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Redox Chemistry of Nickel Complexes in Aqueous Solutions

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1. Introduction

Before 1970, information concerning the redox chemistry of nickel in solution in general and in water in particular was very scarce. A handful of complexes featuring “atypical” oxidation numbers had been reported[1−4] but were generally regarded as chemical curiosities. During the last 3 decades, however, a number of hypervalent nickel complexes containing Ni^{III} and even Ni^{IV} as well as hypovalent Ni^{I} complexes have been prepared and characterized.

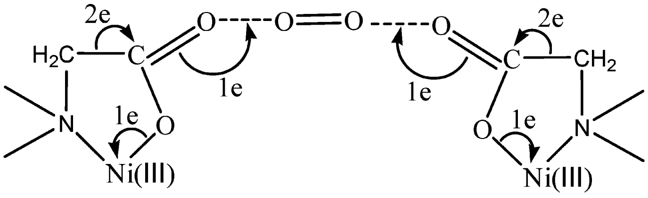
The increasing body of evidence of the involvement of Ni^{III} species in a number of enzymes, such as (NiFe)−hydrogenases,[5−9] both Ni^{I} and Ni^{III} (as Ni−CH_3) species in CO dehydrogenases[10−15] and in acetyl CoM synthase,[10−13,16−18] and more recent Ni^{III} in Ni−SOD[19,20] and Ni^{I} in methanogenic bacteria,[20−25] is the reason for the special attention on the redox chemistry of nickel.

The requirements for the stabilization of the d^6−d^9 nickel ions, Ni^{I}−Ni^{IV}, have been reviewed several times in the last 2 decades.[26−30] This review deals with the redox chemistry of nickel in aqueous solutions because the authors believe in its relevance to industrial−environmental as well as bioinorganic (enzymes) issues. The material is arranged by the redox couples, i.e., $Ni^{3+/2+}$, $Ni^{2+/+}$, and $Ni^{4+/3+}$ or/and $Ni^{4+/2+}$, with further subdivision in terms of the ligand donor type for $Ni^{3+/2+}$.

2. The $Ni^{3+/2+}$ Couple

2.1. Complexes with Amines and Amino-carboxylates as Donor Groups

Saturated amines provide a ligand field significantly greater than that of water and allow oxidation of Ni^{II} under a variety of conditions. Early studies indicated that indeed $Ni^{III}(NH_3)_n$ (**1**), $Ni^{III}(glycine)_2$ (**2**), and $Ni^{III}en_2$ (**3**) can be formed in slightly alkaline aqueous solutions, but these complexes are short-lived and decompose via oxidation of the ligands.[31−32] Furthermore, nickel is an electrocatalyst for the oxidation of these ligands.[33] Surprisingly, the Ni^{III} complexes with the amino-carboxylate ligands edta (**4**) and nta (**5**), via oxidation of the corresponding divalent complexes by hydroxyl radicals, are kinetically stable in deaerated solutions.[34−36] However, these Ni^{III} complexes react with dioxygen. The mechanism of this reaction was solved 20 years later using high-pressure pulse radiolysis and proved to be a cooperative oxidation of the ligands of two complexes by one molecule of dioxygen and the two central trivalent nickel ions,[37] probably via



EPR measurements pointed out that the electronic configuration of these Ni^{III} complexes is the low-spin one, although these ligands are usually weak field ligands.[34] In methanolic solutions, even the complex $[Ni^{II}en_2Cl_2]$ (**6**) can be oxidized by Cl_2; the trivalent complex thus obtained has an axial EPR spectrum consistent with a tetragonally elongated low-spin Ni^{III} complex.[38] Sulfate ions have a stabilizing effect on the complex as with tetraaza-macrocyclic complexes, see below. $[Ni^{II}bpy_3]^{2+}$ (**7**) and other tris(polypyridyl) (**8**) complexes can be oxidized electrochemically in 2 M $HClO_4$.[39] The $[Ni^{III}bpy_3]^{3+}$ has a lime-green color and has a redox potential of +1.72 V versus NHE.

These early studies indicated that trivalent nickel complexes can be stabilized in aqueous solutions. However, the observation that the Ni^{III} complexes

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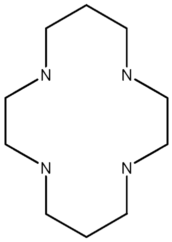
Dan Meyerstein was born in Jerusalem, Israel, in 1938. He received his M.Sc., in 1961, and Ph.D., in 1965, at The Hebrew University of Jerusalem. After a postdoctoral fellowship at Argonne National Laboratory in IL, he joined the faculty of the Ben-Gurion University, where he is a Professor Emeritus. Since 1995, he has been President of The College of Judea and Samaria in Ariel, Israel. He was president of the Israel Chemical Society. He received the Humboldt–Meitner research prize and the Kolthof prize. His research interests include mainly the kinetic and mechanistic studies of redox processes of transition-metal complexes in aqueous solutions with an emphasis on radical processes.

Eric Maimon was born in Beer-Sheva, Israel, in 1963. He graduated with a B.Sc. from Ben-Gurion University of the Negev in 1989. In 1992, he received his M.Sc. under the direction of Prof. Dan Kost in organic chemistry at Ben-Gurion University of the Negev. He worked until 1997 in the chemical industry as an organic chemist. In 1997, he joined the Analytical Chemistry Department at NRCN as a research scientist. The same year he started his Ph.D. studies at Ben-Gurion University of the Negev under the supervision of Prof. Dan Meyerstein and Prof. Haim Cohen. He received his Ph.D. in 2002, and since then, he has been a senior research scientist and the head of the analytical laboratory at NRCN. Dr. Maimon's main fields of interest are inorganic synthesis, especially metallo-macrocyclic compounds, redox chemistry of transition metals in solutions, and kinetics and mechanistic aspects of copper and nickel complexes studied by UV–vis and NMR techniques.

Haim Cohen was born in Rehovot, Israel, in 1945. He received his B.Sc. in Chemistry from Tel-Aviv University in 1968. He received his M.Sc. and Ph.D. in chemistry from the Feinberg Graduate School in the Weizman Institute of Science in Rehovot, Israel. He obtained his Ph.D. in physical chemistry in 1975 under the supervision of Prof. Dan Meyerstein and Prof. Ora Kedem. Since 1968 until 2004, he was employed in the NRCN as a chemist, and since 1975, he was employed as a senior research scientist. Since 1991, he has also been involved in research in the Chemistry Department at Ben-Gurion University as an adjunct associate professor, and in 2005, he was appointed as a professor in the Department of Biological Chemistry in the College of Judea and Samaria in Ariel. He spent sabbatical periods in Santa Barbara, CA, with Prof. Peter C. Ford, Witten-Hedrdecke, Germany, with Prof. Rudi van Eldik, Leiden, Holland, with Prof. Jan Redijk, and Calgary, Canada, with Prof. Fari Goodarzi. Prof. Cohen's main fields of interest are bioinorganic and homogeneous catalytic aspects of transition-metal complexes, metal carbon σ bonds chemistry, coal and ash chemistry and radiation chemistry as a tool to study uncommon oxidation states of transition metals.

Israel Zilbermann was born in Galati, Romania, in 1964. He received his B.Sc., M.Sc., and Ph.D. in chemistry from the Ben-Gurion University of the Negev. He received his Ph.D. in inorganic chemistry in 1995 under the supervision of Prof. Dan Meyerstein and Prof. Haim Cohen. Since 1994, he has been employed by NRCN as a research scientist, and since 1998, he has been employed as a senior research scientist in the Physical Chemistry Department. From 2002 until 2003, he spent a sabbatical year at the Radiation Laboratory at Notre Dame University, IN, with Prof. Dirk Guldi, working on the radiation chemistry and photochemistry of porphyrin–fullerene assemblies. Dr. Zilbermann's main fields of interest are the redox chemistry of first-row transition metals in solutions, bioinorganic and homogeneous catalytic aspects of nickel and copper complexes, metalloporphyrin chemistry and radiation chemistry as a tool to study uncommon oxidation states of transition metals.

with tetraaza-macrocyclic ligands can be stabilized in aqueous solutions by the axial binding of oxo-anions[40] opened the door to many studies. The complex with the symmetric 14-membered ring, cyclam-[14]aneN4 (**9**), is thermodynamically most stable[40–42] with an ideal $Ni^{II}-N$ bond length of 2.06 Å and of 1.97 Å for $Ni^{III}-N$.[27c] The Ni^{III} species, characterized by EPR methods, show the expected elongated tetragonal geometry with axial coordination of the solvent or counteranions confirmed by hyperfine interactions.[41,43]



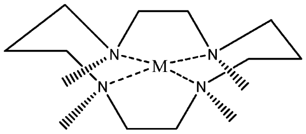
cyclam

The trivalent nickel complexes are usually obtained electrochemically or by oxidation with $S_2O_8^{2-}$.[43–47] The latter approach enables production of solutions containing high concentrations of the Ni^{III} complexes and eventually the precipitation of $NaNi^{III}L(SO_4)_2$ or $NaNi^{III}L(PO_4H)_2$.[47,48] When the study of short-lived Ni^{III} complexes in aqueous solutions is desired, the oxidation by strong single-electron oxidants, usually radicals, e.g., $^{\cdot}OH$, $Br_2^{\cdot -}$, etc., using the pulse-radiolysis technique is the preferred approach.[45–50] Even the $HO_2^{\cdot}$ and probably the $O_2^{\cdot -}$ radicals can oxidize Ni^{II}(cyclam) (**9**) in the presence of stabilizing anions, e.g., sulfate and phosphate, to form the trivalent complexes $LNi^{III}X_2$ (where L = [14]aneN_4 (**9**) or Me_6-[14]aneN_4 (**11**) and X = SO_4^{2-} and $H_2PO_4^{-}$).[51–53] Similar reactions in biological media may explain some of the mechanisms of Ni^{II} toxicity. Some $Ni^{III}L$ complexes with relatively low redox potential, e.g., those with L = some peptides,[54,55] can be obtained even by the oxidation of the corresponding $Ni^{II}L$ complex with dioxygen. Of special interest is that the $Ni^{II}L$ complexes with L = 1-(2-aminoethyl)-1,4,8,11-tetraazacyclotetra-decane (**12**), L = 6,6-bis(4-amino-2-azabutyl)-1,4-diazacycloheptane (**13**), and L = 2,5,9,-12,16,19-hexaaza-7-spiro[6,13]eicosane (**14**) are oxidized to the corresponding $Ni^{III}L$ complexes even by perchlorate.[56,57]

