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An investigation into the electronic and structural properties of nickel complexes of tetradentate N_2S_2 ligands

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Abstract

A series of Ni(II) complexes of the ligands; *N,N'*-dimethylene-, *N,N'*-trimethylene-, *N,N'*-tetramethylene- and *N,N'*-pentamethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate) (L $n=2$, 3, 4, 5) have been prepared where the bridging alkyl chain between the two nitrogens varies from two to five methylene groups. Ligands field transitions occur at 15 150, 14 950 and 14 750 cm^{-1} for Ni $n=2$, 3, and 4, respectively, energies comparable to tetra-thiolate ligand systems. Red shifts in both LF and LMCT transitions indicate a shift to more tetrahedral symmetries in the series as additional methylene groups are incorporated into the diamine bridge. The compounds exhibit reversible one electron reductions and oxidations, which also show trends explained by a changing coordination environment. The Ni(II) complex of *N,N'*-tetramethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate) ($n=4$) has a solid state effective magnetic moment of 3.20 $\beta\mu$, and, in solution, exhibits an equilibrium between planar and tetrahedral geometries, which gives rise to isotropic Fermi contact shifts of proton resonances. These and other data from infrared spectroscopy and cyclic voltammetry indicate increasing distortion from planarity toward a pseudo-tetrahedral coordination geometry as the length of the bridge increases, and suggest the geometrical environment around the Ni(II) is controlled by the ligand.

Introduction

The bioinorganic chemistry of nickel has become increasingly important in the past few years, primarily because nickel has been shown to lie at the active site of several very important classes of metalloenzymes, including, most notably, the nickel hydrogenases [1–3]. In addition, nickel(II) has been utilized as a spectroscopic probe in metal replacement studies of other metalloenzymes [4–8]. Common to many investigations into nickel metalloenzymes is the proposition of four coordinate, distorted geometries, involving nitrogen and sulfur ligand groups at the active sites. For example, experiments using electron spin resonance, X-ray diffraction and X-ray absorption techniques suggest from one to four sulfurs bind a monomeric nickel ion at a hydrogenase active site [9–12]. Recent magnetic circular dichroism experiments have revealed the magnetic susceptibility of the nickel site in native hydrogenases is likely diamagnetic, considerably narrowing possible model geometries [13]. Nickel(II) replacement studies involve various type 1 Cu(II) containing metalloenzymes where the metal is thought to be coordinated by two nitrogen and two sulfur groups. It has been shown that at least one Ni(II) derivative absorbs radiation in the near IR region [7], characteristic of tetrahedral, or pseudo-tetrahedral, d^8 symmetries.

The catalytic properties of hydrogenases arise from the remarkably low oxidation potential for the Ni(II)/Ni(III) redox couple (-390 to -640 mV versus SCE), which enables activation of dihydrogen [14–19]. Few synthetic complexes have been able to match these low potentials [15], considering the typical potential for the oxidation wave of Ni(II) complexes lies positive of $+500$ mV versus SCE [2, 20–22]. Factors that affect the stability of trivalent Ni(III), while not well understood, normally involve different combinations of donor ligands and coordination geometries [2 ,20–22]. In an effort to better understand the spectral properties of both enzymatic systems, we have designed a series of tetradentate $[N_2S_2]^{2-}$ ligands with flexibility that allows the attainment of both square planar and pseudo-tetrahedral coordination geometries. We have undertaken detailed studies in order to characterize the soluble Ni(II) complexes of this series, which possess a consistent nitrogen and sulfur donor set, but systematically

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varying stereochemistries. Some information on Ni(II)N_2S_2 systems with tetradentate ligands has been collected [23–33]. Recently, in an effort to mimic the low oxidation potentials experienced in the Ni(II) hydrogenases, Krüger and Holm [15] reported the effect of placing Ni(II) in an anionic $[N_2S_2]^{4-}$, planar coordination environment. We anticipated that by combining an electron rich $[N_2S_2]^{2-}$ environment and pseudo-tetrahedral coordination geometry, even lower oxidation potentials could be attainable. Finally, while many treatments of isotropic contact shifts of bis-bidentate Ni(II)N_2S_2 complexes appear in the literature, to our knowledge, this work offers the first treatment involving tetradentate $[N_2S_2]^{2-}$ ligands. Results will be discussed and compared to studied of native nickel metalloenzymes, Ni(II) substituted type 1 copper(II) proteins, and other Ni(II)N_2S_2 complexes.

Experimental

Materials

All reagents and solvents were commercially obtained from either Fisher Scientific or Aldrich Chemicals and used without further purification. Tetraalkylammonium salts, used as supporting electrolytes, were obtained from Southwestern Analytical Chemicals, dried for 12 h at 70 °C, and dissolved without additional recrystalization in Aldrich Gold Label solvents.

