Articles

Nickel(II) in an N₄S Donor Environment: An Unprecedented Alcoholysis Reaction through the Activation of a Carbon−Nitrogen Single Bond

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Pentadentate N₄S ligands based on methyl 2-aminocyclopent-1-ene-1-dithiocarboxylate with flexible pyrazolyl arms ((Me₂pzCH₂)₂NC₂H₃RNHC₅H₆CSSCH₃ (R = H, **Hmmecd** and R = CH₃, **Hmmpcd**) undergo a nickel(II)-induced alcoholysis reaction through the activation of a saturated C−N bond linkage. The products obtained are square-planar complexes **1**−**4** containing a modified ligand structure possessing an N₃S donor set and a pendant arm that holds the alkoxy group provided by the solvent. [Ni(N₃S)-CH₂OMe]ClO₄ **1** crystallizes in the triclinic space group $P\bar{1}$ with $a = 10.4886(5)$ Å, $b = 10.706(1)$ Å, $c = 11.487(1)$ Å, $\alpha = 108.784(4)°$, $\beta = 108.887(6)°$, $\gamma = 95.139(6)°$, $V = 1128.0(4)$ Å³, and $Z = 2$; while [Ni(N₃S)′-CH₂ OPr^n]ClO₄ **4** has the monoclinic space group $P2_1/n$ with $a = 8.875(2)$ Å, $b = 18.629(2)$ Å, $c = 15.399(2)$ Å, $\beta = 91.37(2)°$, $V = 2545(1)$ Å³, and $Z = 4$ per unit cell. Complexes **1**−**4** with acyclic ligand environments have interesting electrochemical behavior in acetonitrile, involving a reversible Ni(II)/Ni(I) reduction, $E_{1/2}$ ca. −1.0 V, and a Ni(II)/Ni(III) irreversible oxidation, E_{pa} ca. 1.0 V vs Ag/AgCl as the reference. The coulometrically reduced solution of **2** displays a rhombic EPR spectrum at 77 K characteristic of nickel(I) with $g_1 = 2.217$, $g_2 = 2.170$, and $g_3 = 2.054$.

Introduction

Pentacoordination in nickel is a relatively unexplored area.[1] In recent years, such species have been thought to be present as active sites in at least three bacterial enzymes that utilize redox-active nickel centers as prosthetic groups during their turnover.[2] The oxidation states, nuclearity status, turnover mechanism, and the set of donor atoms around nickel in these biosites are, thus far, only partially revealed. Nevertheless, thiol-dominated coordination environments are conceived in these nickel biochromophores as evidenced by their X-ray absorption spectra,[3−6] low Ni(III)/Ni(II) redox potentials,[7] and crystal-structure data.[8] Consequently, studies on pentacoordinate nickel complexes of heterodonor (S, N, O) ligands have gathered renewed interest in recent years because of their apparent biological relevance to nickeloprotein active sites.[9−18]

The ligands, methyl ((2-(β-bis((3,5-dimethylpyrazol-1-yl)-

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methyl)amino)ethyl)amino)cyclopent-1-ene-1-dithiocarboxyl-ate (**Hmmecd**) and its propyl homologue (**Hmmpcd**),[19] are both pentadentate, having a pair of flexible pyrazolyl arms and a carbodithioate functionality, which behaves more like an electronic analogue of thiol when coordinated to a metal center.[20,21]

R = H, **Hmmecd**
= CH$_3$, **Hmmpcd**
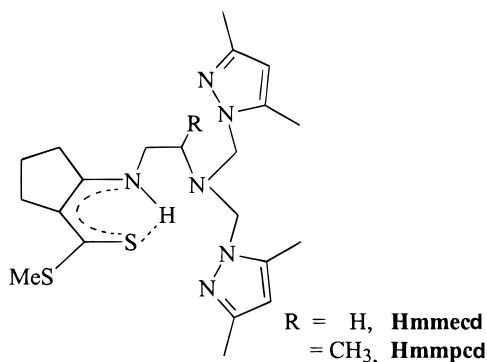
The interesting combination of hard−soft donor atoms in the set (N$_4$S) and sufficient flexibility in the ligand backbone promise enough scope for the extension of this study to nickel pentacoordination chemistry in a N/S environment.