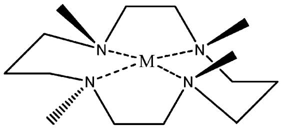
The Ni(cyclam) complex has in principle five possible conformational isomers.[58] Of these configurational isomers, the *trans*-I and the *trans*-III isomers are the most stable. Recent studies point out that the isomerization reaction

$$trans\text{-I-Ni}^{III}(\text{cyclam})(H_2O)^{3+} \rightarrow trans\text{-III-Ni}^{III}(\text{cyclam})(H_2O)_2{}^{3+} \quad (1)$$

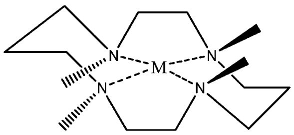
proceeds via the deprotonation of a coordinated N−H and inversion, presumably via the *cis-V* isomer.[59,60]



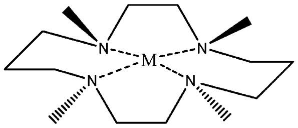
Trans I **(15)**



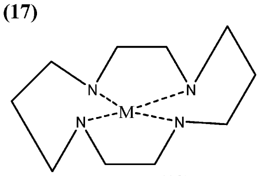
Trans II **(16)**



Trans III **(17)**



Trans IV **(18)**

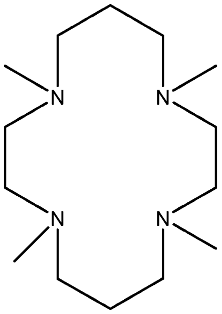


Cis V **(19)**

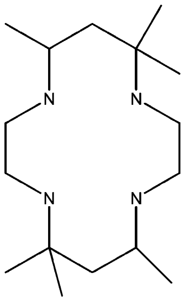
This mechanism explains the reason for a faster isomerization step in the case of nickel for the trivalent complex versus the divalent complex. This mechanism corroborates also the pH effect in the case of the $[Ni^{II}(L^1)]^{2+}$ (**9**) complex.

The size of the tetraaza-macrocyclic ligand clearly affects the redox potential and the stability of the trivalent nickel complex. Thus, the redox potentials for Ni([13]aneN_4) (**20**), Ni([14]aneN_4) (**9**), and Ni([15]aneN_4) (**21**) are +0.90, +0.70, and +1.0 V versus Ag/AgCl, respectively.[61]

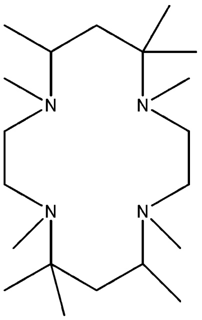
Methyl substituents on the macrocyclic backbone affect the redox potential of the couple $Ni^{III}L(H_2O)_2{}^{3+}$/$Ni^{II}L^{2+}$ by shifting it anodically from +0.94 V[40] for Ni([14]aneN_4-cyclam) (**8**) to +1.22 V for the C-substituted complex *meso*-Ni(Me_6[14]N_4-hexamethylcyclam) (**11**)[46]and to +1.63 V > $E_{1/2}$ > +1.3 V for the C- and N-substituted complex *trans*-III-NiMe_{10}-([14]N_4-decamethylcyclam) (**22**) (all of the potentials versus NHE).[62] This effect of the methyl substituents is probably mainly due to the increase in the radii of the complexes and their larger hydrophobicity, which decreases their solvation energies.[63] Interestingly and in accordance with expectations, the addition of two non-ligating nitrogens to the cyclam backbone, Ni([14]aneN_6-diazacyclam) (**23**), does not affect the redox potential of the couple Ni^{III}/Ni^{II}, +1.00 V versus NHE.[64]



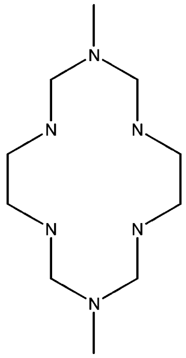
$Me_4[14]N_4$-Tetramethylcyclam **(24)**



$Me_6[14]N_4$-hexamethylcyclam**(11)**



$Me_{10}[14]N_4$-decamethylcyclam**(22)**



diazacyclam**(23)**

Electron-withdrawing substituents on the carbon backbone of the macrocyclic ligand, which render the nitrogens poorer σ donors, induce as expected an anodic shift of the redox potential of the central cation. Thus, for example, Ni^{II} complexes of fluorine-substituted cyclams, on the carbon skeleton, have been prepared. It was found that upon fluorination, the higher oxidation state Ni^{III} becomes successively destabilized with respect to Ni^{II}.[65]

The central nickel(III) cation in *trans*-III-$Ni^{III}L(H_2O)_2{}^{3+}$, L = a tetraaza-macrocyclic ligand, is a strong hard acid and thus tends to replace the aquo ligands by better σ donor ligands, especially by oxo anions. The axial binding of these ligands stabilizes the trivalent nickel species of cyclam, C-substituded cyclam, and diazacyclam complexes, i.e., shifts cathodically the redox potentials of the $LNi^{3+/2+}$ couples (Table 1). Thus, complexes with a large variety of axial ligands, e.g., chloride,[41,47,57,66] sulfate, phosphate,[46,47,51,64,67] pyrophosphate,[68] ATP,[68] and to a lesser extent bromide or fluoride[41,49,64,69] or organic anions like formate, acetate, benzoate, pivalate,[64] and phthalate,[47] were prepared and their stability constants have been determined.[41,45−47,64,68] The results indicate that the major factors affecting the binding constant are the charge and the charge density of the anionic ligand. It is of interest to note that pyrophosphate[68] and ATP[68] seem to form the thermodynamically most stable complexes, although the ATP complex decomposes via oxidation of the axial ligand. The

Table 1. Redox Potentials for Several of the Couples $Ni^{3+/2+}L$ Measured in Aqueous Solutions[a]

complex	$E_{1/2}$ versus NHE (V)[b]	reference
$Ni(bpy)_3$ (**7**)	+1.72	39
$Ni([13]aneN_4)$ (**20**)	+1.12	61
$Ni([14]aneN_4)$ (**9**)	+0.92	61
$Ni([15]aneN_4)$ (**21**)	+1.22	61
meso-$Ni(Me_6[14]aneN_4)$ (**11**)	+1.22	46
$Ni([14]aneN_6)$ (**23**)	+1.00	64
$Ni([14]dioxoaneN_4)$ (**28**)	+0.89	77
$Ni([9]aneN_3)_2$ (**37**)	+1.015	42
$Ni([10]\ aneN_3)_2$ (**38**)	+1.014	42
NiCR (**47**)	+1.3	113
$Ni[H_{-3}(gly)_4]$ (**41**)	+0.79	54
$Ni[H_{-2}(gly)_2hisgly]$ (**43**)	+0.960	90b
$Ni[H_{-2}(gly)_2ha]$ (**44**)	+0.928	90b
Ni_{aq} (**54**) calculated	+2.26	151a and b

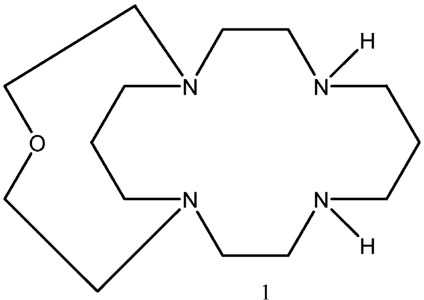
[a] The bold numbers refer to the numbered complexes in the paper. [b] The potentials were measured under different experimental conditions. It should be noted that axial binding of anions to the tetraaza-nickel(III) complexes affects the redox potential considerably.

binding of axial ligands renders the central trivalent nickel more stable both thermodynamically and kinetically, i.e., $t_{1/2}$ of minutes–hours of the trivalent species even at neutral and slightly alkaline pHs.[64] It should be noted that for the *trans*-I isomers and sterically hindered complexes often only one anion binds axially.[27c,60]

Naturally, also hydroxides are good axial ligands, and therefore, the pK_a values of the axial water ligands are relatively low.[27c,43] The central trivalent cation also increases the acidity of the secondary amino ligands. However, the debate concerning the pK_a of the amino ligand in Ni^{III}cyclam is still not solved.[43,70,71] It is of interest to note that kinetic data suggest that some of the $Ni^{III}L(OH^-)^{2+}$ complexes are pentacoordinated.[27c,43]

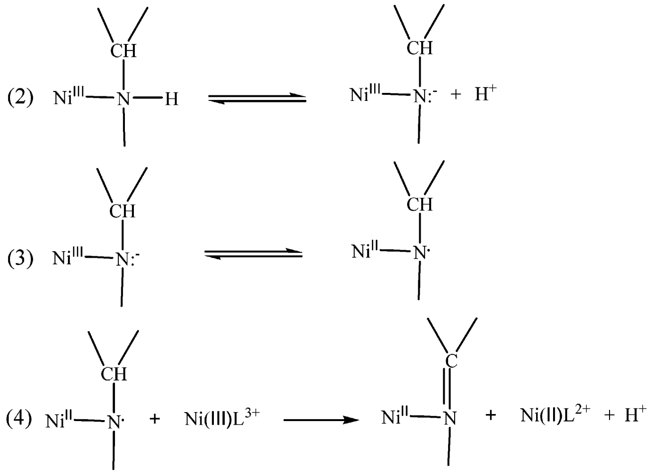
The central nickel(III) cation in some cases also considerably lowers the pK_a of the macrocyclic ligand. Of special interest are the pK_a values of the diallylic CH_2 group of the nickel complexes with the ligands: 1,13-dimethyl-1,4,7,11-tetraazacyclotrideca-10,13-diene (**25**) and 1,13-ditrifluoromethyl-1,4,7,11-tetraazacyclotrideca-10,13-diene (**26**), for which the pK_a of the Ni^{II} complexes is lower than that of the corresponding Ni^{III} complexes.[72] This unexpected result was attributed to the special electronic configuration of the Ni^{II} complexes in this case.

The kinetics and mechanisms of the substitution reactions were reported.[41,45] Substitution reactions of the axial ligands of Ni^{III} complexes have been studied primarily with cyclam-based ligands.[41,43,45] As expected, these reactions are relatively fast for a trivalent central cation because of the Jahn–Teller effect. The rate of substitution at $[Ni^{III}[14ane]N_4(H_2O)_2]^{3+}$ was found to be $[Cl^-]$-dependent and $[H^+]$-independent.[41] The results are in accordance with a dissociative interchange mechanisms.[27c,41] In a recent study in which L^1 (**27**), a cyclam derivative was used, the substitution rate was found to be both $[Cl^-]$- and $[H^+]^{-1}$-dependent.[73] It was suggested that the pH effect is due to the detachement of the ether oxygen from the central Ni^{III} cation, which is accompanied by hydrogen bonding of the axial-bound water molecule to the ether oxygen atom. A pK_a of this water molecule might change the rate of the chloride insertion.