Syntheses

The ligands *N,N'*-dimethylene, *N,N'*-trimethylene-, *N,N'*-tetramethylene- and *N,N'*-pentamethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate) were prepared by methods previously described [34] with only slight modifications [30]. Yellow crystalline powders of each complex were isolated, analyzed for purity by elemental analyses and NMR, and used directly for subsequent reactions. $C_{16}H_{24}N_2S_4$: (L $n=2$) melting point (m.p.) 210 °C. *Anal.* Calc.: C, 51.6; H, 6.50; N, 7.52; S, 37.0. Found: C, 51.5; H, 6.52; N, 7.49; S, 34.5%. $C_{17}H_{26}N_2S_4$: (L $n=3$) m.p. 157 °C. *Anal.* Calc.: C, 52.8; H, 6.76; N, 7.25; S, 34.4. Found: C, 52.9; H, 6.86; N, 7.29; S, 33.1%. $C_{18}H_{28}N_2S_4$: (L $n=4$) m.p. 180 °C. *Anal.* Calc.: C, 54.0; H, 7.06; N, 6.99; S, 32.0. Found: C, 53.9; H, 7.12; N, 7.29; S, 31.6%. $C_{19}H_{30}N_2S_4$: (L $n=5$) m.p. 110 °C. *Anal.* Calc.: C, 55.0; H, 7.31; N, 6.76; S, 30.9. Found: C, 54.9; H, 7.31; N, 6.76, S, 30.9%.

The corresponding Ni(II) and Zn(II) complexes were synthesized according to previously reported methods [32, 33]. Analytical data on Ni $n=2$, 3, 4 and 5 are reported below. $NiC_{16}H_{22}N_2S_4 \cdot CH_2Cl_2$: (Ni $n=2$) slow evaporation of saturated chloroform solution produced dark green prismatic crystals. *Anal.* Calc.: C, 44.7; H, 5.13; N, 6.53; S, 29.8. Found: C, 44.7; H, 5.19; N, 6.50; S, 29.8%. $NiC_{17}H_{24}N_2S_4$: (Ni $n=3$) slow evaporation of a saturated chloroform solution yielded reddish-brown, chunky crystals. *Anal.* Calc.: C, 46.0; H, 5.40; N, 6.30; S, 28.0. Found: C, 46.1; H, 5.40; N, 6.30; S, 28.9%. Found: C, 46.1; H, 5.49; N, 6.26; S, 28.8%. $NiC_{18}H_{26}N_2S_4$: (Ni $n=4$) slow evaporation of a chloroform solution produced reddish-brown, chunky crystals. *Anal.* Calc.: C, 47.3; H, 5.69; N, 6.13; S, 28.0. Found: C, 47.3; H, 5.77; N, 6.10; S, 27.9%. $NiC_{19}H_{28}N_2S_4$: (Ni $n=5$) a rust-colored microcrystalline solid resulted from repeated recrystallizations from saturated chloroform solutions; rapid decomposition hindered the collection of physical characteristics. *Anal.* Calc.: C, 48.4; H, 5.94; N, 5.94; S, 27.2. Found: C, 48.6; H, 6.00; N, 6.15; S, 27.0%.

Zinc(II) complexes of *N,N'*-dimethylene-, *N,N'*-trimethylene- and *N,N'*-tetramethylene-bis(methyl-2-amino-1-cyclopentenedithiocarboxylate) were synthesized using zinc acetate and the same procedure as with the analogous Ni(II) complexes. Elemental analyses revealed slight ligand impurities, however further characterization by NMR supported a 1:1 ligand to metal complex formation.

Physical measurements

IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer over the range 4000–400 cm^{-1} using potassium bromide optics and pellets.

Electronic absorption spectra of chloroform solutions were recorded on a Cary 2300 spectrophotometer over the UV–vis and near IR region. The data were collected and manipulated with an Apple IIe computer.

Elemental analyses were obtained from Atlantic Microlabs, Atlanta, GA, U.S.A.

Electrochemical properties were determined in solutions of methylene chloride and dimethylformamide, with tetraalkylammonium perchlorate salts as supporting electrolytes, and using conventional three compartment 'H' cells. A BAS CV 27 potentiostat and YEW Model 3022 A4 X-Y recorder were used in all cyclic voltammetry experiments. Measurements were made using a platinum disk working electrode and platinum wire auxiliary electrode, with potentials standardized against a saturated calomel electrode.

NMR spectra were obtained on either a GE 500 MHz Omega FT-NMR spectrometer equipped with variable temperature apparatus, or a GE 300 MHz Omega FT-NMR instrument. All ^1H spectra were obtained using $CDCl_3$ solutions with TMS as an internal standard.

Results

Infrared spectroscopy

Absorptions in the IR regions near 1570, 1460 and 1350 cm^{-1} correspond to vibrations from delocalized C=C, C=C and C=N, and C=C and C=S bonds, respectively [33], and indicate inclusion of Ni(II) in a six-membered chelate ring. A slight shift in the C=S band from 1370 cm^{-1} for Ni $n=2$ to 1340 cm^{-1} for Ni $n=4$ is also noticed, suggesting increased delocalization throughout the ring as n increases.