Unlike the copper(II)/zinc(II) chemistry as described earlier,[20] the nickel(II) coordination chemistry with these ligands is not straightforward. The latter metal atom appears to promote solvolytic cleavage of an otherwise unreactive C−N single bond of the coordinated ligands in alcohols solvent, thus possibly providing a rare example of a nickel(II) induced C−N single-bond activation process. Herein we report the synthesis, crystal and molecular structures, spectroscopic characterizations, and redox properties of a series of square-planar nickel(II) complexes, **1**−**4**, formed during this unprecedented alcoholysis reaction.

Experimental Section

The ligands **Hmmecd** and **Hmmpcd** were prepared as described earlier.[20] Solvents were purified and dried from appropriate reagents[22] and distilled under nitrogen prior to their use. All other reagents are available commercially and were used as received. Unless stated otherwise, all manipulations in the following preparations were carried out under an atmosphere of purified dinitrogen.

Syntheses. [Ni(N$_3$S)-CH$_2$OMe]ClO$_4$ 1.[23] To a stirred, freshly prepared methanolic solution (15 mL) of **Hmmecd** (0.22 g, 0.5 mmol) was added with continuous stirring an equimolar amount (0.18 g) of nickel(II) perchlorate hexahydrate in 10 mL of methanol. The resulting green solution was stirred at room temperature for 5 h, filtered, concentrated to ca. a 10 mL volume, and refrigerated (at 4 °C) overnight

to obtain a green crystalline solid. Recrystallization from methanol gave shining green crystals. Yield: 0.11 g (42%). Anal. Calcd for NiC$_{17}$H$_{27}$N$_4$S$_2$-ClO$_5$: C, 38.84; H, 5.14; N, 10.66. Found: C, 38.4; H, 5.3; N, 10.7. IR (KBr disk): ν(CC), 1565s; ν(CN)/pyrazole ring, 1545s; ν(CN + CC), 1470s; ν_{as}(ClO), 1100s; δ(OClO), 630s cm^{-1}.

[Ni(N$_3$S)′-CH$_2$OMe]ClO$_4$ 2. To a freshly prepared solution of **Hmmpcd** (0.22 g, 0.5 mmol) in methanol (15 mL) was added quickly with stirring a methanolic solution (10 mL) of nickel(II) perchlorate hexahydrate in equimolar quantity (0.18 g, 0.5 mmol). The color of the reaction mixture immediately changed to green from which moss-green crystalline solid began to appear within 10 min. The stirring was continued for ca. 2 h to ensure completion of the reaction. The product was filtered off, washed with chilled methanol/ether (2:1 v/v) mixture (4 × 10 mL), and finally dried in vacuo. The product was recrystallized from an acetone/*n*-hexane mixture. Yield: 0.18 g (66%). Anal. Calcd for NiC$_{18}$H$_{29}$N$_4$S$_2$ClO$_5$: C, 40.06; H, 5.38; N, 10.38. Found: C, 40.0; H, 5.5; N, 10.3. IR (KBr disk): ν(CC) + ν(CN)/pyrazole ring, 1555s; ν(CN + CC), 1460s; ν_{as}(ClO), 1100s; δ(OClO), 630s cm^{-1}.

[Ni(N$_3$S)′-CH$_2$OEt]ClO$_4$ 3. A freshly prepared solution of **Hmmpcd** (0.22 g, 0.5 mmol) in ethyl alcohol (15 mL) was combined with a stoichiometric (1:1 mol ratio) amount of nickel(II) perchlorate hexahydrate (0.18 g, 0.5 mmol), also in ethyl alcohol (10 mL). The resulting green solution was refluxed for 4 h and then filtered. The filtrate was allowed to stand overnight in a freezer (at 0 °C) when microcrystalline green solid separated from the solution. The product was filtered, washed with ethyl alcohol/ether (2:1 v/v) mixture (2 × 10 mL), and dried in vacuo. Repeated recrystallization (two to three times) from a dichloromethane/*n*-hexane combination afforded shining green crystals. Yield: 0.11 g (40%). Anal. Calcd for NiC$_{19}$H$_{31}$N$_4$S$_2$ClO$_5$: C, 41.21; H, 5.60; N, 10.12. Found: C, 41.2; H, 5.4; N, 10.2. IR (KBr disk): ν(CC), 1560s; ν(CN)/pyrazole ring, 1550s, ν(CC + CN), 1460s; ν_{as}(ClO), 1100s; δ(OClO), 630s cm^{-1}.