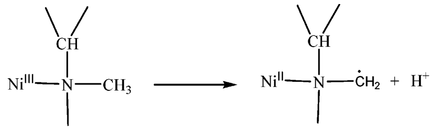
L^1

It has been shown that the decomposition of $[Ni^{III}LX_2]^{(3-2n)+}$ (L = cyclam, diazacyclam, and C-substituted cyclam) in aqueous solutions containing coordinating anions, X^{n-}, proceeds primarily through the aquo complex $[Ni^{III}L(H_2O)_2]^{3+}$, which is the strongest oxidant.[47,64] The oxidation is base-catalyzed and was proposed to proceed via the following mechanism:[74]



The intermediates involved in this mechanism were not fully elucidated although extensive studies have been performed on this issue.[48–50,70,75]

Because this type of mechanism is not possible for the decomposition of N(coordinated)-substituted macrocycles complexes, such as *trans*-III-$Ni(Me_{10}[14]N_4$-decamethylcyclam) (**22**) and *trans*-III-$Ni(Me_4[14]N_4$-tetramethylcyclam) (**24**), the latter once obtained in aqueous solutions by electrolysis at +1.5 V versus SCE (at pH 3) is relatively long-lived with rates of decomposition considerably lower than the nonsubstituted analogues at neutral and slightly alkaline pHs (7–10).[62] The reactions of decomposition obey a first-order rate law though the oxidation of both the ligands or the water are two electron processes indicating that the rate-determining step involves some type of rearrangement, isomerization of the trivalent complex followed by a fast reaction with a second trivalent complex.[62] The mechanism of this process is probably similar to that of the corresponding Cu^{III} complex,**[75]** i.e.,

(5)


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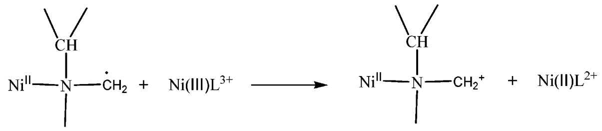

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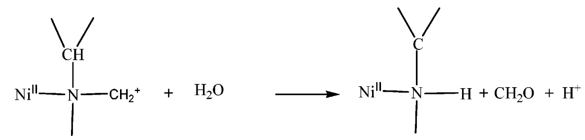
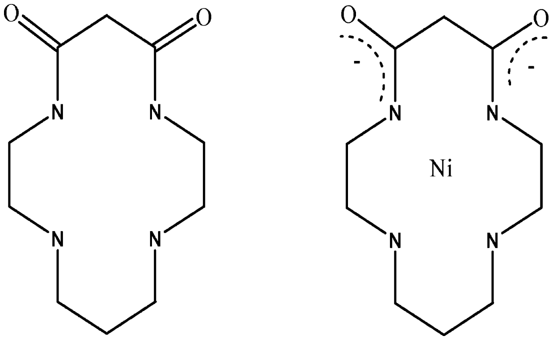


Oxo derivatives of the tetraaza macrocycles, e.g., dioxocyclam, stabilize tetragonally elongated nickel(III) complexes in aqueous solutions because the amide ligands are stronger σ donors than the secondary amines.[76,77] These complexes are not stabilized in the presence of coordinating anions, e.g., sulfate, because of the smaller effective charge on the central Ni^{III} cation.



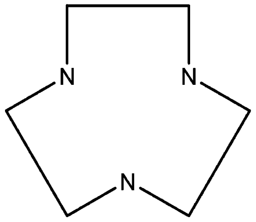
dioxocyclam(**28**)

Pendant arms, usually bound to the nitrogen donor atoms, with substituents that can axially bind to the central nickel ion, shift the redox potential of the complex cathodically, i.e., stabilize the trivalent complex. Such substituents are $-CH_2CH_2NH_2$ (**29**), $-CH_2COOH$[77-79] (**30**), and $-CH_2CH_2OH$ (**31**)[80], for example. Similar stabilization is obtained also with analogous substituents bound to the carbon skeleton of the macrocyclic ligands, e.g., $-CH_2CH_2NH_2$ (**32**) and $-C_6H_4OH$ (**33**).[81-83] Axial coordination of the pyridine nitrogen proven by EPR spectra in the case of $[Ni^{III}([14]aneN_4CH_2CH_2py])^{3+}$ (**34**) has little effect on the reduction potential in contrast to what was shown for axial coordination of Ni^{III} species by other pendant arms, which ligate to the central nickel cation,[77] whereas the 13-membered species with a pendant pyridine N oxide showed a significant decrease in reduction potentials.[77]

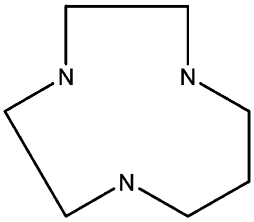
However, the electrochemical oxidation of *trans*-I-$[Ni^{II}([14]aneN_4(CH_3COO^-)_4)]$ (**35**) proceeds via the degradation of the acetate arms.[79] This is attributed to the oxidation of the pendant arm by the combined effect of the electrode and the central nickel cation. When Ni^{III}(1,4,8,11-tetraacetato-1,4,8,11-tetraazacyclotetradecane) is prepared via single-elctron oxidizing agents in deaerated solutions, the trivalent complex is relatively stable. However, it decomposes in the presence of dioxygen in a process analogous to that observed for Ni^{III}edta (**4**).[79a]

Of special interest is the observation that $[Ni^{III}[14]aneN_4(H_2O)_2]^{3+}$ readily oxidizes CH_3NH_2 and $(CH_3)_2NH$, while the cyclam ligand, which has four secondary amine groups bound to the Ni^{III} ion and axially bound pendant primary amine groups, which are covalently linked to the macrocyclic ligand, is relatively stable to oxidation by the trivalent metal cation. This difference in the behavior is attributed to the free rotation of the axially bound $N(CH_3)_iH_{3-i}$ ligands that are required for the oxidation to proceed.[48] This finding also explains the difference in the stability of the meso(**11**)- and rac(**36**)- isomers of Ni^{III}-$Me_6([14]N_4$-hexamethylcyclam).[46] It is tempting to propose that the relative stability of the $Ni^{III}L$ complexes and other high-valent transition-metal complexes, for L = tetraaza-macrocyclic ligands versus that for L = open-chain amines,[31-33] is due to analogous arguments.

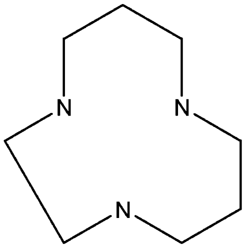
The small nine-membered triaza macrocycle $[9]aneN_3$ (**37**) forms a Ni^{III} complex in which the six-coordinate geometry is imparted by two triaza rings. This complex is thermodynamically more stable than the analogous complexes with either $[10]aneN_3$ (**38**) or $[11]aneN_3$ (**39**).[27c,84a]



$[9]aneN_3$ (**37**)

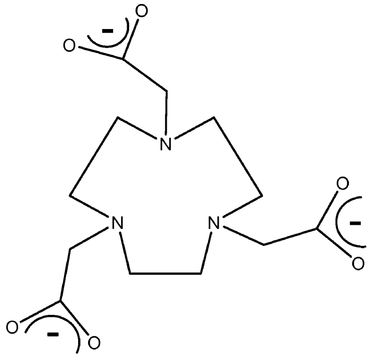


$[10]aneN_3$(**38**)



$[11]aneN_3$(**39**)

When the entropy changes for the reactions of $Ni^{III}L + e^- \rightarrow Ni^{II}L$ for L = $[9]aneN_3$ (**37**) and $[9]aneN_3$-*N′*,*N″*,*N‴*-triacetate (**40**) in NaCl solutions were measured, it was found that ΔS°_{rc} of the half-reaction for the former is positive, while for the latter, it is negative. This result demonstrates that polynegatively charged ligands as $[9]aneN_3$-*N′*,*N″*,*N‴*-triacetate favor access to high oxidation states of the metal because of a very favorable entropy term.[84b]



[9]aneN$_3$-N',N'',N'''-triacetate**(40)**

Nickel(III)−peptide complexes were discovered in the early seventies when it was found by Margerum et al. that $[Ni^{II}(H_{-3}Glyglyglygly)]^{2-}$ (**41**) reacts with dioxygen in neutral aqueous solutions to yield a new species with absorption maxima at 240 nm (ϵ = 11 000 M^{-1} cm^{-1}] and at 325 nm (ϵ = 5240 M^{-1} cm^{-1}]. The identification of the product as $[Ni^{III}(H_{-3}Glyglyglygly)]^-$ was confirmed by EPR.[54,55] The redox potentials for the Ni^{III}−peptide species are similar to those of the tetraaza-macrocyclic complexes because of the similar equatorial ligand field stabilization energy.[27c,54] These complexes have also a tetragonally elongated geometry as confirmed by EPR measurements.[85−87] Binding of axial ligands to these complexes were monitored by their effect on the redox potentials of the Ni^{III}−peptide complexes.[88]

$Ni^{III}(H_{-2}Gly_2His)$ (**42**) oxidatively decomposes at the histidyl residue via C-terminal decarboxylation.[89] The self-decomposition of the Ni^{III} doubly deprotonated peptide complex occurs by base-assisted oxidation of the peptide. In this case in neutral and slightly acidic solutions, the oxidative decarboxylation is a minor pathway of decomposition, with the major one being a 4-electron oxidation at the α carbon of the N-terminal glycyl residue to finally yield after hydrolysis ammonia and oxalylGlyHisGly.[90a]

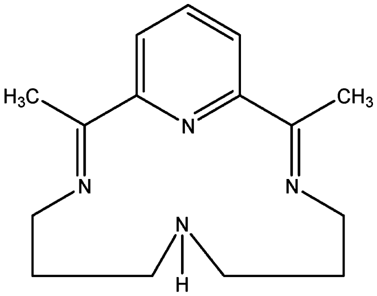
The decomposition kinetics of the Ni^{III} complexes of Gly2HisGly (**43**) and GlyHa (Ha = histamine) (**44**) were recently studied as a function of pH.[90b] In these reactions, at least two Ni^{III} complexes are reduced to Ni^{II} while oxidizing a single peptide ligand. The rate of Ni^{III} loss is first order at low pH, mixed order at pH 7.0−8.5, and second order at higher pH. The transition from first-order to second-order kinetics is attributed to the formation of an oxo-bridged Ni^{III}−peptide dimer.

