potential electrolysis beyond this potential affords an EPR-active product ($g_1 = 2.17$, $g_2 = 2.11$, $g_3 = 2.07$) formulated as the mixed-valent $Ni^{II/III}$ dimer $[Ni(memta)]_2^+$, although this was not structurally characterized. Oxidation of the dimeric complex $[Ni(P\{o\text{-}C_6H_4S\}_3)]_2^{2-}$ ($E_{1/2} = -0.57$ V *vs* SCE in DMF) also affords a valence-delocalized $Ni^{II/III}$ species, $[Ni(P\{o\text{-}C_6H_4S\}_3)]_2^-$ ($g_1 = 2.12$, $g_2 = 2.09$, $g_3 = 2.03$):[715] the oxidation is accompanied by a substantial structural rearrangement (Figure 40), from a centrosymmetric dimer of square-planar Ni^{II} centers linked by arms of the ligands [Ni–S = 2.174(4)–2.233(4) Å], to a dimer of square-pyramidal $Ni^{2.5+}$ ions with two bridging thiolate donors [Ni–S = 2.238(2)–2.260(2) Å]. The mononuclear analogue $[Ni(PhP\{o\text{-}C_6H_4S\}_2)(S\text{-}2\text{-}Ph\text{-}C_6H_4)]$ shows no oxidative behavior. It remains to be seen whether a similar structural rearrangement, possibly involving the noncoordinated thioether donor, plays a role in the stabilization of $[Ni(memta)]_2^+$. In contrast to these results, reversible *reductive* processes ($E_{1/2} = ca.$ −0.85 V *vs* Ag/AgCl) were observed by cyclic voltammetry for other S-bridged Ni dimers containing amine and pyridyl thiolate chelates,[806] including $[Ni(pemta)]^{2+}$ (pemtaH = *N*-[2-(2-pyridyl)ethyl]-*N*-[2-(2-methylthio)ethyl]-2-aminoethanethiol) which is structurally analogous to $[Ni(memta)]_2$ but for the presence of one terminal pyridyl, rather than thiolate, donor per nickel ion.[739] The one-electron electroreduction of ^{61}Ni-enriched $[Ni(pdmt)]_2$ ($E_{1/2} = -1.21$ V *vs* SCE in DMF) affords an EPR-active product showing hyperfine coupling to two ^{61}Ni centers, leading to its formulation as the valence-delocalized $Ni^{II/I}$ dimer $[Ni(pdmt)]_2^-$.[642]

Several Ni^{II} amine/thioether macrocyclic complexes show chemically reversible oxidative behavior within the range $0.8 < E_{1/2} < 1.3$ V *vs* Fc/Fc^+ (Table 6).[779,780,783–785,788,789,807] Examination of the $Ni^{II/III}$ couples in MeCN for the series $[Ni(L)_2]^{2+}$ (L = [9]-aneN$_3$, $E_{1/2} = +0.56$ V *vs* Fc/Fc^+;[807] L = [9]aneSN$_2$, $E_{1/2} = +0.79$ V;[807] L = [9]aneS$_2$N, $E_{1/2} = +0.88$ V;[784] L = [9]aneS$_3$, $E_{1/2} = +0.98$ V;[710,711] **68**) shows that replacement of an amine donor by a thioether in these complexes raises the $Ni^{II/III}$ oxidation potential, despite the steric compression on the metal ion for thia over aza macrocyclic complexes caused by the increased bulk of the macrocyclic sulfur heteroatoms.[701] This trend in $Ni^{II/III}$ oxidation potentials has also been noted for Ni complexes of other polychelate and macrocyclic amine/thioether ligands.[758,789] All oxidized $[Ni^{III}(L)]^{n+}$ species of this type show EPR spectra consistent with octahedrally coordinated d^7 ions, some examples like $[Ni(bc\text{-}[19]aneSN_4)(F)]^{2+}$ (bc-[19]aneSN$_4$ = 15-thia-1,5,8,12-tetraazabicyclo[10.5.2]-nonadecane, **77**)[783] showing anion or solvent coordination to complete the Ni^{III} coordination sphere