[Ni(N$_3$S)′-CH$_2$OPr^n]ClO$_4$ 4. This compound was prepared following a procedure essentially identical to that described for **3**, but with *n*-propanol being the solvent. A prolonged refluxing time (ca. 24 h) was required for the completion of this reaction. The product was obtained as a dark green solid and recrystallized twice from dichloromethane/*n*-hexane. Yield: 20%. Anal. Calcd for NiC$_{20}$H$_{33}$N$_4$S$_2$ClO$_5$: C, 42.31; H, 5.81; N, 9.87. Found: C, 42.0; H, 6.0; N, 9.8. IR (KBr disk): ν(CC) + ν(CN)/pyrazole ring, 1550s; ν(CN + CC), 1470s; ν_{as}(ClO), 1100s; δ(OClO), 630s cm^{-1}.

[Ni(N$_3$S)-CH$_2$Me$_2$pz]ClO$_4$ 5. To a hot (45 °C) solution containing **Hmmecd** (0.44 g, 1 mmol) and Me$_2$pz (0.25 g, 2.6 mmol) in methanol (20 mL) was added with stirring a methanolic solution (5 mL) of nickel(II) perchlorate hexahydrate (0.36 g, 1 mmol). The resulting brown solution was refluxed for 2 h and filtered, and the filtrate was cooled to room temperature. To this was added diethyl ether (10 mL), and the solution was refrigerated at 4 °C overnight. The dirty yellow solid appearing at this stage was discarded, and the filtrate volume was reduced to 5 mL by rotoevaporation and left in the air for 2 h to yield a dark brown crystalline product, which was washed with methanol−ether (2:1 v/v) and dried. Yield: 0.25 g (42%). Anal. Calcd for NiC$_{21}$H$_{31}$N$_6$S$_2$ClO$_4$: C, 42.77; H, 5.26; N, 14.25. Found: C, 42.5; H, 5.4, N, 13.9. IR (KBr disk): ν(CC) + ν(CN)/pyrazole ring, 1550s; ν(CN + CC), 1475s; ν_{as}(ClO), 1100s; δ(OClO), 630s cm^{-1}.

Caution! Perchlorate salts of metal complexes are potentially explosive and should only be handled in small quantities.

Physical Measurements. Details of elemental analyses and IR and UV/visible spectroscopic measurements were described elsewhere.[24] Electrochemical measurements were performed with a Bioanalytical system model 100 B/W workstation. For cyclic voltammetry, a Pt disk (ϕ = 1.7 mm) working electrode and a Pt wire counter electrode were utilized along with an Ag/AgCl electrode as a reference. Concentrations of sample solutions were ca. 10^{-3} M and contained 0.1 M TEAP as the supporting electrolyte. For coulometry, a platinum-gauze working electrode was used. Successful coulometric experiments were done at

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(19) Abbreviation used: **Hmmecd**, methyl ((2-(β-bis((3,5-dimethylpyrazol-1-yl)methyl)amino)ethyl)amino)cyclopent-1-ene-1-dithiocarboxyl-ate; **Hmmpcd**, methyl ((2-(β-bis((3,5-dimethylpyrazol-1-yl)methyl)-amino)propyl)amino)cyclopent-1-ene-1-dithiocarboxylate; TEAP, tetraethylammonium perchlorate; Me$_2$pz, 3,5-dimethylpyrazole; TBP, trigonal bipyramid.

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(23) During the preparations of **1**−**4**, the original N$_4$S ligands undergo alcoholysis reaction through the activation of a C−N single bond. The modified forms of the coordinated ligands are represented by their respective set of donor atoms. Details are given in Scheme 1.