In the past few years, Ni^{III}−peptide complexes containing histidine as the third amino acid residue have been used in site-specific DNA cleavage,[91−93] RNA-cleavage,[94] protein−protein cross linking,[95−97] and protein affinity labeling.[98] Furthermore, evidence suggests that the Ni-containing SOD contains a histidyl nitrogen bound axially to a Ni^{III} ion.[99]

Site-specific DNA cleavage occurs also by binding the peptide GlyGly-L-His to the amine glycyl terminus of a DNA-binding agent and adding Ni^{II}_{aq} and oxidizing agents. Ni^{III} intermediates were proposed as the cleavage agents.[100] Nickel complexes with tetraazamacrocyclic ligands[44,71,92,101−109] and with peptide ligands[91,92,109,110] were shown to catalyze the oxidation of DNA by peroxomonosulfate, monoperoxyphthalate, H_2O_2, etc., via specific oxidation at N7 of the exposed guanine bases and via the catalyzed autoxidation of sulfite.[92,109−111] Some of these complexes are also active in other oxidation processes involving various oxidants, e.g., NaOCl in the epoxidation of alkenes.[112,113] The nature of the active species in these catalytic oxidations has not yet been identified. In some systems, $SO_4^{\cdot -}$ radicals[5] or analogous radicals were proposed to be the active species, whereas in other complexes of the type LNi^{III}-($OSO_3^{\cdot -}$) and LNi^{IV}-(OSO_3^{2-}) were proposed to be the active oxidants.[109] Various nickel complexes were studied, and the nature of the ligand L has a major effect on the catalytic properties of the complexes. The correlation between the effect of the ligands on the redox properties of the central nickel ion and the flexibility of the ligand[44,106] were discussed as plausible sources for this effect.

Two relatively recent studies on $Ni^{II}L$ complexes (L = pyridyl pendant dioxocylam (**45**) and C-methylated derivatives)[114] and on a binuclear Ni^{II} complex of tris(2-hydroxyiminopropyl) amine (**46**)[115] report on O_2 activation to cleave plasmid DNA in one case[114] and to oxidize methanol and benzylamine in aqueous solutions in the second case.[115] Although in neither of these studies Ni^{III} species are proposed as the active species, it is reasonable to propose formation of intermediates of the type Ni^{III}-OO^-.

The reactions of Ni^{III}[14]aneN$_4$ (**9**) and Ni^{III}CR (**47**) with three nucleotides GMP (guanosine-5′-monophosphate), AMP (adenosine-5′-monophosphate), and ApG [adenylyl-(3′-5′)guanosine-monophosphate] were recently investigated.[116] The two trivalent nickel complexes react with the three nucleotides to a different extent. Ni^{III}CR oxidizes GMP gradually but does not react with AMP. Ni^{III}([14]aneN$_4$) does not oxidize either GMP or AMP (at the 1:1 concentration used). Both trivalent nickel complexes oxidize ApG, Ni^{III}([14]aneN$_4$) to a lesser extent than Ni^{III}CR.



CR

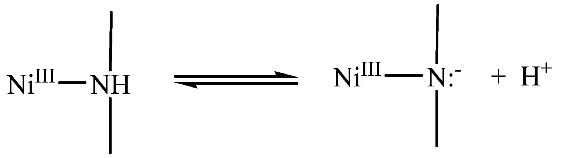
Because the electrochemical studies in aqueous solutions have shown that many of the Ni^{III} complexes discussed above are relatively strong oxidants (from +0.7 to +1.3 V versus NHE) and are stable enough to enable studies of their redox reactivity,[48,54,67,79,80,82,83,117] several such studies were carried out.

The outer-sphere oxidation reactions by the octahedral species: $[Ni^{III}([9]aneN_3)_2]^{3+}$ and [Ni^{III}([10]-

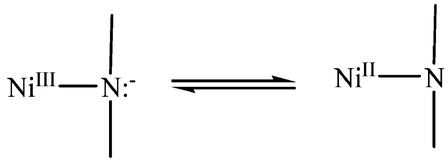
aneN$_3$)$_2$]$^{3+}$ of a series of metal-poly(pyridine) complexes have been studied.[42,118,119] The self-exchange rates for the Ni$^{III/II}$ couples were derived. Recent studies showed a very good agreement between the experimentally estimated activation volume for the [Ni([9]aneN$_3$)$_2$]$^{3+/2+}$ couple (-8.2 cm^3 mol^{-1}) and the theoretically calculated value (-7.5 cm^3 mol^{-1}), indicating that the electron self-exchange of this couple occurs via the outer-sphere mechanism in-acidic aqueous solutions.[120]

[Ni^{II}([9]aneN$_3$)$_2$]$^{2+}$ (**37**) was used as a reductant in a series of cross reactions with other Ni^{III} macrocyclic and Ni^{III}−peptide complexes. Self-exchange values of $0.5-10 \times 10^5$ M^{-1} s^{-1} were derived for most of the unsubstituted cyclam derivatives and for the peptide complexes, while values of $0.008-30$ M^{-1} s^{-1} were obtained for complexes in which there is a relatively high inner coordination sphere reorganization needed or the presence of methyl groups in the tetra and hexamethyl cyclam derivatives increases the barrier to axial solvation.[27c,121−126]

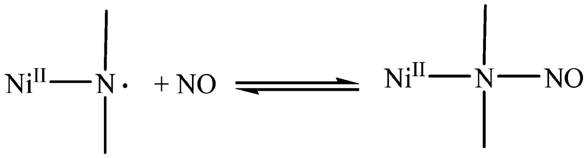
Several Ni^{III} complexes were used as oxidants in a variety of processes. Thus, for example, nitrite is oxidized by [Ni^{III}([9]aneN$_3$)$_2$]$^{3+}$ to form the divalent nickel complex and nitrate. The rate-determining step in this reaction is proposed to be the electron transfer from the nitrite to the trivalent nickel complex. The reaction of SCN$^-$ with [Ni^{III}([9]aneN$_3$)$_2$]$^{3+}$ shows kinetic inhibition by the product [Ni^{II}([9]aneN$_3$)$_2$]$^{2+}$ (**37**), and with a large excess of the Ni^{II} complex, the reaction exhibits pseudo-second-order behavior. This observation is attributed to the formation of the corresponding Ni^{II} complex and the radical anion (SCN)$_2^{\cdot -}$ in equilibrium.[127] The reaction of NO with the same trivalent nickel complex surprisingly leads to decomposition of the complex probably via nitrosation of the N-deprotonated conjugate base form of the Ni^{III} complex.[128] It was proposed that the NO attacks the lone pair of the conjugate base along with an internal electron transfer to the central Ni^{III} cation.[128] Alternatively, it is reasonable to propose that the mechanism can be described by the following sequence:

(8) 

$$\mathrm{Ni^{III}{-}NH} \rightleftharpoons \mathrm{Ni^{III}{-}N{:}^-} + \mathrm{H^+}$$

(9) 

$$\mathrm{Ni^{III}{-}N{:}^-} \rightleftharpoons \mathrm{Ni^{II}{-}N\cdot}$$

(10) 

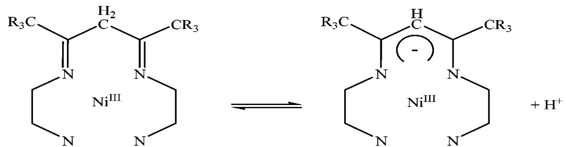
$$\mathrm{Ni^{II}{-}N\cdot} + \mathrm{NO} \rightleftharpoons \mathrm{Ni^{II}{-}N{-}NO}$$

Analogous reactions of NO with high valent transition-metal complexes were recently reported.[129,130]

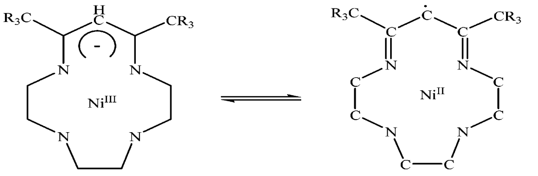
Ni^{III}(Me$_6$[14]aneN$_4$) oxidizes formate in slightly acidic solutions via an inner-sphere, single-electron, rate-determining step. The rate of oxidation of formate in [Ni^{III}(Me$_6$[14]aneN$_4$)(H$_2$O)(HCO$_2^-$)]$^{2+}$ is considerably faster than in [Ni^{III}(Me$_6$ [14]aneN$_4$)(H$_2$PO$_4^-$)(HCO$_2^-$)]$^+$ and in [Ni^{III}(Me$_6$[14]aneN$_4$)(HCO$_2^-$)$_2$]$^+$ in accordance with expectations because of the effect of the axial ligands on the redox potential of the central nickel cation. The results obtained in this system point out that formate has an ambivalent role in this process both as a reducing agent and as a stabilizer of the trivalent nickel complex.[131]

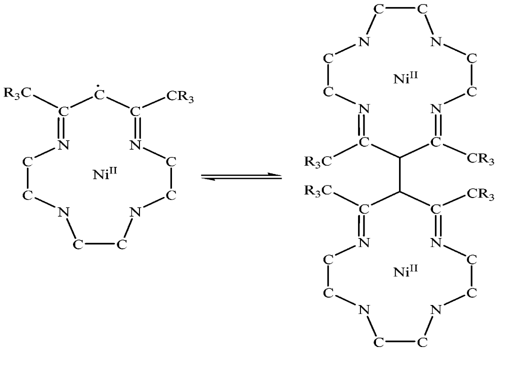
Ascorbate is oxidized in neutral aqueous solutions by [Ni^{III}(Me$_6$[14]aneN$_4$)(H$_2$O)(HPO$_4^-$)]$^+$, [Ni^{III}(Me$_6$-[14]-aneN$_4$)(HPO$_4^-$)$_2$]$^-$ via the outer-sphere mechanism, and [Ni^{III}([14]aneN$_6$)(H$_2$O)$_2$]$^{3+}$ via the inner-sphere mechanism, where the first transient observed is the unexpected complex [Ni^{II}([14]aneN$_6$(A$^{\cdot -}$)]$^+$.[67]

Some Ni^{III} complexes, e.g., those with a −N=CRCH$_2$CR=N− group, have a pK_a where one of the hydrogens bound to the central carbon is lost. This loss is usually followed by an intramolecular electron transfer from the anionic ligand to the central Ni^{III} cation, forming a carbon-centered radical, which can dimerize, as outlined in the following scheme.[72,132]

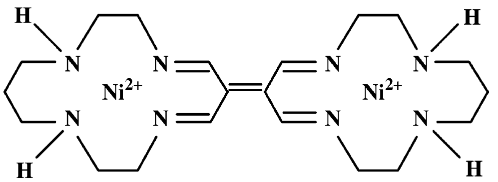
(11) 

R = H, F

(12) 