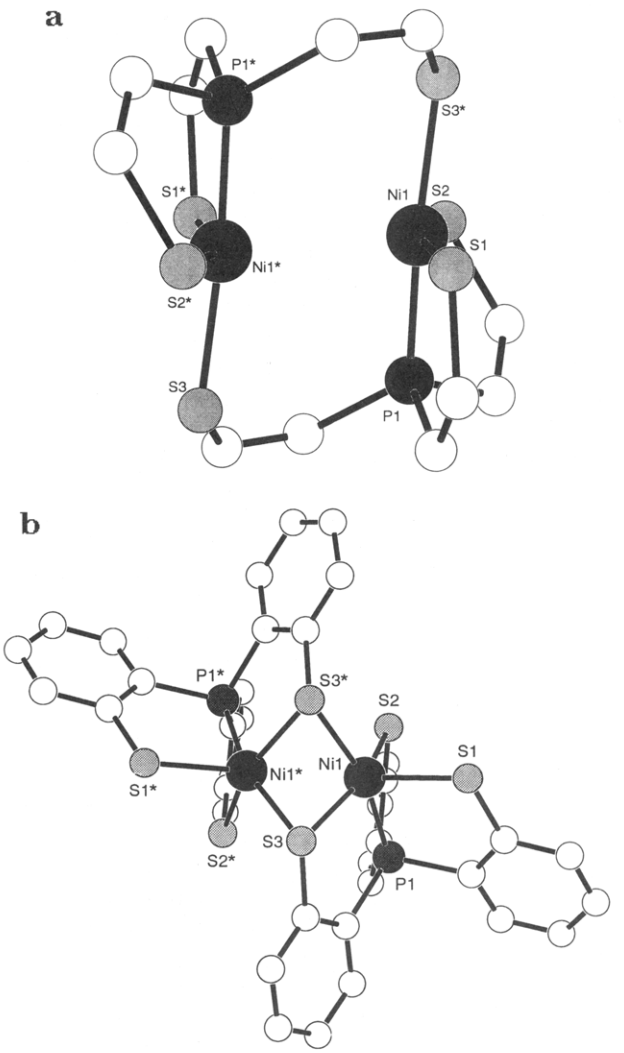
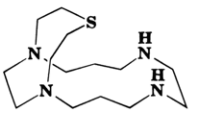


Figure 40. Structures of (a) $[Ni(P\{o\text{-}C_6H_4S\}_3)]_2^{2-}$, (b) $Ni(P\{o\text{-}C_6H_4S\}_3)]_2^-$. (Reprinted from ref 715. Copyright 1992 American Chemical Society.)



bc-[19]aneSN$_4$
77

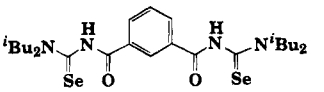
(Table 6). Unusually, some octahedral Ni^{III} species containing amine/thioether donor ligands exhibit EPR spectra with $g_{\|} > g_{\perp}$, consistent with a $(d_{x^2-y^2})^1$ ground state and implying a tetragonally compressed stereochemistry about the Ni^{III} ion.[757,759,788]

Several of the above compounds, together with other Ni^{II} complexes of linear chain amine/thioether chelates, also exhibit quasireversible or irreversible reductive processes by cyclic voltammetry, typically with $-0.7 \geq E_{1/2} \geq -1.2$ V *vs* SCE,[768,783-785,788,793,794,796] although very few reduced products derived from these complexes have been detected spectroscopically. The instability of these Ni^{I} species may arise from radical-induced C–S bond cleavage within the ligand backbone (section V.B),[384] or may reflect the stereochemical preference of Ni^{I} for four- or five-coordination;[7,8] the one-electron reduction of $[Ni([9]aneS_2N)_2]^{2+}$ (**68**) is followed by rapid loss of one macrocyclic ligand and the formation of tetrahedral Ni^{I} products in MeCN (reaction 69; X = NH; L = MeCN, PPh_3).[784]

The $Ni^{II/I}$ couple shown by [Ni(BME-DACO)] (**43**; $E_{1/2} = -1.94$ V *vs* NHE) becomes dramatically less negative upon methylation of the ligand thiolate donors (Table 6);[796] the observed $Ni^{II/I}$ potentials show a dependence on the halide anion present, consistent with the weak anion coordination observed for $[Ni^{II}(R_nBME\text{-}DACO)]X_n$ (**43**; $X^- = Cl^-$, Br^-, I^-; R = Me, n = 1, 2; $R_2 = C_3H_6$, CH_2OCH_2, n = 2) in the solid state.[794,796] The reduced products [Ni(MeBME-DACO)] and $[Ni(Me_2BME\text{-}DACO)]^+$ exhibit axial EPR spectra typical of square planar or square pyramidal Ni^{I} species, with $g_{\|} = 2.25$ and $g_{\perp} = 2.07$.[796] These two complexes, together with some macrocyclic [Ni(alkyl)BME-DACO)]$^+$ thioether derivatives[794] and $[Ni(N\{C_2H_4SR\}_3)(CO)]^+$ (R = Pr^i, Bu^t; Figure 25, *vide supra*), are the only Ni^{I} thioether complexes not containing abiological coligands[808,809] that are stable enough to be observed in bulk solutions.