Electronic absorption

Absorption spectra for the series were obtained in the UV–vis and near IR regions over the range 40 000–5000 cm^{-1}. The results are presented in Table 1. All absorptions higher in energy than 23 000 cm^{-1} (435 nm) correspond to intraligand electronic transitions. A comparison of the spectra of free and coordinated ligands shows a persistent intraligand band at 30 000 cm^{-1} (333 nm). A common ligand to metal charge transfer occurs between 22 570 and 21 790 cm^{-1} (453–459 nm) for each Ni(II) complex, and is assigned as a πS–Ni(II) transition. The red shift associated with this LMCT parallels the increase in the length of the bridging group, suggesting increased sulfur-nickel(II) π backbonding interactions. The spectrum of Ni(II)N$_2$S$_2$ $n=2$ shows a strong LMCT peak at 21 140 cm^{-1} flanked by a shoulder at both lower and higher energies, possibly assignable to additional LMCTs. By analogy to Ni $n=2$, each broad absorption in the 22 570 and 21 790 cm^{-1} region of the spectra of Ni(II)N$_2$S$_2$ $n=3$ and Ni(II)N$_2$S$_2$ $n=4$ consists of three LMCTs also tentatively assigned as πS–Ni(II) and σS–Ni(II) transitions.

TABLE 1. Optical absorption bands for Ni(II)N$_2$S$_2$ ($n=2$, 3, 4)[a]

Complex	Position (cm^{-1})	ϵ (M^{-1} cm^{-1})	Assignment
Ni(II)N$_2$S$_2$	28070	16510	CT
$n=2$	23840	4500	CT
	22570	6500	CT
	21100	4050	CT
	15150	130	d–d
Ni(II)N$_2$S$_2$	26850	8370	CT
$n=3$	24690	5200	CT
	22070	5850	CT
	14950	170	d–d
Ni(II)N$_2$S$_2$	26525	6000	CT
$n=4$	21800	3700	CT
	14750	200	d–d

[a] All spectra recorded using CHCl$_3$ and 1 cm matched quartz cells.

A ligand field transition appears within the 14 000–18 000 cm^{-1} range for Ni $n=2$, $n=3$ and $n=4$ typical for square planar complexes [35]. As the length of the bridging group between the nitrogens increases, the ligand field band red shifts, decreasing in energy from 15 150 cm^{-1} (660 nm) for Ni $n=2$ to 14 750 cm^{-1} (678 nm) for Ni $n=4$, suggesting distortion of the coordination geometry away from planar and towards a pseudo-tetrahedral stereochemistry.

Careful analysis of electronic absorptions in the 6500–14 000 cm^{-1} region required inspecting difference spectra calculated from baseline corrected spectra of the Ni(II) complexes and Zn(II) derivatives. No bands appear in the near IR region of the spectra of the complexes.

Electrochemistry

The Ni(II)N$_2$S$_2$ complexes were characterized electrochemically by cyclic voltammetry (CV) in both coordinating and non-coordinating solvents (DMF and CCl$_2$H$_2$). $E_{1/2}$ values are reported in Table 2. Each complex undergoes a quasi-reversible oxidation at +550 mV or greater versus SCE, and a reversible reduction at −1300 mV or lower versus SCE. Both are one electron processes, as shown by $i_{p,c}/i_{p,a}$ ratio analyses. Comparing the three complexes, the potential difference between the oxidative and reductive half waves decreases as a result of increasing the length of the methylene bridge. The oxidation half wave potentials become more negative by approximately 160 mV, while the reduction half wave potentials shift 370 mV more positive. Another effect of increasing the bridge length is to distort the oxidation waves, and subsequently lose reversibility.

The addition of small amounts of the Lewis bases thiophene and triphenylphosphine to solutions during voltammetric studies showed marked effects on the shape of the oxidation waves, but not the reduction waves. Increased current flow at the oxidation potential appears as the only distortion in the CV

TABLE 2. Cyclic voltammetry of Ni(II)N$_2$S$_2$ ($n=2$, 3, 4)[a]

Nickel complex	$E_{1/2}$ (V)	
	Oxidation	Reduction
$n=2$	0.75	−1.54
$n=3$	0.68	−1.43
$n=4$	0.59	−1.27

[a] All voltages vs. SCE; DMF solutions with 0.10 M TEAP as supporting electrolyte.

shape. The effect is less severe when the bridging group is lengthened, suggesting a steric effect governing the adduct formation of nickel(II) complex and electron donor molecule. Similar experiments with pyridine showed no changes in the shapes of the cyclic voltammagrams of each complex.

Nuclear magnetic resonance

Initially, NMR was used simply as a technique to verify deprotonation of free ligand, and check purity of synthetic products. The absence of amide proton at approximately 12.42 ppm signified deprotonation and chelation. The room temperature proton NMR chemical shifts of the free ligands, Ni(II) complexes and Zn(II) complexes are collected in Table 3.