(13) 2 

The mechanism of oxidation of Ni^{II}(cyclam) (**9**) by peroxomonosulfate to yield the dimer



probably follows a similar mechanism.[133]

Methyl radicals were shown to react with $Ni^{II}L$ (**9**), L = cyclam, to form a relatively stable, formally Ni^{II}, intermediate[134−136]

$$Ni^{II}L^{2+} + {}^{\cdot}CH_3 \rightleftarrows LNi^{III}\text{-}CH_3{}^{2+} \qquad K = 6.5 \times 10^8\ M^{-1} \tag{14}$$

In the presence of dioxygen, this reaction is followed by[134,135]

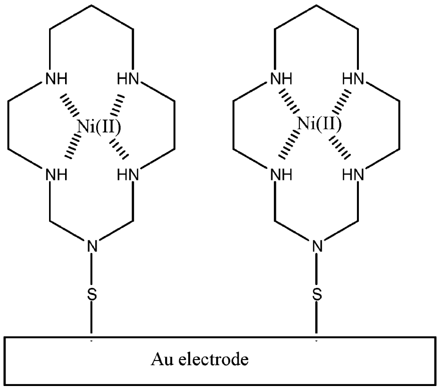
$$^{\cdot}CH_3 + O_2 \rightarrow CH_3O_2{}^{\cdot} \tag{15}$$

$$CH_3O_2{}^{\cdot} + Ni^{II}L^{2+} \rightarrow LNi^{III}\text{-}OOCH_3{}^{2+} \tag{16}$$

$$LNi^{III}\text{-}OOCH_3{}^{2+} + H^+ \rightarrow Ni^{III}(H_2O)_2{}^{3+} + HOOCH_3 \tag{17}$$

Reactions of this type might be of importance in radical-induced biological deleterious processes and in various radical-induced catalytic processes.[137]

The capability of axial anion binding and thermodynamic stabilization (cathodic shift of the redox couple $Ni^{3+/2+}$ of trivalent nickel species) was exploited by using modified electrodes with bound divalent nickel cyclam-like complexes as anionic sensors in aqueous solutions. Dinickel(II)(2,2-bis-(1,3,5,8,12-pentaazacyclotetra decane-3-yl)-diethyldisulfide) (**48**) was adsorbed from methanolic solutions onto gold electrodes to yield self-assembled electroactive monolayers. Cyclic voltammetric measurements revealed that the latter-modified gold electrodes can sense electrochemically various nonelectroactive anions, e.g., $NO_3{}^-$, CF_3COO^-, $SO_4{}^{2-}$, $H_2PO_4{}^-$, $HPO_4{}^{2-}$, $ClO_4{}^-$, $PF_6{}^-$, and SCN^- from the variation of the formal potential $E°$ in aqueous solutions in the presence of the different anions.[138]



Modified graphite paste electrodes with a Ni^{II} mixed ligand complex (cyclam and thiocyanate) on applying a potential of +1.25 V versus Ag/AgCl catalyze the oxidation of phenol at pH 7.2 through a Ni^{III} intermediate.[139]

2.2. Complexes with Nitrogen/Oxygen and Sulfur/Nitrogen Donor Atoms

The severe stability limitation of the thiolate-ligated higher oxidation states of nickel is due to internal electron transfer leading to metal reduction and formation of disulfide species

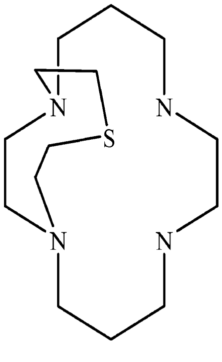
$$2Ni^{III}\text{-}{}^{-}SR \rightarrow 2Ni^{II} + RS\text{-}SR \tag{18}$$

The thermodynamic factors controlling this process have been analyzed.[140] The process can be blocked by lowering the metal redox potential via co-ligands or other controls. In nickel hydrogenases, the $Ni^{3+/2+}$ potential is < −0.4 V versus NHE, and here, the $Ni^{III}\text{-}{}^{-}SR$ moiety is well-sustained.[141] However, no such model complexes are known in aqueous solutions, although many have been prepared in organic solvents.[18,142,144]

On the other hand, thioethers are considerably more resistant toward oxidation. Thus, indeed, the $Ni^{III}L^2$ (**49**) complex was generated chemically in aqueous solutions.[145] The $[Ni^{III}L^2(H_2O)]^{3+}$ complex has an EPR spectrum characteristic of a low-spin d^7 ion in a distorted octahedral environment. When aqueous solutions of $[Ni^{III}L^2F]^{2+}$ are frozen, an axial EPR spectrum consistent with a coordinated fluoride anion is obtained. The EPR behavior permitted the examination of the anation reaction of $[Ni^{III}L^2(H_2O)]^{3+}$ with fluoride ions. The equilibrium was found to be dependent on $[H^+]$ as expected in view of the pK_a of HF. The value of K for the reaction:

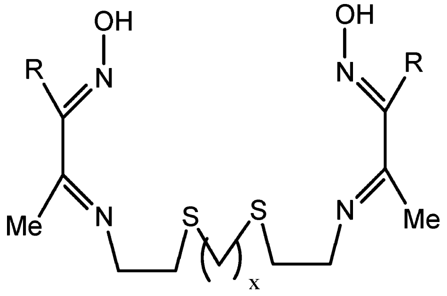
$$[Ni^{III}L^2(H_2O)]^{3+} + F^- \rightarrow [Ni^{III}L^2F]^{2+} + H_2O \tag{19}$$

is $3.1 \times 10^4\ M^{-1}$. This value is considerably higher than those reported for the first anation step of $[Ni^{III}([14]ane)(H_2O)_2]^{3+}$ with chloride and bromide, which are 210 and 34 M^{-1}, respectively.[32] Although a rearrangement to a five-coordinated species instead of a second anation step was proposed for both Ni^{III} complexes of cyclam (**9**)[69] and [16]-aneN_5 (**50**),[146] the results for $Ni^{III}L^2$ (**49**) definitely provide evidence for a six-coordinate Ni^{III} species.



L^2

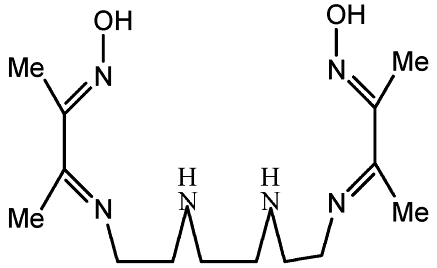
The EPR spectra of $Ni^{III}L^3$ [147] can be compared with the Ni−C form of *Desulfovibrio gigas* hydrogenase.[148] In aqueous solutions, the Ni^{III} complex exists in the deprotonated form $Ni(R_xS)^+$ at pH > 5. A monoprotonated state similar to $Ni(HMe_2N)^{2+}$ ($pK_a = 4.05$)[149] may exist at a lower pH. The redox potentials ($Ni^{3+/2+}$ and Ni^{4+}/Ni^{3+} of the $Ni(S_2N_4)(L^3)$ (**51**) complexes are lower than those of the $Ni(N_6)(L^4)$ (**52**) complex. This effect is explained by the authors[147] by the thermodynamic weakness of the metal−thioether bondcompared to the metal−amine bond in a primarily σ-bonded complex.



H_2RxS

R=Me,Ph ; x=2,3

L^3



H_2Me2N

L^4

2.3. Other Ligands

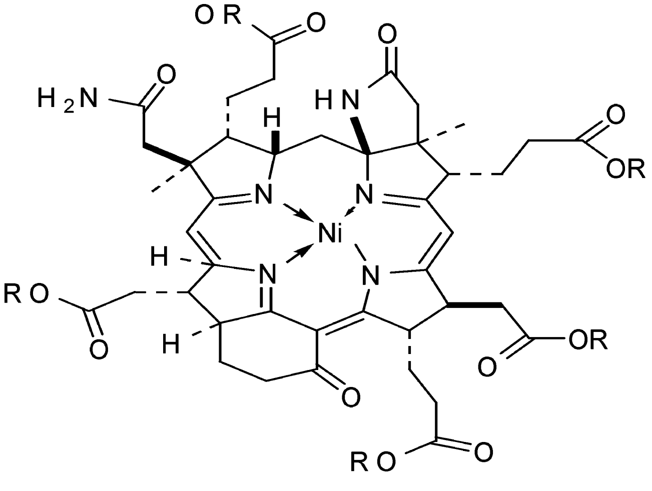
The Ni^{III} complex anion, trans-$[Ni(CN)_4(H_2O)_2]^-$ (**53**), which has labile axial water molecules that are readily replaced by other ligands, has been prepared in aqueous solutions. New Ni^{III} complexes were prepared by water exchange with NCO^-, Cl^-, $NCCH_3$, pyridine, N_3^-, imidazole, ammonia, and bpy. EPR spectra of all of these complexes are tetragonally elongated complexes with two equivalent axial donor ligands.[150]

No direct information on the E^0_{298} value for the $Ni^{3+/2+}{}_{aq}$ (**54**) couple is available, presumably with the latter being too positive to be observable. Using the similarity between $bpyO_2$ and H_2O as oxygen donor ligands, with D_q values closely similar and the same spin state for the metal, a linear plot of the redox potentials of $M(H_2O)_6{}^{3+}/M(H_2O)_6{}^{2+}$ versus $M(bpyO_2)_3{}^{3+}/M(bpyO_2)_3{}^{2+}$ (M = Cr, Mn, Fe, and Co) (bpy = 2,2′-bipyridine 1,1′-dioxide) was received. Extrapolation of the line to the E^0_{298} value for the $Ni^{3+/2+}{}_{aq}$ couple affords a formal potential of 2.26 ± 0.12 V versus NHE.[151a] Recently, a DFT calculation yielded a similar redox potential.[151b]

3. The Ni$^{2+/+}$ Couple

The discovery that tetraaza-macrocyclic ligands stabilize monovalent nickel in aqueous solutions[152a,b,153] induced a variety of studies on the role of these complexes in catalytic,[154−157] electrocatalytic,[157−160] and photocatalytic reactions.[161]

The discovery of the nickel-containing tetrapyrrole-derived factor 430 (**55**), F_{430}, in the enzyme methyl-coenzyme M reductase (MeCoM)[21,24,162−163] and the proposal[164−166] (which is nowadays almost a certainty[167−169]) that the active enzyme (MCRred1) contains F_{430} in the Ni^I oxidation state, which is directly involved in the catalytic cycle of methane formation, induced a variety of studies, although only a few in aqueous solutions,[170−173] to understand the mechanism of the reaction in which Ni^I is involved in MeCoM.