D. Nickel Complexes of Selenolate and Selenoether Ligands

Although the existence and properties of [FeNiSe] H_2-ase are now well documented, the literature concerning Ni selenolate and selenoether complexes is extremely sparse.[691,830] Only two homoleptic Ni^{II} complexes of saturated selenolate ligands have thus far been described: $[Ni(Se_4)_2]^{2-}$ [831,832] and $[Ni(eds)_2]^{2-}$ [833] ($edsH_2$ = ethane-1,2-diselenol) both exhibit square planar structures in the solid state with Ni–Se bonds of 2.30–2.32 Å. In addition to these, the following square-planar complexes of unsaturated diselenolates and their oxidized derivatives have been reported: $[Ni(bzds)_2]^-$ ($bzdsH_2$ = benzene-1,2-diselenol),[834] $[Ni(tds)_2]^{2-/-}$ ($tdsH_2$ = bis(trifluoromethyl)ethene-1,2-diselenol),[835-837] $[Ni(Se_2C{=}C\{CN\}_2]_2^{2-}$,[838] $[Ni(C_3S_xSe_{5-x})_2]^{2-/-}$ (x = 0, 2, 3),[839-845] $[Ni(Se_2CNR_2)_2]$,[846] $[Ni(Se_2COR)_2]$,[847] and $[Ni(Se_2PR_2)_2]$.[848] These generally exhibit structural and (where reported) redox chemistry similar to their sulfur analogues (section IX.B), so that 1,2-diselenolenes form oxidized species with predominantly Ni^{II}-stabilized ligand radical cation character,[834,837,845,849] while the cation $[Ni^{IV}(Se_2CNBu^n_2)_3]^+$ [850,851] has been structurally characterized. Interestingly, the complex $[Ni^{IV}(Se_2C{=}C\{CN\}_2)_3]^{2-}$ has also been isolated;[838] the analogous dithiolate species could not be obtained. The mixed chalcogen donor complexes $[Ni(tbs)_2]^{2-}$ ($tbsH_2$ = *o*-mercaptobenzeneselenol),[852] $[Ni(SeSCNR_2)_2]$ (R = alkyl),[853] $[Ni(SeSC{=}C\{CN\}_2)_2]^{2-}$,[854] and $[Ni(SeOCNBu_2)_2(PPh_3)_2]$[855] have been synthesized, while the crystal structure of $[Ni(Bu^iphthSe)]_2$ ($Bu^iphthSeH_2$ = 1,1,1′,1′-tetraisobutyl-3,3′-isophthaloylbis(selenourea), **78**) has recently been described [Ni–Se = 2.281(2), 2.251(2) Å].[856]



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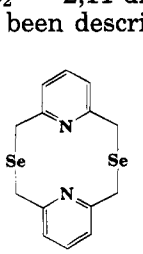
Mascharak *et al.* have communicated the structures of the mixed N/Se-donor trigonal-bipyramidal complexes $[Ni(Me_2phen)(SePh)(\mu\text{-}SePh)]_2$ and [Ni(terpy)$(SeR)_2$], and the tetrahedral $[Ni(Me_2phen)(SeR)_2]$ (R = 2,4,6-Pr^i_3-C_6H_2; Me_2phen = 2,9-dimethyl-1,10-phenanthroline).[857] The Ni–Se distances in the five-coordinated compounds are comparable with those in [NiFeSe] H_2-ase, at 2.39–2.47 Å; however, [Ni(terpy)$(SeR)_2$] shows only reductive redox chemistry, forming an observable Ni^{I} species upon reaction with dithionite in DMF that exhibits an EPR spectrum similar to that given by $[Ni(terpy)(SR)_2]^-$ (Table 6, section IX.C), with $g_{\|} = 2.249$ and $g_{\perp} = 2.103$. While $[Ni(terpy)(SeR)_2]^-$ readily affords a CO adduct, unlike the corresponding thiolate complexes,[530] no Ni^{I} hydride adduct was formed upon reaction of [Ni(terpy)$(SeR)_2$] with BH_4^-, which is consistent with the proposal that substitution of Se for S at the active site of H_2-ase may decrease the stability of a hydrido intermediate in the enzymic catalytic cycle. The Ni^{I} hydroselenide complex [Ni(tdpme)(SeH)] (tdpme = $MeC\{CH_2PPh_2\}_3$) has been synthesized,[858] as have some square-planar Ni^{II} complexes of N/O/Se-donor *ortho*-selenoxybenzaldimino,[859,860] *ortho*-selenoxybenzofurylaldimino,[861] and 3-selenoxypyrazol-4-ylaldimino[862,863] Schiff base ligands, some of which have been structurally characterized and show square-planar/tetrahedral equilibria in solution.[860,862,863]