Variable temperature NMR spectra were recorded in order to analyze isotropic contact shifts common to other four coordinate Ni(II) complexes with paramagnetic susceptibility. Spectra of the respective complexes dissolved in $CDCl_3$ were inspected over the temperature range from 20 to 60 °C. The shifts of proton resonances of the Zn(II) derivatives of the complexes were employed as diamagnetic references when calculating shift contributions from the paramagnetic Ni(II) center. Only Ni $n=4$ exhibited significant paramagnetic shifts, and shift values are reported in Table 4. At 58 °C the 8-CH_2 protons shifted downfield by 3.224 ppm to 6.788 ppm, the 5-CH_2 shifted downfield by 1.155 ppm to 3.875 ppm, and the 7-CH_2 shifted upfield by 1.222 ppm to 1.598 ppm. The percentage of tetrahedral isomer, or proportion of distortion from planarity, can be calculated from values of isotropic contact shifts, and the activation energy governing the equilibrium can be assessed.

Discussion

Molecules of the Lewis structure shown in Fig. 1 have been synthesized where the number of methylene groups, n, bridging the two nitrogens ranges from 2 to 5. Earlier, we published the molecular structures and characteristics of a similar series of neutral, four coordinate Cu(II) complexes, where the symmetry around the Cu(II) varied from pseudo-square planar to pseudo-tetrahedral as a function of n [36–38]. The dihedral angle between the two Cu(II)NS planes grew from 20 to 54 to 57°, with $n=2$, 3 and 4, respectively [36–38]. Previous characterizations of Ni $n=2$ and Ni $n=3$ indicated both as planar and diamagnetic in solution [32, 33], while earlier work on Ni $n=4$ in these laboratories suggested we could isolate two isomers, one diamagnetic and one paramagnetic [39]. Further experimentation, however, supports our hypothesis that Ni $n=3$ is slightly distorted from square planar geometry, while Ni $n=4$ is more twisted and exists only as a pseudo-tetrahedral isomer. The stabilization of square planar Ni(II) compounds by thiolate and pseudo-thiolate ligands is well documented [23], but behavior of the N_2S_2 ligands in the Cu(II) series raised some questions about the characteristics of the Ni(II) complexes. In order to more fully characterize the present series of Ni(II) compounds, we have studied the molecules using IR, NMR, electronic absorption and cyclic voltammetry.

The stereochemistries of the compounds can best be described by the dihedral angle between the two Ni(II)NS planes. The planarity of the six membered chelate rings including Ni(II) is established by NMR, supporting deprotonation of the amide, and IR, showing the expected delocalized streching frequencies. Infrared bands corresponding to delocalized vibrations from the ring shift to lower energies,

TABLE 3. ^1H NMR resonances of $n=2$, 3 and 4 ligands, Ni(II) complexes and Zn(II) complexes[a]

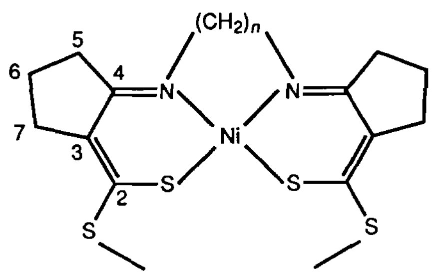
Compound	Protons						
	1-CH_3	5-CH_2	6-CH_2	7-CH_2	8-CH_2	9-CH_2	N-H
$L(H_2)N_2S_2$ $n=2$	2.593	2.710	1.837	2.800	3.632	–	12.42
$n=3$	2.593	2.715	2.029	2.815	3.567	1.890	12.42
$n=4$	2.598	2.703	1.895	2.820	3.340	1.822	12.42
$Ni(II)N_2S_2$ $n=2$	2.622	2.620	1.876	2.5622	3.354	–	
$n=3$	2.595	2.515	1.873	2.617	3.640	1.861	
$n=4$	2.595	2.144	1.820	3.142	5.043	1.742	
$Zn(II)N_2S_2$ $n=2$	2.598	2.714	1.943	2.807	3.528	–	
$n=3$	2.598	2.722	1.950	2.822	3.586	1.898	
$n=4$	2.603	2.720	2.037	2.820	3.564	1.898	

[a]All spectra recorded in $CDCl_3$ at room temperature with TMS as an internal standard. All shifts reported in ppm from TMS.

TABLE 4. ^1H NMR isotropic contact shifts for $Ni(II)N_2S_2$ $n=4^a$

Temperature (K)	5-CH_2	7-CH_2	8-CH_2
298	−0.743	0.636	1.738
308	−0.855	0.700	2.118
318	−1.013	0.872	2.496
323	−1.095	0.972	2.788
328	−1.174	1.086	3.055
331	−1.222	1.155	3.224

[a] All resonances in ppm relative to TMS internal standard.



$Ni(II)N_2S_2$ n=2, 3, 4, and 5

Fig. 1. Lewis structures of $Ni(II)N_2S_2$ complexes.

indicating increased electron delocalization throughout the chelate rings of the ligand. This effect accompanies the apparent shift to more pseudo-tetrahedral geometries.