NiF_{430}

Monovalent nickel complexes with tetraaza-macrocyclic ligands are stabilized in aqueous solutions mainly via N-alkylation of the macrocyclic ligand.[27c,153−155] This observation is surprising because alkyl substituents are better σ donors than hydrogen atoms.

Several explanations were offered to explain the results:

(1) N-Alkylation of the macrocyclic ligand induces an increase of the cavity of the ligand because of the steric hindrance induced by the N-alkylation.[174] On the other hand, it was shown that an increase in the size of the macrocyclic ligand does not stabilize monovalent nickel complexes.[152b]

(2) Tertiary amines are poorer σ donors than secondary amines and thus stabilize low valent transition-metal complexes.[152b,153]

(3) N-Alkylation of the macrocyclic ligand increases the hydrophobicity of the ligand, thus stabilizing low valent transition-metal complexes[74,153,175]. The effect is dual: (a) As a result of N-alkylation, no hydrogen bonds with the solvent are possible; thus, charge delocalization is inhibited.[153,175] This also transforms the N atom into a poorer σ donor.[74] (b) N-Akylation increases the radius of the complex, thus decreasing its solvation energy.[74]

The observations that the electron self-exchange rates of the *N*-methylated complexes are considerably faster than those of the corresponding nonmethylated complexes[153,175] and that $\Delta S°$ for the reduction of Ni-

Table 2. Redox Potentials for Several of the Couples $NiL^{2+/+}$ Measured in Aqueous Solutions[a]

complex	$E_{1/2}$ versus NHE (V)[b]	reference
$Ni([14]aneN_4)$ (**9**)	−1.34	153, 175
meso-$Ni(Me_{10}[14]aneN_4)$ (**22**)	−0.74	153, 175
NiL^5 (**56**)	−1.01	175
meso-$Ni(Me_6[14]aneN_4)$ (**11**)	−1.18	153, 175
transIII-$Ni(Me_4[14]aneN_4)$ (**24a**)	−0.91	153, 175
NiF_{430}	− 0.65	20, 172
NiL^6 (**57**)	−1.09	182

[a] The bold numbers refer to the numbered complexes in the paper. [b] The potentials were measured under different experimental conditions.

$(Me_{10}[14]N_4ane)^{2+}$ (**22**) is considerably smaller than that of $Ni([14]N_4ane)^{2+}$ (**9**)[175] are in accordance with this argument.

The monovalent tetraaza-nickel complexes in aqueous solutions are mainly obtained either electrochemically or radiolytically using powerful single-electron reducing agents, e.g., e^-_{aq} ($E° = -2.87$ V versus NHE[176]) and $CO_2^{\cdot -}$ ($E° = -1.90$ V versus NHE[177]). Ni^I tetraaza-macrocyclic complexes are powerful one electron reducing agents, and when the grade of N-alkylation is changed on the cyclam or cyclam-like macrocyclic frame, the redox potential for the couple $LNi^{2+/+}$ (Table 2) can be finely tuned over a range of 600 mV (−1.58 V versus SCE for ($[14]aneN_4$,cyclam) (**9**), until −0.98 V versus SCE for ($Me_{10}[14]N_4$-decamethylcyclam) (**22**).[153,175] It is of interest to note that the redox potential of the couple $Ni(H_2O)_n^{2+/+}$ was estimated to be equal to or more negative than those of the couples $Ni(Me_4[14]N_4\text{-tetramethylcyclam})^{2+/+}$ and $Ni(Me_{10}[14]N_4\text{-decamethylcyclam})^{2+/+}$.[178] This result leads to the surprising conclusion that the stability constants for the binding of these macrocyclic ligands to Ni^I are higher or equal to those for Ni^{II}.

Several phenomena observed indicate that the reduction of the divalent complexes are often accompanied or followed by isomerization processes:[175]

(1) Fast reductions, applying pulse radiolysis experiments, point out that the fast reduction reaction of the nickel tetraaza-macrocyclic complexes is followed by a reaction that obeys first-order kinetics causing considerable shifts in the absorption spectra of the Ni^I complexes.[153,175]

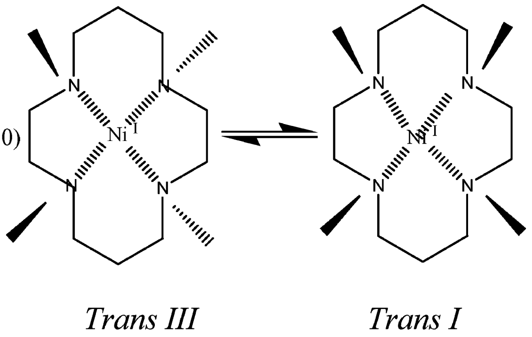
(2) The lifetimes of the monovalent complexes obtained radiolytically often differ considerably from the presumably identical complexes obtained electrochemically.[175]

(3) The kinetics of decomposition of Ni^IL (L = cyclam or diazacyclam or alkylated derivatives) complexes obey first-order rate laws, although they clearly involve second-order processes.[175]

(4) The observation that the electrochemical reductions are always only quasireversible, i.e., that $\Delta E_{peak-Ni^{2+/+}} > 60$ mV.[175]

The preparation of *trans*-III(**24a**) and *trans*-I(**24b**)-$Ni^I(Me_4[14]N_4\text{-tetramethylcyclam})$ is followed by the isomerization reaction,

(20)



resulting in an equilibrium mixture of 3:1 of *trans*-III/*trans*-I within several hours.[179−181] This reaction is many orders of magnitude faster than the corresponding reaction of the analogous divalent complexes. Recently, a similar result was reported for the isomerization of *trans*-III(**17**)-$Ni^I(cyclam)^+$.[182] The faster isomerization of the monovalent complexes is attributed to the weaker Ni−N bond, which enables its dissociation followed by inversion.

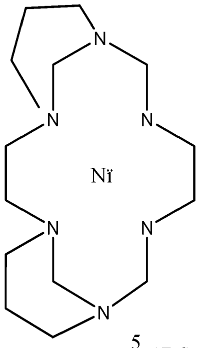
Ligands such as formate[153] or CO[60,159−161,182] can bind axially to these Ni^I complexes producing significant changes in the UV−vis spectra. While LNi^I-CO^+ complexes in aqueous solutions were primarily proposed as transients in the electrocatalytic reduction of CO_2,[159−161] they were later spectrally characterized by application of the pulse radiolysis technique.[60,182]

The reductions of alkyl halides, RX, and alkyl peroxides by $Ni^I(Me_4[14]N_4\text{-tetramethyl-cyclam})^+$ is followed by the formation of LNi^{II}−alkyl complexes.[179−181] The reduction of a variety of alkyl halides was studied. The results indicate that the reduction step obeys a first-order dependence on each reactant, and the reactivity decreases in the order X = I > Br > Cl,[27c,180] and for R, the reactivity order observed is methyl > primary > secondary. Although the monovalent complex was prepared by the reduction of *trans*-III-$Ni^{II}(Me_4[14]N_4\text{-tetramethylcyclam})$ (**24a**), the study probably involved a blend of *trans*-III- and *trans*-I-$Ni^I(Me_4[14]N_4\text{-tetra-methylcyclam})^+$. The kinetic and spectral data obtained for the reactions of the alkyl halides with the monovalent nickel complexes have been interpreted in terms of a rate-determining one-electron transfer from the Ni^IL^+ complex to RX either via the outer-sphere mechanism or via halogen atom transfer to yield the alkyl radical $R^{\cdot}$. The alkyl radical reacts further with a second Ni^IL^+ species to yield $[LNi-R]^+$. The latter complexes decompose heterolytically, yielding the alkane RH and $Ni^{II}L^{2+}$. The $[LNi-R]^+$ complexes react also with the alkyl halides to form alkanes and alkenes.

In the case of the reaction of $Ni^I(Me_4[14]N_4\text{-tetramethylcyclam})^+$ with *tert*-butyl hydroperoxide, the presence of two, one-electron-transfer steps was confirmed by the detection of $[LNi-CH_3]^+$.[179]

The reactions of Ni^IL^i [i = cyclam (**9**), *meso*-Me_6-cyclam (**11**), *trans*-I-Me_4cyclam (**24b**), and 1,3,6,10,12,15-hexaazatricyclo[13.3.1.1^{8,12}]eicosane-L^5 (**56**)] with

2,2-dibromomethyl-1,3-propane-diol were recently studied.[157]



NïL^5 **(56)**

The nickel(I) complexes were produced radiolytically, reducing the divalent analogues by e^-_{aq} and/or $CO_2^{\cdot -}$. The $Ni^IL^{i\,+}$ complexes thus formed react with the organic substrates, RBr

$$\mathrm{Ni^IL^{i\,+}} + \mathrm{RBr} \xrightarrow{k_3} \mathrm{Ni^{II}L^{i\,2+}} + \mathrm{R^{\cdot}} + \mathrm{Br^-} \tag{21}$$

When the radical yield in this reaction is relatively low, i.e., when low pulse intensities are applied, and in the presence of a relatively high concentration of $Ni^{II}cyclam^{2+}$ (**9**), the reaction of the $R^{\cdot}$ radicals thus formed with $Ni^{II}L^{2+}$ is observed

$$\mathrm{Ni^{II}L^{2+}} + \mathrm{R^{\cdot}} \rightarrow \mathrm{(LNi^{III}\text{-}R)^{2+}} \tag{22}$$

The plot of log k_3 versus $E°$ ($Ni^{II/I}L$) yields a straight line. Because the rates of the electron self-exchange reactions of the couples $Ni^{II/I}L^i$ are relatively low[153,175] and because the self-exchange for the $RBr/RBr^{\cdot -}$ couple is probably not high and the free-energy gain in the outer-sphere reduction

$$\mathrm{Ni^IL^{i\,+}} + \mathrm{RBr} \rightarrow \mathrm{Ni^{II}L^{i\,2+}} + \mathrm{RBr^{\cdot -}} \tag{23}$$

is also not high, because of the instability of $RBr^{\cdot -}$, it is proposed that the reduction of RBr by $Ni^IL^{i\,+}$ proceeds via the inner-sphere mechanism. However, the straight line of the plot suggests that steric hindrance does not considerably slow the reduction reaction. It is of interest to note that when formate is present in the solution the reduction becomes a chain reaction