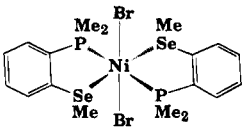
The complexation of Ni^{II} halides by some di- and linear tetraselenoether chelates has been investigated, with octahedral complexes of general formula $\{[NiL_2X_2]\}_x$ (L = $Pr^iSeC_2H_4SePr^i$, $X^- = Cl^-$, Br^-;[864] $L_2 = \{MeSeC_2H_4Se\}_2C_3H_6$, $X^- = I^-$ [865]) being obtained. No Ni complex of a homoleptic polyselenoether crown has thus far been reported, although the structure of the octahedral complex *cis*-$[Ni(Py_2Se_2)(OH_2)_2]^{2+}$ (Py_2Se_2 = 2,11-diselena[3.3](2,6)pyridinophane, **79**) has been described (Ni–Se = 2.48



79

Å, Ni–N = 2.08 Å, Ni–O = 2.07 Å).[866] Several other Ni^{II} Se-ligated complexes containing organometal-

lic[867] or P-donor[868,869] ligands have also been synthesized, although none has been crystallographically characterized; in particular, [Ni{*o*-C_6H_4(PMe_2)(SeMe)}$_2$$Br_2$] (**80**) is oxidized by Br_2 to the corresponding cationic Ni^{III} derivative ($\langle g \rangle$ 2.15, $\langle A\{^{79,81}Br\} \rangle$ 43 G),[869] which is thus far the only known Ni^{III} complex to contain a Se-donor.



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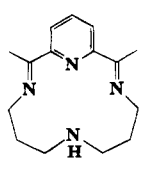
E. Reactivity of Nickel Complexes toward H_2 and the Reduction of H^+

The first report of a non-organometallic Ni^{II} complex interacting directly with H_2 was described by Crabtree *et al.*, who reported that the square-planar (in solution) N_2S_2 complex [Ni(tssH_2)$_2$]$^{2+}$ (**50**) catalyzes H^+/D_2 exchange (reaction 54) between D_2 and the hydroxyl proton on the tssH_2 ligand under acidic conditions.[870] This was proposed to occur via hydrogen bonding between a dangling tssH_2 hydroxyl group and an η^2-coordinated H_2 ligand (Figure 41), although this result has subsequently proven difficult to reproduce.[871] The 1:1 complex [Ni(tss)]$_2$ also catalyzes silane alcoholysis,[871] a reaction generally considered indicative of η^2-Si-H binding.[872] This reaction was shown to proceed through a Ni–H intermediate, leading to the proposed mechanism shown in Figure 42. The alcoholysis reaction was also inhibited by H_2, suggesting competitive H_2 binding at the Ni active site (Figure 42), although neither in this case nor in the H^+/D_2 exchange reaction was a Ni(η^2-H_2) species directly observed. No Ni^{II} dihydrogen complexes are known;[872,873] the isoelectronic species *trans*-[Pt(PBu^t_3)$_2$H(H_2)]$^+$ is the only d^8 η^2-H_2 complex to have been unambiguously characterized to date.[874]

While no synthetic Ni-containing H_2 oxidation homogeneous catalyst has been described, the reduction of H^+ to H_2, which is also catalyzed by most H_2-ases, is technically easier to study and has therefore received more attention.[875] The square-planar Ni^{II}-stabilized ligand radical anion [Ni^{II}(PydieneN$_4^{\bullet-}$)]$^+$ (PydieneN$_4$ = 2,12-dimethyl-3,7,11,17-tetraazabicyclo-[11.3.1]heptadeca-1(17),2,11,13,15-pentaene, **81**), which



81

had previously been shown to react with a variety of substrates to form five-coordinate Ni^I adducts,[528] also reduces protons.[876] This was proposed to proceed by protonation of the reduced cation to form a Ni^{III}–hydrido species, which could then react with a second electron and proton (reactions 82–85), although none of the postulated intermediates was detected.