The electronic spectra of the complexes also suggests that bonding interactions between S and Ni(II) increase as the dihedral angle increases. Both LMCTs and ligand field transitions undergo red shifts characteristic of small geometric changes within the same coordination environment [37]. These shifts in charge transfer energies are consistent with greater polarization of the sulfurs brought on by structural rearrangement of the ligand. It appears that as n increases the nitrogens are forced to rotate out of the NiSS′ plane, allowing the sulfurs to increase π-backbonding with Ni(II). This is consistent with similar trends reported for the $Cu(II)N_2S_2$ $n=2$, 3 and 4 complexes. The short two carbon bridge in Ni $n=2$ limits the coordination geometry to a pseudo-planar stereochemistry, which is most stabilized by thiolate and pseudo-thiolate ligands [23]. When the bridge is lengthened to 3 and 4 carbons the strain in the ligands forces the nitrogens out of the Ni(II)SS′ plane [36].

While the LMCTs provide insight into the ligand to metal bonding, the ligand field transitions aid in the assignment of the symmetry of the metal ion site. The band in each complex around 15 000 cm^{-1}, with molar extinction coefficients between 70–200 M^{-1} cm^{-1}, must be assigned as a d–d transition of a planar or pseudo-tetrahedral species. The bands are similar to low energy d–d transitions in $Ni(II)S_4$ molecules [40, 41], yet considerably lower than similar $Ni(II)N_2S_2$ [26]. The absence of the characteristic peak between 6500–10 000 cm^{-1} in the spectra of each complex indicates no tetrahedral isomers exist in solution [35]. The molar extinction coefficients increase as a function of the number of methylene groups as expected from a coordination site that loses a pseudo-inversion center.

The electrochemical potentials reveal oxidation and reduction potentials common for Ni(II) complexes [2, 20–22, 24]. The effect of increasing n, or increasing the dihedral angle, produces a drop in oxidation and reduction potentials. Repeated attempts to electrochemically produce Ni(III) under various conditions, resulted in significant decomposition of the starting complex. Irreversible oxidations in complexes coordinated by thiolate and pseudo-thiolate ligands exists as a common problem in similar situations [14, 15, 42]. Plots of $E_{1/2,\ \mathrm{ox}}$ versus ν_{max} and $E_{1/2,\ \mathrm{red}}$ versus ν_{max} yield straight lines, indicating an electron added during electrochemical processes enters or is removed from the same orbitals that are involved with photochemical charge transfer bands [36], and, as such, both oxidation and reduction waves represent metal centered processes.

Pyridine, thiophene and triphenylphosphine were used as axial bases in a study of the steric hindrance around the Ni(II) center. In the presence of thiophene and triphenylphosphine, Ni $n=2$ showed large increases in current flow at the oxidation potential, suggesting a possible electrocatalytic process. A threefold increase in current flow combined with a shift in the coupled reduction peak suggest adduct formation possibly producing a somewhat stable five coordinate environment surrounding a trivalent nickel ion. The effect diminished considerably in the case of Ni $n=3$ and $n=4$, and in the presence of pyridine no reaction was noted with any of the complexes. This suggests the metal interacts with the small molecules via π bonding, since S and P donors notably have more π than σ character as coordinating ligands, and undergo pπ–dπ backbonding more proficiently than does N. The evaluation of inductive π bonding has been the focus of other studies involving similar NiN_2S_2 complexes, and is believed as important factor in molecular O_2 binding [26].

Characterization of the planar ⇔ tetrahedral equilibrium by NMR techniques has been studied extensively [43–48]. Shifts in ^1H resonances are very sensitive to small changes in the electronic and magnetic state of a complexed metal ion. Shifts due to paramagnetic metals in chelate complexes can be separated into two components, dipolar and contact. Dipolar shifts arise from through space interactions and are considered negligible for systems similar to the present series of compounds [45]. Paramagnetic contact shifts are caused by electron–electron and nuclear–electron magnetic coupling between unpaired electrons on the metal and electrons centralized on the ligand, and then between electron spin from the ligand and the nuclei of neighboring protons. The nature of the observed shifts indicate they arise from a Fermi contact mechanism which delocalizes odd spin throughout the ligand orbitals. Since the shifts exhibit a linear relationship with temperature, the following relationship holds true [45]

$$\Delta f_o/f_i = -a_i(\gamma_e/\gamma_H)\{[g\beta S(S+1)]/6SkT\} \times [\exp(-\Delta G/RT)+1]^{-1} \qquad (1)$$

In eqn. (1) Δf_o is the shift in resonance for any given proton between diamagnetic and paramagnetic molecule, f_i is the frequency of the NMR instrument, a_i is the electron-nuclear hyperfine coupling constant in Gauss, and g is the g value of the paramagnetic form. The remaining symbols have their usual meanings. The bracketed exponential term, $[\exp(-\Delta G/RT)+1]^{-1}$, represents N_t, the fraction of tetrahedral isomer present in solution at temperature T, or the fractional proportion of twist from square planar to tetrahedral geometry. The analogous Zn(II) derivatives were utilized as diamagnetic references for calculating the isotropic contact shifts of the Ni(II) complexes.