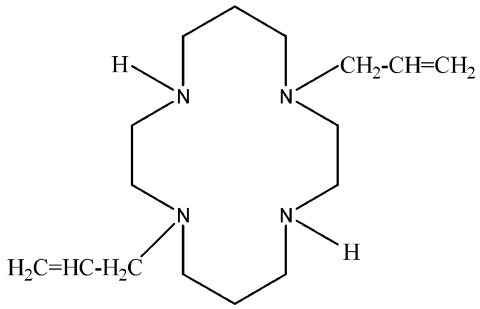
$$\mathrm{Ni^{II}L^{i\,2+}} + \mathrm{CO_2^{\cdot -}} \rightarrow \mathrm{Ni^IL^{i\,+}} + \mathrm{CO_2} \tag{24}$$

$$\mathrm{Ni^IL^{i\,+}} + \mathrm{RBr} \rightarrow \mathrm{Ni^{II}L^{i\,2+}} + \mathrm{R^{\cdot}} + \mathrm{Br^-} \tag{25}$$

$$\mathrm{R^{\cdot}} + \mathrm{HCO_2^-} \rightarrow \mathrm{RH} + \mathrm{CO_2^{\cdot -}} \tag{26}$$

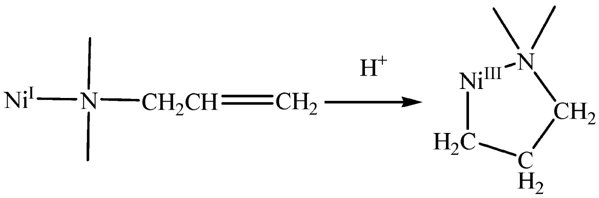
The complexes $Ni^{II}L^{i\,2+}$ act also as elecrocatalysts for the reduction of RBr.[157]

The allylic substituents on the cyclam frame shift the redox potential of the couple $(NiL^6)^{2+/+}$ (**57**) anodically relative to $Ni(cyclam)^{2+/+}$ as expected from the hydrophobic effect.[182] However, the lifetime of $(Ni^IL^6)^+$ is surprisingly shorter than that of



L^6

Ni^Icyclam. Pulse radiolysis experiments reveal that the allylic substituents are reduced by the central Ni^I ion. The first step in this reduction is a general acid-catalyzed process. The results suggest that this step involves schematically the reaction

(27)


The latter transient decomposes slowly with a half-life time of several minutes.

$Ni^{II}(cyclam)^{2+}$ (**9**) and analogous complexes were shown to be electrocatalysts,[159-161] photoelectrocatalysts,[183] and photocatalysts[161] for the reduction of CO_2 in aqueous solutions. The general interest in this subject as well as the fact that the catalytic cycle involves Ni^IL species required a detailed mechanistic analysis.[175] In principle, the catalysis might proceed via one of the following mechanisms:

(a) Reduction of CO_2 by NiL^+_{aq}

$$\mathrm{NiL^+_{aq}} + \mathrm{CO_2} \overset{k_4}{\rightleftarrows} \mathrm{NiL^{2+}_{aq}} + \mathrm{CO_2^{\cdot -}} \tag{28}$$

followed by the reaction of $CO_2^{\cdot -}$ with a second NiL^+_{aq}. However, because the redox potential of the couple $Ni(cyclam)^{2+/+}$ is ~ −1.34 V versus NHE and $k_{-4} = 2 \times 10^9\ M^{-1}\ s^{-1}$, one calculates $K_{-4} \sim 10^{9.5}$ and $k_4 \sim 3\ s^{-1}$. The latter rate is too low to explain the high electrocatalytic currents observed.

(b) Reduction via a two-electron redox reaction, i.e., via

$$\mathrm{NiL^+_{aq}} + \mathrm{CO_2} + 2\mathrm{H_3O^+} \rightarrow \mathrm{NiL^{3+}_{aq}} + \mathrm{CO} + 3\mathrm{H_2O} \tag{29}$$

Because $E°(Nicyclam^{2+/+}{}_{aq}) \sim -1.34$ V versus NHE and $E°(Nicyclam^{3+/2+}{}_{aq}) = +1.00$ V versus NHE,[28] one calculates $E°(Nicyclam^{3+/+}{}_{aq}) = -0.17$ V and $E°(CO_2 + 2H_3O^+/CO + 3H_2O) = -0.103$ V;[184] then, the latter reaction is exothermic only at pH < 1. However, the electrocatalytic currents are pH-independent at pH < 5.[159]

(c) Two NiL^+_{aq} reduce one CO_2 molecule coherently. Two routes are envisaged: (1) Disproportionation

$$2NiL^+_{aq} \rightleftarrows NiL^\circ + NiL^{2+} \quad (30)$$

followed by

$$NiL^\circ + CO_2 + 2H_3O^+ \rightarrow NiL^{2+}_{aq} + CO + 3H_2O \quad (31)$$

This mechanism does not fit the observations because the disproportionation reaction is very slow and the NiL^+_{aq} complex is a relatively long-lived species. Furthermore, the decomposition of NiL^+_{aq} complexes seems to require isomerization reactions prior to decomposition (as already mentioned above), and it is difficult to envisage that the reduction of CO_2 by NiL° will then yield back NiL^{2+} in its stable conformation. (2) NiL^+_{aq} forming a complex with CO_2

$$NiL^+_{aq} + CO_2 \rightleftarrows LNi^{+\cdot}CO_2 \quad (32)$$

followed by the reduction of this complex by the electrode

$$LNi^{+\cdot}CO_2 + 2H_3O^+ + e^- \rightarrow NiL^{2+}_{aq} + CO + 3H_2O \quad (33)$$

This reaction seems to be in accordance with all of the results reported on the electrocatalytical reduction, which indicate that NiL^+_{aq} when formed is adsorbed to the Hg electrode.[160]

Alternatively the reduction might proceed via

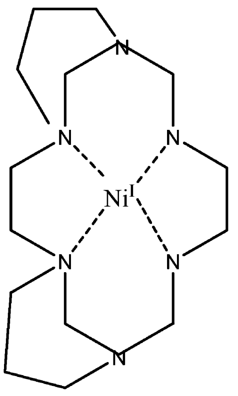
$$LNi^{+\cdot}CO_2 + NiL^+_{aq} + 2H_3O^+ \rightarrow NiL^{2+}_{aq} + CO + 3H_2O \quad (34)$$

This reaction, taking into account the low stability constant of the complex $LNi^{+\cdot}CO_2$, explains the low yields of the photocatalytic processes.

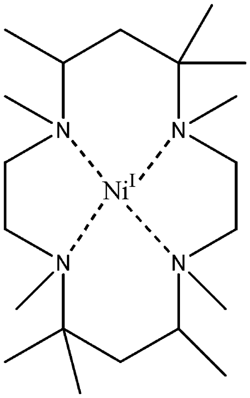
The relevance of Ni^I in the activity of cofactor F_{430} induced many studies both with model complexes and with the purified cofactor itself, although only a few of them in water.

Incubation of the purified $Ni^{II}F_{430}$ (**55**) with titanium(III)citrate leads to the formation of Ni^IF_{430}. The same process occurs when MCRox1, the inactive form of methyl coenzyme M reductase (MCR), is reacted with Ti^{III}citrate to form MCRred1, the active form of the enzyme.[166,167]

When deaerated solutions containing methyl coenzyme M were added to solutions containing the monovalent complexes $Ni^I(Me_{10}[14\text{-ane}]N_4)^+$ and $Ni^I(L^5)^+$,



Ni(I)L^5



Ni(I)(Me$_{10}$[14-ane]N$_4$)$^+$

the complexes produced radiolytically yielded traces of methane at pH 7.4 but yielded 10% of methane at pH 9.4.[172] These complexes were chosen because of their relatively low redox potentials for the couple $Ni^{2+/+}$ in aqueous solutions, -1.25 and -0.98 V versus SCE for $Ni^I(L^5)^+$ and $Ni^I(Me_{10}[14\text{-ane}]N_4)^+$, respectively.[153,175] These redox potentials are similar to that of $Ni^{2+/+}F_{430}$, the native cofactor, -0.89 V versus SCE.[185] The yield of methane was calculated assuming that two Ni^I complexes are required for the production of a methane molecule.

Two plausible routes were proposed: (a)

$$Ni^IL^+_{aq} + CH_3SCH_2CH_2SO_3^-(\text{MeCoM}) \rightarrow Ni^{II}L^{2+}_{aq} + {}^\cdot CH_3 + {}^-SCH_2CH_2SO_3^- \quad (35)$$

followed by

$$Ni^IL^+_{aq} + {}^\cdot CH_3 \rightarrow LNi^{II}\text{-}CH_3{}^+_{aq} \quad (36)$$

$$LNi^{II}\text{-}CH_3{}^+_{aq} + H_2O \rightarrow Ni^{II}L^{2+}_{aq} + CH_4 + OH^- \quad (37)$$

or by

$$Ni^{II}L^{2+}_{aq} + {}^\cdot CH_3 \rightarrow LNi^{III}\text{-}CH_3{}^{2+}_{aq} \quad (38)$$

$$LNi^{III}\text{-}CH_3{}^{2+}_{aq} + H_2O \rightarrow Ni^{III}L^{3+}_{aq} + CH_4 + OH^- \quad (39)$$

Analogous reactions were observed for the reactions of monovalent[179,186,187] and divalent[134,136] nickel complexes with tetraaza-macrocyclic ligands with alkyl radicals. (b)

$$Ni^IL^+_{aq} + CH_3SCH_2CH_2SO_3^-(\text{MeCoM}) + H^+ \rightarrow Ni^{II}L^i_{aq} + CH_4 + {}^\cdot SCH_2CH_2SO_3^- \quad (40)$$

followed by

$$Ni^IL^+_{aq} + {}^\cdot SCH_2CH_2\,SO_3^- + H^+ \rightarrow Ni^{II}L^{2+}_{aq} + HSCH_2CH_2\,SO_3^- \quad (41)$$

or by

$$2^{\cdot}SCH_2CH_2SO_3^- \rightarrow {}^-{}_3OS(CH_2)_2SS(CH_2)_2SO_3^- \quad (42)$$

followed by

$$Ni^{I}L^{+}_{aq} + {}^-{}_3OS(CH_2)_2SS(CH_2)_2SO_3^- \rightarrow Ni^{II}L^{i}_{aq} + HSCH_2CH_2SO_3^- + {}^{\cdot}SCH_2CH_2SO_3^- \quad (43)$$

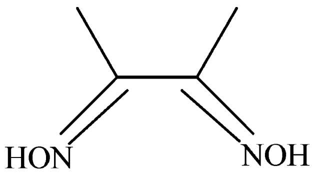
Blank experiments in which solutions containing high concentrations (0.1−0.3 M) of $(CH_3)_2SO$ (as a source of methyl radicals) and MeCoM (0−4 mM) were irradiated in N_2O saturated aqueous solutions yielded methane not as a major product, pointing out that MeCoM competes with $(CH_3)_2SO$ for $^{\cdot}CH_3$. This explains why other model systems failed to produce methane.