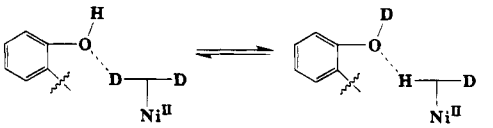


Figure 41. Proposed mechanism of D_2/H^+ exchange catalysis by [Ni(tssH_2)$_2$]$^{2+}$ (tssH_2 = *o*-(OH-C_6H_4CH=NNHC(S)NH_2, **50**). Adapted from ref 870.

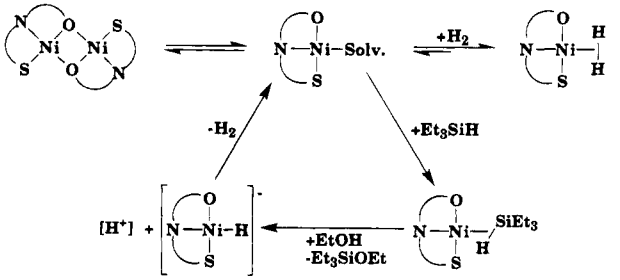


Figure 42. Proposed mechanism of silane alcoholysis by [Ni(tss)]$_2$ (tssH_2 = *o*-(OH)-C_6H_4CH=NNHC(S)NH_2, **50**) and its inhibition by H_2. Adapted from ref 871.

$$[Ni^{II}(L)]^{2+} + e^- \rightarrow [Ni^{II}(L^{\bullet-})]^+ \quad (82)$$

$$[Ni^{II}(L^{\bullet-})]^+ + H^+ \rightarrow [H{-}Ni^{III}(L)]^{2+} \quad (83)$$

$$[H\text{-}Ni^{III}(L)]^{2+} + e^- + H^+ \rightarrow [H_2{-}Ni^{II}(L)]^{2+} \quad (84)$$

$$[H_2{-}Ni^{II}(L)]^{2+} \rightarrow [Ni^{II}(L)]^{2+} + H_2 \quad (85)$$

The aqueous reduction of H^+ by several other electrogenerated Ni^I species has been noted, most commonly as a side reaction to the aqueous electro- or photoreduction of CO_2 (section VII.B),[489,502,507,512,877] and is believed to follow a similar double reduction/double protonation mechanism.[502] The catalytic reduction of protons by [Ni^{II}(qdt)$_2$]$^{2-}$ (**67**)[681] and their stoichiometric reduction by [Ni^{II}_2(P{*o*-C_6H_4S}$_3$)$_2$]$^{2-}$ [878] (section IX.C, Figure 40) have recently been communicated; both reactions presumably pass through Ni^{III} intermediates, although full mechanistic details are not yet available. The reduction of H^+ by [Ni^I(mnt)$_2$]$^{3-}$ at a dropping Hg electrode has been noted;[879] a theoretical study of this reaction supported a mechanism very similar to that above (reactions 82–85), with a coordinated thiolate donor facilitating proton transfer to the Ni-bound hydride (Figure 27).[880]

The catalytic electroreduction of protons by Ni^{II} halides in the presence of cysteine, cystine, selenocysteine, or cysteinyl dipeptides has been extensively studied by Calusaru, Banica, and co-workers,[881–889] and proceeds via the two-electron reduction of a [Ni^{II}(cys)(L)$_x$]$^{n+}$ precursor to a Lewis basic Ni^0 species containing bound cysteine, which has then been proposed to react as in Figure 43. The authors have remarked that, excepting the differences in Ni oxidation states, this mechanism is similar to that favored by several authors for H_2 oxidation by H_2-ase.[889]

Although not a Ni complex, [Cp*Ru(dppm)H] (Cp* = $C_5Me_5^-$; dppm = $Ph_2PCH_2PPh_2$) has been shown to serve as a functional H_2-ase model, in that it catalyzes the reduction of analogues of NAD^+ (a biological redox cofactor that is reduced by several H_2-ases *in vivo*) by H_2 in the presence of base (Figure 44).[890] All intermediates shown in the catalytic cycle

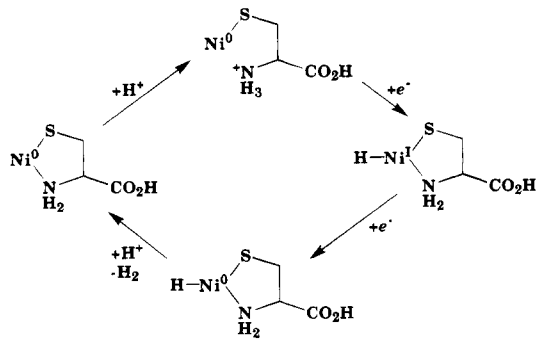


Figure 43. Proposed mechanism for the electrocatalytic reduction of protons by Ni cysteine complexes. Adapted from ref 889.