Ni $n=2$ and Ni $n=3$ show only small shifts in proton resonances when compared to the corresponding Zn(II) complexes. These changes are attributed to slight electronic distortions caused by geometrical restraints imposed by chelation rather than contact shifts. In solution the two structures appear to be most stable in diamagnetic, square planar geometries. Even at elevated temperatures both complexes show no paramagnetic influence, although the optical results do point out small differences between the two coordination geometries.

Ni $n=4$, however, shows considerable shifts at room temperature. In analyzing spectra recorded between 25 and 58°C, the shifts in the 5-CH_2 and 7-CH_2 resonances exhibit a linear relationship with inverse temperature, as plotted in Fig. 2. In order to estimate N_t utilizing eqn. (1), the g value must be calculated from the effective magnetic moment, $\mu_{eff}=3.20\ \beta\mu$ [39], while a_i values must be imported from similar tetrahedral complexes [45]. Using an a_i range of -0.683 to -0.386, and the isotropic shifts of the 5- and 7-protons we have calculated a range for the percentage of tetrahedral isomer of $0.02<N_t<0.03$ (i.e. 2–3%). ΔG for the equilibrium can then be estimated. It is obvious from the variable temperature readings that the equilibrium process is endothermic, since shifts increase with temperature between 293 and 331 K. The ΔG required to shift the geometry from planar towards pseudo-tetrahedral coordination is approximately 2.2 kcal/mol. Intuitively this makes sense in that the Ni(II) prefers to coordinate in a planar geometry, yet ligand strain imposed by the Ni $n=4$ bridging group attempts to force the coordination into a pseudo-tetrahedral symmetry.

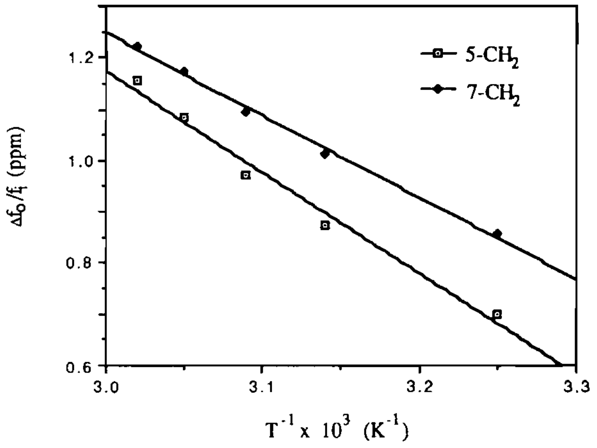


Fig. 2. Temperature dependence of contact shifts for Ni(II)N_2S_2 $n=4$ (I) protons.

The mechanism of spin transfer is thought to be a ligand to metal antiparallel spin transfer as seen in similar bis-bidentate Ni(II)N_2S_2 complexes [45]. As a result of this mechanism, net excess spin resides on the nitrogen, the sulfur and the 3-carbon of the chelate ring. The transfer is predominantly a π effect leaving excess odd spin in the ligand-based HOMO forming an odd-alternate spin pattern as just described. The outerlying protons of the cyclopentene moiety also experience the effects of the paramagnetic component of the Ni(II). The resonance of the 7-CH_2 protons shift downfield as a result of increased shielding from spin distributed from the 3-C of the delocalized ring system. The opposite effect is seen in the 5-CH_2 protons, where the resonance shifts upfield due to a combination of π and σ bonding effects from the 4-C of the chelate ring. The π density at the 5-C decreases as a result of the ligand to metal spin transfer, which causes polarization of the C–H bond. As the temperature is raised the 7-CH_2 and 5-CH_2 peaks grow farther apart. The 6-CH_2 protons of the cyclopentene moiety show no shift in resonance. The distance from the Ni(II) ion and the combined contributions from the two neighboring methylenes leave the resonance unaffected.

The peak shifted farthest downfield is that of the 8-CH_2 protons. Transmission of spin through the σ orbitals of the nitrogen and into the alkyl bridge causes a large shift in the first protons of the bridge. The σ effect quickly attenuates, however, and does not shift the resonance of the next protons in the bridge. This result is seen in similar complexes [29, 45]. The strong singlet from the S-CH_3 protons also remains unaffected by the paramagnetic Ni(II) because of distance. It is interesting to note the combinations of π and σ influences as compared to previously studied bis-bidentate structures, which involved extended π systems.