Route (a) seems to best explain the results in which transients as LNi^{II}-CH_3^+ and LNi^{III}-CH_3^{2+} are involved and in which most of the methyl radicals react with MeCoM to yield products different than methane.

4. The $Ni^{4+/2+}$ or/and $Ni^{4+/3+}$ Couples

A key question concerning Ni^{IV} complexes is whether their reduction to Ni^{II} complexes invariably proceeds through a Ni^{III} intermediate or if there are circumstances favoring a direct $2e^-$ transaction for this conversion.

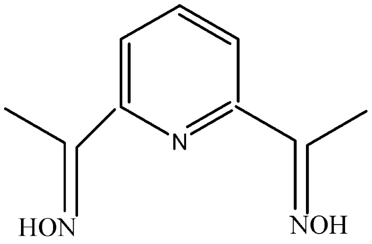
In combination with other nitrogen donor atoms, oximes provided the right environment for stabilizing high oxidation states of nickel, especially Ni^{IV}. One of the best characterized Ni^{IV} complexes is $[Ni^{IV}(dmg)_3]^{2-}$ (**58**). Alkaline solutions of the latter tetravalent nickel complex are kinetically relatively stable.[188,189]



$dmgH_2$

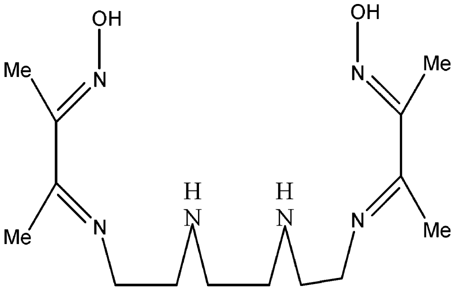
The complex is inert to substitution but is sensitive to acid and protonates with a pK_a of 10.8.[28,190] One-electron reduction at pH 12.4 yields the trivalent nickel complex,[191−193] although this complex differs from that formed via the one-electron oxidation of the divalent complex.[194] There is also a report of a two-electron reduction in 1.5 M NaOH.[195]

Persulfate oxidation of $[Ni^{II}(dapd)_2]^{2-}$ (**59**) in alkaline media yields violet needles of $[Ni^{IV}(dapd)_2]$. The complex is inert to substitution as evidenced by the observation that it can be dissolved in concentrated HNO_3.[196−197]



$dapdH_2$

Chemical and electrochemical oxidation of $[Ni^{II}Me_2LH_2]^{2+}$ (**52**) oxidation results in the highly colored diamagnetic $[Ni^{IV}Me_2L]^{2+}$ in which both oxime groups are deprotonated.[198−199]



Me_2LH_2

The complex of Me_2L with Ni^{IV} exists as a pair of optical isomers, sufficiently inert to allow optical resolution.[200,201]

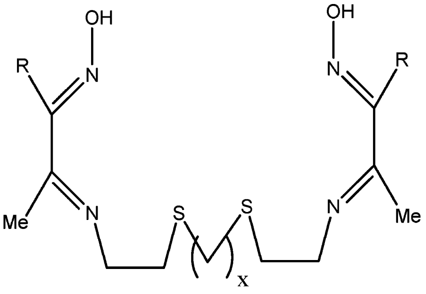
The kinetics of the redox comproportionation reaction

$$[Ni^{IV}Me_2L]^{2+} + [Ni^{II}Me_2L] \rightleftarrows 2[Ni^{III}Me_2L]^{+} \quad (44)$$

have been studied as a function of pH. Above pH 5, the reduction of $[Ni^{IV}Me_2L]^{2+}$ by $[Ni^{II}Me_2L]$, $[Ni^{II}Me_2LH]^{+}$, and $[Ni^{II}Me_2LH_2]^{2+}$ takes place with kinetics that obey second-order rate laws. At more acidic pHs, the disproportionation of $[Ni^{III}Me_2L]^{+}$ is dominated by its reaction with $[Ni^{III}Me_2LH]^{2+}$.[202]

Changing the N_6 donor set of the former ligand to the S_2N_4 donor set of the H_2R_xS ligands, affords brown, paramagnetic Ni^{II} complexes (**51**), which, upon oxidation with concentrated HNO_3, yield the violet diamagnetic $Ni^{IV}(R_xS)^{2+}$ complexes.[147] The complexes $Ni^{IV}(Me_xS)(ClO_4)_2$ ($x = 2$ and 3) decompose, regenerating the initial Ni^{II} complexes via $Ni^{III}(HMe_xS)^{2+}$ and/or $Ni^{III}(Me_xS)^{+}$. A comparison with the related NiN_6 complexes revealed that replacement of the amine donors by thioether donors increases $E°$.

This is attributed to the lower thermodynamic stability of the Ni−S(thioether) bond.[147]

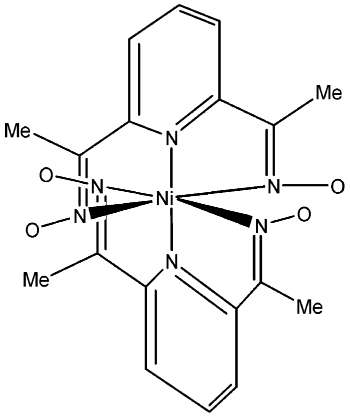


H_2RxS

R=Me,Ph ; x=2,3

Redox reactions involving Ni^{IV} are also subject to divalent metal ion catalysis.[203,204] Oxidations by $[Ni^{IV}(dmg)_3]^{2-}$ of the two-electron reductant ascorbate[192] and the one-electron reductant $[Fe(CN)_6]^{4-}$ [205] have been investigated. Both reactions have as the rate-determining step the transfer of one electron from the reductant to Ni^{IV} in an outer-sphere process to yield an undetected Ni^{III} transient. On the other hand, the data for the Cu^{II}-catalyzed oxidation of phenylhydrazine by the same Ni^{IV} complex are insufficient to unequivocally establish whether electron transfer in the rate-determining step proceeds by formation and decomposition of a precursor intermediate or by two successive $1e^-$ steps.[206]

Another complex of Ni^{IV} studied is that of 2,6-diacetylpyridine dioxime-$Ni^{IV}L^7$ (**60**). This complex is stable enough at low pH values to allow redox studies involving aquated metal cations as reductants.[207]



Ni(IV)L^7**(60)**

Aqueous solutions of Fe^{II}, Sn^{II}, I^-, and U^{IV} reduce $Ni^{IV}L^7$ cleanly to yield the divalent analogue $Ni^{II}L$.[7] $Ni^{IV}L^7$ reacts very slowly with H_3PO_2 and H_3AsO_3.

There is no evidence for the accumulation of the intermediate state Ni^{III} even with the oxidant in large excess. The rate laws of the reactions with Fe^{II}, Sn^{II}, and I^- strongly depend on $[H^+]$, reflecting partial protonation of the oxidant. Reductions by Sn^{II} are strongly catalyzed by Cl^-. Reductions by U^{IV} at $[H^+]$ below 0.02 M are catalyzed by UO_2^{2+} with rates proportional to $([U^{VI}][U^{IV}])^{1/2}$. The overall kinetic picture of the $Ni^{IV}-U^{IV}$ system supports a sequence in which a reactive intermediate, a U^V species, undergoes one of two competing processes: reduction of Ni^{IV} or reversible disproportionation to U^{VI} and U^{IV}. Each of the steps is a single-electron transfer. These results taken together show that the conversion of Ni^{IV} to Ni^{II}, a net $2e^-$ process, usually entails pairs of $1e^-$ steps.[207]

However, the oxidation of sulfite by $Ni^{IV}L^8$ (L^8 = 6-amino-3-methyl-4-azahex-3-en-2-one oxime) (**61**) and $Ni^{IV}(Me_2L)$ (**52**) proceeds via single-step two-electron transfer processes in slightly acidic solutions.[163] A distinct biphasic process with faster initial one-electron reduction of Ni^{IV} followed by a slower reduction of Ni^{III} was observed at higher pHs. Under these conditions in the presence of an excess of the complex, the product is a mixture of dithionate and sulfate, pointing out that the reduction at least partially proceeds via single-electron-transfer steps. However, at pH > 8, with $([S^{IV}]/ [Ni^{IV}])$ = 2:1, dithionate is the major product.[208]

The kinetics of oxidation of thiosulfate by the same tetravalent nickel complexes was studied under pseudo-first-order conditions with an excess of thiosulfate in the range of pH 2.5−8.0.[164] A monophasic two-electron transfer was found at $3.0 \leq pH \leq 5.0$ in the case of NiL^8 and at $2.50 \leq pH \leq 4.0$ for $Ni^{IV}Me_2L$. Above these pH regions, both reactions showed biphasic decomposition with a faster initial one-electron reduction of Ni^{IV} followed by a slower reduction of Ni^{III}. The reduction of Ni^{IV} to Ni^{III} is assumed to proceed via an outer-sphere mechanism, whereas the reduction Ni^{III} proceeds via an inner-sphere route.[209]

Azide is oxidized in aqueous solutions by $Ni^{IV}L^8$ and $Ni^{IV}L^9$ (L^9 = 3,14-dimethyl-4,7,10,13-tetraazahexadeca dioxime) (**62**).[210] The reactions are overall second-order reactions, first-order both in [azide] and $[Ni^{IV}]$, and exhibit a strong dependence on $[H^+]$. Single-step two-electron transfer are encountered for $Ni^{IV}L^8$ at $2.0 \leq pH \leq 6.0$ and for $Ni^{IV}L^{8,9}$ at $2.0 \leq pH \leq 4.5$.[210] Above these pH regions until pH 8.0, both reactions showed biphasic decomposition with a faster initial one-electron reduction of Ni^{IV} to Ni^{III}, followed by a slower conversion of Ni^{III} to Ni^{II}. As in the case of thiosulfate, the reduction of Ni^{IV} to Ni^{III} is assumed to follow an outer-sphere mechanism, whereas the reaction Ni^{III} to Ni^{II} follows an inner-sphere route.[2]

In a relatively recent report[211] using the tridentate bisamide ligand 2,6-bis[*N*-(phenyl)carbamoyl]pyridine in its deprotonated form, nickel complexes in three consecutive oxidation states, II (**63**), III, and IV, have been prepared and the di- and tetravalent complexes were structurally characterized. A linear correlation between the $Ni^{3+/2+}$ reduction potentials and the reciprocal of solvent dielectric constants was obtained in line with the free energy of solvation as predicted by the Born equation. Surprisingly, no such trend was depicted for the $Ni^{4+/3+}$ couples. The reported redox potentials in water for the couples $Ni^{4+/3+}$ and $Ni^{3+/2+}$ are +0.66 and +0.275 V versus SCE, respectively.

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