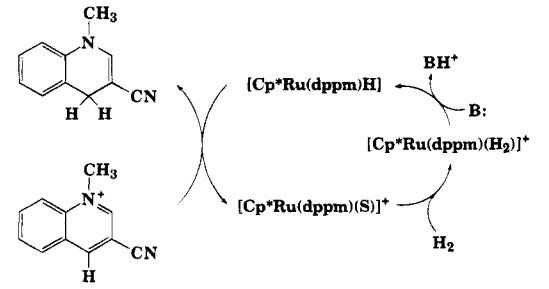


Figure 44. The catalytic reduction of 3-cyano-*N*-methylquinolium, a NAD^+ model compound, by [Cp*Ru(dppm)H] and H_2 (Cp* = $C_5Me_5^-$, dppm = $Ph_2PCH_2PPh_2$). Adapted from ref 890.

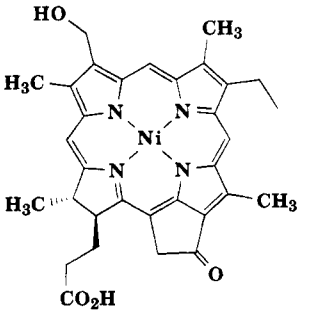
were spectroscopically characterized, while the Ru → substrate hydride transfer was shown to be a single-step process.

X. Concluding Remarks

In writing this article we have tried to demonstrate the currently limited knowledge of the structural and catalytic chemistry of the four currently recognized Ni enzymes and, by describing the current state of the art in relevant Ni coordination chemistry, to suggest areas of investigation by which the inorganic chemist might contribute to the biochemists' perception of these problems. Conversely, we have also tried to summarize the biochemical data from these enzymes in the language of the inorganic chemist, and to highlight what we believe to be relevant areas where knowledge of Ni coordination chemistry is currently lacking.

For what at one time appeared to be a simple Ni^{II} complex, containing nonredox-active Ni^{2+} ions in an octahedral N/O donor ligand environment, the spectroscopic and magnetic properties of urease have thus far defied more detailed analysis; the coordination geometry about the two Ni^{2+} ions in the urease active site, their relationship to each other and their roles in enzyme catalysis are all still open to considerable debate. In particular, there are inconsistencies between the currently favored interpretation of the magnetic properties of urease, which have been proposed to arise from a mixture of magnetically isolated high-spin and low-spin five-coordinate Ni^{2+} fractions within the enzyme, and the properties of analogous substituted Ni enzymes and model complexes which show exclusively high-spin configurations. There has been only limited interest in the structural and functional modeling of urease by inorganic chemists, possibly because of a perceived mundanity of the enzymic Ni coordination sphere and the generally limited efficiency of Ni^{2+} as a Lewis acid catalyst *in vitro*. The resultant lack of relevant dinuclear Ni_2 model complexes makes it extremely difficult to draw conclusions from chemical data obtained from the enzyme, however, while the factors contributing to the extraordinarily efficient hydrolytic catalysis by such a nominally poor Lewis acid as Ni^{2+} in urease are still unknown.

Although the role of Ni in the catalytic cycle of MCR has not been settled, the Ni complex in MCR is probably the best defined of the four enzymes described in this article, in that the enzymic Ni content is known to be present as the Ni tetrapyrrole F_{430}, axially ligated to (probably two) N/O donors. In this case, biomimetic chemistry has made significant contributions to the understanding of this enzyme. Model studies have shown F_{430} to have a high affinity for axial ligation and to possess the necessary flexibility within the corphin ligand to accommodate redox processes at Ni, and both $Ni^{I}F_{430}$ and other reduced Ni tetrapyrroles have been shown to be active toward the cleavage of C−X (X = halide) and activated C−S bonds. In the case of [Ni(OEiBC)], which of all known Ni tetrapyrroles most closely reproduces the redox and structural chemistry of F_{430}, these cleavage reactions occur via a nucleophilic attack of Ni^{I} at the C−X bond; this nucleophilicity is enhanced by axial ligand binding to Ni, as observed upon incorporation of F_{430} into the MCR polypeptide. Hence, much of the structural and reaction chemistries that F_{430} might be expected to undergo *in vivo* seem established, although in the absence of corroborating mechanistic data from MCR these conclusions must still be regarded as tentative. Given the role played by F_{430} in methanogenic bacterial metabolism, it is intriguing that an unusual Ni tetrapyrrole (tunichlorin, **86**) which appears to perform an



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Tunichlorin

as yet unknown metabolic function[891] has been isolated from a tunicate.[892] The chemical properties of this novel product have not been analyzed, however.