Comparisons can be made between Ni $n=2$, 3 and 4 and the Ni(II) substituted blue copper(II) proteins. Physical characteristics of Ni(II) derivatives of Azurin and Stellacyaninin are found in the literature [6, 7] along with other synthetic Ni(II)N_2S_2 complexes [26, 29]. The original purpose of metal substitution studies was to examine the rigidity of the secondary protein structure in the presence of various metals. Ni(II) substituted Azurin has revealed electronic absorption in the near IR region indicative of tetrahedral coordination similar to Cu(II) Azurin [7]. Although LMCTs of the synthetic n-series seem to match the Ni(II) substituted proteins rather closely, the NMR data characterizes the geometry of the most distorted Ni $n=4$ complex as having only a small dihedral angle in solution. High resolution NMR studies of Ni(II) Azurin show a resonance shifted to 30 ppm, and assigned as the methyl protons of Met-121. Ni $n=4$ shows no resonance shifted that far downfield, yet it is interesting to note that the synthetic complex and Ni(II) Azurin have the same magnetic susceptibility, $\mu_{\text{eff}}=3.20\ \beta\mu$, a value consistent with a low symmetry, pseudo-tetrahedral coordination geometry, or possibly a pseudo-octahedral one. The Ni $n=4$ value was measured in the solid state, however. Solvation apparently gives rise to the planar$\Leftrightarrow$tetrahedral equilibrium, allowing stabilization of the pseudo-planar geometry by the thiolate-like ligand [29, 45].

Conclusions

We have succeeded in synthesizing a series of Ni(II)N_2S_2 complexes where the coordination geometry changes in a stepwise manner from square planar to pseudo-tetrahedral. By distorting the pseudo-D_{4h} site symmetry around Ni(II) and blocking coordination axially, the oxidation potential drops, but not to values seen in the native hydrogenases. Producing more tetrahedral geometries also allows increased synergistic bonding between the sulfurs and the metal, lowering the energy required for πS–Ni(II) charge transfers. Comparisons with the similar Cu(II) series support the theory that the coordination geometry is dictated predominantly by the preference of the particular metal ion, and that the nitrogens twist out of the NiSS′ plane, leaving the sulfurs in position to maximize π backbonding. The strain imposed by the ligands pushes the Ni(II) structures toward pseudo-tetrahedral geometry, while it keeps the Cu(II) complexes from attaining larger dihedral angles. Therefore, we offer support to the theory that the coordination geometry in native N_2S_2 proteins is dictated by the protein fold.

If indeed a crossover point exists where the spin state abruptly changes from singlet to triplet, Ni $n=2$, 3 and 4 must still be considered as ground state singlets in solution. Nevertheless, the visible absorption bands of ni $n=4$ reveal ligand field transitions indicative of intermediate four coordinate geometry when compared with other Ni(II)N_2S_2 complexes [26, 29]. Representative of pseudo-tetrahedral coordination is Ni(tsaltbu)$_2$ [26], with d–d transitions at 7.00 (30 M^{-1} cm^{-1}) and 9.00 (25 M^{-1} cm^{-1}) kK. At the planar end of the four coordinate symmetries is Ni(sacac)en [29], with a d–d transition at 16.53 kK (70 M^{-1} cm^{-1}). Ni $n=4$ occupies an intermediate position within the range of possible stereochemistries with a d–d transition at 14.75 kK (200 M^{-1} cm^{-1}). A similar comparison can be made between ^1H NMR resonances of Ni $n=4$ and Ni(tsaltbu)$_2$. The isotropic contact shifts are not as large in the former as they are in the latter. The single crystal X-ray diffraction analyses of the Ni n-series is underway, and we anticipate the results will show a smooth transition from square planar to pseudo-tetrahedral geometries [49].

References

1 R. P. Hausinger, *Microbiol. Rev., 51* (1987) 22.
2 R. Cammack, *Adv. Inorg. Chem., 32* (1988) 297.
3 J. Lancaster, (ed.), *The Bioinorganic Chemistry of Nickel,* VCH, New York, 1988.
4 R. Cammack, D. S. Patil, E. C. Hatchikian and V. M. Fernande. *Biochim. Biophys. Acta, 98* (1987) 912.
5 D. L. Tennent and D. R. McMillin, *J. Am. Chem. Soc., 101* (1979) 2307.
6 V. Lum and H. B. Gray. *Isr. J. Chem., 21* (1981) 23.
7 H. R. Engeseth, D. R. McMillin and E. L. Ulrich, *Inorg. Chim. Acta, 67* (1982) 145.
8 J. A. Blaszak, E. L. Ulrich, J. L. Markley and D. R. McMillin, *Biochemistry, 21* (1982) 6253.
9 D. V. DerVartanian, H.-J. Krüger, H. D. Peck, Jr. and J. LeGall, *Rev. Port. Quim., 27* (1975) 70.
10 S. P. J. Albracht, A. Kroger, J. W. Van der Zwaan, G. Unden, R. Bocher, H. Mell and R. D. Fontijn, *Biochim. Biophys. Acta, 874* (1986) 116.

11 P. A. Lindahl, N. Kojima, R. P. Hausinger, J. A. Fox, B. K. Teo, C. T. Walsh and W. H. Orme-Johnson, *J. Am. Chem. Soc., 106* (1984) 3062.