It is instructive to compare the properties of the Ni sites in CODH and H_2-ase. The Ni K-edge XAS spectra reported for CODH show only small differences from those obtained from H_2-ase, the data for both enzymes being consistent with five-coordinate Ni ions containing approximately two S- and three N/O-donor ligands (**57**);[442,446,581,582] in each case, structural models containing square-planar Ni tetrathi-

olate ions (**56**) have also been proposed.[443,444,578] In addition, the most recent structural data has led to the proposition that the Ni centers in both CODH and H_2-ase may be chemically linked to a $[Fe_4S_4]$ cluster via a thiolate or sulfide bridge (**40**);[446,582] for the CODH center A, this proposition is supported by EPR spectroscopy. In addition, the EPR spectra of the [center A-CO]$_{red}$ (Ni^I) site in CODH and of CO-inhibited H_2-ase, which probably contains Ni^I, have each been interpreted on the basis of a $S = {}^1/_2$ Ni ion possessing a $(d_{z^2})^1$ ground state with comparable, although not identical, g values. However, despite these similarities, the redox properties of the two Ni sites are very different, in that CODH shows reductive chemistry with no observable Ni^{III} state, while that of H_2-ase shows facile oxidative behavior, being isolated as a Ni^{III} species in air; the involvement of the Ni^I state in the H_2-ase redox cycle remains to be proven. Given this fundamental difference, despite the XAS results it seems unlikely that the $[Ni(\mu\text{-}S)\text{-}Fe_4S_4]$ structural motif can be present in both enzymes without substantial differences between them in the arrangement of ligands about the Ni ion, or in the redox properties of the adjoining Fe/S cluster. In addition, while the $Ni^{II/III}$ oxidation potentials of H_2-ase are well reproduced by square-planar Ni tetrathiolates, model studies imply that the reductive chemistry exhibited by CODH could not be shown by an Ni ion with this geometry, unless at least two of the S ligands to Ni were derived from methionine thioether donors, rather than cysteine thiolates.

It is also interesting that for H_2-ase there is conflict between EPR data, which show significant Ni-centered character for paramagnetic redox states of this enzyme, and XAS results which imply little or no change in electron density and stereochemistry about Ni on redox cycling. These data could be taken to show that the unpaired spins at Ni are substantially delocalized onto the surrounding ligand sphere, as is generally the case in the presence of soft, strongly covalently bound ligands such as thiolates. Alternatively, the redox processes concerned might occur at a nearby cysteine or other protein residue that can interact weakly with the Ni ion, rather than involving the Ni ion directly. For some years a similar problem was also present for CODH, where Ni XAS and Mössbauer measurements of the center A and [center A-CO]$_{red}$ clusters imply little change in electron density at Ni *or* Fe between these two states. In the case of CODH, a spectroscopic study was recently presented that shows that the reductive carbonyl binding reaction of the CODH A cluster occurs at the $[Fe_4S_4]$ portion of this center, thus resolving this difficulty and calling into question the role of the Ni ion in acetyl-CoA synthesis.[451] It remains to be seen whether a similar result will be presented for H_2 or CO binding by H_2-ase; although hyperfine coupling to ^{57}Fe was not observed for the (inactive) Ni-A signal,[559] no appropriate enrichment study of the *active* Ni-C state has been described.

While the structural and redox chemistry of a large number of Ni complexes of S-donor ligands have been reported, the number of such complexes relevant to current theories concerning the structures of the CODH and H_2-ase Ni sites is limited; in particular, the number of redox active Ni *thiolate* complexes is extremely sparce, and in no case are EPR ^{61}Ni hyperfine coupling parameters, or structural data from X-ray crystallography or XAS, available from the resultant redox products. Hence, at this point it is difficult for the coordination chemist to contribute to the debate concerning the role of Ni in H_2-ase, and much work in this area remains to be done.