12 R. A. Scott, S. A. Wallin, M. Czechowski, D. V. DerVartanian, J. LeGall, H. D. Peck, Jr. and I. Moura, *J. Am. Chem. Soc., 106* (1984) 6864.

13 A. T. Kowal, I. C. Zambrano, I. Moura, J. J. G. Moura, J. LeGall and M. K. Johnson, *Inorg. Chem., 27* (1988) 1162.

14 H.-J. Krüger and R. H. Holm, *Inorg. Chem., 28* (1989) 1148.

15 H.-J. Krüger and R. H. Holm, *Inorg. Chem., 27* (1988) 3645.

16 J. W. van der Zwaan, S. P. J. Albracht, R. D. Fontijn and E. C. Slater, *FEBS Lett., 179* (1975) 271.

17 M. Teixeira, I. Moura, A. V. Xavier, B. H. Huynh, D. V. DerVartanian, H. D. Peck, Jr., J. LeGall and J. J. G. Moura, *J. Biol. Chem., 260* (1985) 8942.

18 R. Cammack, V. M. Fernandez and K. Schneider, *Biochemie, 68* (1986) 85.

19 R. Cammack, D. S. Patil, E. C. Hatchikian and V. M. Fernandez, *Biochim. Biophys. Acta, 912* (1987) 98.

20 K. Nag and A. Chakravorty, *Coord. Chem. Rev., 33* (1980) 87.

21 R. J. Haines and A. McAuley, *Coord. Chem. Rev., 39* (1981) 77.

22 A. G. Lappin and A. McAuley, *Adv. Inorg. Chem., 32* (1988) 241.

23 M. A. Ali and S. E. Livingstone, *Coord. Chem. Rev., 13* (1974) 101.

24 W. R. Pangratz, F. L. Urbach, P. R. Blum and S. C. Cummings, *Inorg. Nucl. Chem. Lett., 9* (1973) 1141.

25 R. M. C. Wei and S. C. Cummings, *Inorg. Nucl. Chem. Lett., 9* (1973) 43.

26 P. R. Blum, R. M. C. Wei and S. C. Cummings, *Inorg. Chem., 13* (1974) 450.

27 L. S. Chen and S. C. Cummings, *Inorg. Chem., 17* (1978) 2358.

28 M. F. Corrigan and B. O. West, *Aust. J. Chem., 29* (1976) 1413.

29 I. Bertini, L. Sacconi and G. P. Speroni, *Inorg. Chem., 11* (1972) 1323.

30 K. Nag and D. S. Joardar, *Inorg. Chim. Acta, 14* (1975) 433.

31 S. K. Mondal, P. Paul, R. Roy and K. Nag, *Transition Met. Chem., 9* (1984) 247.

32 R. Roy, P. Paul and K. Nag, *Transition Met. Chem., 9* (1984) 152.

33 S. K. Mondal, D. S. Joardar and K. Nag, *Inorg. Chem., 17* (1978) 191.

34 P. Bordas, P. Sohar, G. Matolcsy and P. Berencsi, *J. Org. Chem., 37* (1972) 1727.

35 R. S. Drago, *Physical Methods in Chemistry,* Saunders, Philadelphia, PA, 1977, pp. 387–391.

36 R. D. Bereman, J. R. Dorfman, J. Bordner, D. P. Rilemma, P. McCarthy and G. D. Shields, *J. Bioinorg. Chem.,* (1982) 49.

37 R. D. Bereman, M. W. Churchill and G. D. Shields, *Inorg. Chem., 18* (1979) 3117.

38 R. D. Bereman, G. D. Shields, J. Bordner and J. R. Dorfman. *Inorg. Chem., 20* (1981) 2165.

39 J. R. Dorfman, *Ph.D. Thesis,* North Carolina State University, Raleigh, NC, 1982.

40 C. Furlani and M. L. Luciani, *Inorg. Chem., 7* (1968) 1586.

41 B. G. Werden, E. Billig and H. B. Gray, *Inorg. Chem., 5* (1966) 78.

42 Y. Nakabayashi, Y. Masuda and E. Sekido. *J. Electroanal. Chem. Interfacial Electrochem., 205* (1986) 209.

43 G. N. LaMar, W. D. Horrocks and R. H. Holm, *NMR of Paramagnetic Ions,* Academic Press, New York, 1973, pp. 243–326.

44 R. H. Holm, *Acc. Chem. Res., 2* (1969) 307.

45 D. H. Gerlach and R. H. Holm, *J. Am. Chem. Soc., 91* (1969) 3457.

46 G. W. Everett, Jr., R. H. Holm and A. Chakravorty, *Prog. Inorg. Chem., 7* (1966) 83.

47 G. W. Everett, Jr. and R. H. Holm, *Inorg. Chem., 7* (1968) 776.

48 G. W. Everett, Jr. and R. H. Holm, *J. Am. Chem. Soc., 87* (1964) 2117.

49 E. M. Martin, R. D. Bereman and P. Singh, *Inorg. Chem.,* in press.