In addition to the aforementioned characterization of tunichlorin (**86**), there are other partially characterized aspects of Ni biochemistry that may in time provide material of interest to the coordination chemist. In particular, the mechanisms of Ni accumulation and transport in Ni-dependent organisms are not understood, although genes responsible for Ni insertion into all four Ni enzymes have been identified.[18,19] One such Ni-transport protein from a ureolytic bacterium ("UreE") has recently been isolated and characterized as binding 6 mol of Ni^{2+} in an octahedral histidine-rich N/O-donor environment.[893] The discovery of a [NiFe] H_2-ase that exhibits activity toward both proton reduction and sulfur reduction (to H_2S)[894] is also intriguing, although it is not known whether this latter reaction is Ni-dependent, while there is circumstantial evidence to suggest that Ni may play a role in a cobalamin-dependent metabolic pathway in mammals.[895] Clearly, much of the biochemistry of nickel remains to be elucidated.

Note Added in Proof

Since the original submission of this article, additional results relevant to the biochemistry and modeling of urease,[896] MCR,[897,898] CODH,[899-902] and H_2-ase[903-910] have appeared.

XI. Acknowledgments

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XII. Abbreviations

asp^-, aspH	aspartic acid
BME-DACOH$_2$	*N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane
bpy	2,2'-bipyridine
Bu	butyl
Bu^t	*tert*-butyl
CoA, $CoAS^-$	coenzyme A
CODH	carbon monoxide dehydrogenase
cyclam	1,4,8,11-tetraazacyclotetradecane
cys^-, cysH	cysteine
DAPA	2,6-bis[1-(phenylimino)ethyl]pyridine
DMF	dimethylformamide
DMSO	dimethyl sulfoxide
DPV	differential pulsed voltammetry
$edta^{4-}$, edtaH$_4$	1,2-diaminoethane-*N,N,N',N'*-tetraacetic acid
EPR	electron paramagnetic resonance
ENDOR	electron-nuclear double resonance

$edtH_2$	ethane-1,2-dithiol
Et	ethyl
EXAFS	extended X-ray absorption fine structure
Fc	ferrocene
glu^-, gluH	glutamic acid
hmc	5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane
H_2-ase	hydrogenase
his^-, hisH	histidine
iBC^{2-}	2,3,7,8-tetrahydroporphyrin (isobacteriochlorin) dianion
MCD	magnetic circular dichroism
MCR	Methyl-*S*-coenzyme-M methylreductase
Me	methyl
Me_2-bpy	4,4′-dimethyl-2,2′-bipyridine
MeIm	*N*-methylimidazole
mes	mesityl
MeSCoM	*S*-methyl-coenzyme M ($MeSC_2H_4SO_3^-$)
$mntH_2$	dimercaptomaleonitrile (*cis*-1,2-dicyanoethene-1,2-dithiol)
$mptdsH_2$	bis[2-[(2-mercaptophenyl)thio]ethyl] sulfide
$ndtH_2$	norbornane-2,3-*exo*-*cis*-dithiol
NMR	nuclear magnetic resonance
$OEiBC^{2-}$	2,3,7,8,12,13,17,18-octaethylisobacteriochlorin dianion
oep^{2-}	2,3,7,8,12,13,17,18-octaethylporphyrin dianion
$pdtcH_2$	pyridine-2,6-bis(thiocarboxylic acid)
$pdmtH_2$	2,6-di(mercaptomethyl)pyridine
Ph	phenyl
$porph^{2-}$	porphyrin dianion
Pr	propyl
Pr^i	isopropyl
py	pyridine
$salenH_2$	1,2-bis[[(2-hydroxyphenyl)methylene]amino]ethane
$SDPDTP^-$	5,20-diphenyl-10,15-bis(*p*-tolyl)-21-thiaporphyrin anion
$STPP^-$	5,10,15,20-tetraphenyl-21-thiaporphyrin anion
tdpme	1,1,1-tris[(diphenylphosphino)methyl]-ethane
terpy	2,2′,6′,2″-terpyridine
tmc	1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
$tmtssH_2$	2′-hydroxy-4′,5′-dimethylacetophenone 4-methyl-thiosemicarbazone
Tol	tolyl
$tpttdH_2$	2,2,11,11-tetraphenyl-1,5,8,12-tetrathiadodecane
$tssH_2$	salicylaldehyde thiosemicarbazone
XAS	X-ray absorption spectroscopy
XANES	X-ray absorption near edge spectroscopy
XPS	X-ray photoelectron spectroscopy
[9]$aneS_3$	1,4,7-trithiacyclononane

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