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Table 1. Relevant Crystallographic Data of [Ni(N$_3$S)-CH$_2$OMe]ClO$_4$ **1** and [Ni(N$_3$S)′-CH$_2$OPr^n] ClO$_4$ **4**

compound	**1**	**4**
formula	NiC$_{17}$H$_{27}$N$_4$S$_2$ClO$_5$	NiC$_{20}$H$_{33}$N$_4$S$_2$ClO$_5$
f_w	525.7	567.8
space group	$P\bar{1}$ (No. 2)	$P2_1/n$ (No. 14)
a, Å	10.4886(5)	8.875(2)
b, Å	10.706(1)	18.629(2)
c, Å	11.487(1)	15.399(2)
α, deg	108.784(8)	
β, deg	108.887(6)	91.37(2)
γ, deg	95.139(6)	
V, Å^3	1128(4)	2545(1)
Z	2	4
T, °C	20	21
λ(Mo Kα), Å	0.71073	0.71073
ρ_{calcd}, g cm^{-3}	1.548	1.474
μ, cm^{-1}	11.95	10.6
R^a ($R_w{}^b$)	0.042(0.054)	0.049(0.053)

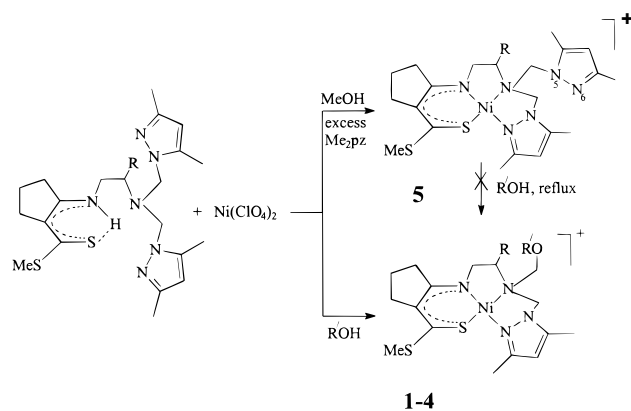^{a} $R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. ^{b} $R_w = [\Sigma w(||F_o| - |F_c||)^2/\Sigma w|F_o|^2]^{1/2}$.

−40 °C or below and the yellow catholyte solutions were immediately frozen at −196 °C before the EPR measurements. Scrupulously dried and freshly distilled deoxygenated acetonitrile was used throughout as the solvent. Potentials are reported relative to Ag/AgCl and are uncorrected for junction potentials. For EPR, a JEOL model JES-RE3X spectrometer combined with an ESR data system JEOL ES−PRIT 300 was used.

X-ray Crystallography. Diffraction-quality crystals of **1** were grown at 0 °C by slow diffusion of *n*-hexane into an acetone solution of the complex. An identical procedure was followed at room temperature to grow the crystals of **4** using *n*-hexane/CH$_2$Cl$_2$ as the solvent combination. A suitable crystal of compound **1** (a yellow-green tablet of dimensions 0.12 × 0.31 × 0.32 mm) was mounted without protection on a glass fiber, while for **4**, a green prism of dimensions 0.22 × 0.25 × 0.50 mm was selected and attached to a glass fiber with epoxy cement. The cell dimensions and orientation matrix were determined from the setting angles of an Enraf-Nonius CAD-4 diffractometer fitted with graphite monochromatized Mo Kα radiation, $\lambda = 0.710\,73$ Å, for 25 centered reflections in the range 15° < θ < 16°. Relevant crystal data are summarized in Table 1. The nickel-atom positions were located from the Patterson maps and the other non-hydrogen atoms by DIRDIF.[25] The expected structures were obtained, and the absence of solvent of crystallization was confirmed in each case. A small empirical absorption correction[26] based on the isotropically refined structure was applied. All non-hydrogen atoms were refined with anisotropic thermal parameters. For compound **4**, in order to ensure a satisfactory convergence, it was necessary to fix the values of x, y, z, and U_{ij} for C(19) and C(20) in the last cycles. Hydrogen atoms were included at calculated, updated positions. For **1**, the perchlorate oxygen atoms had large and appreciably anisotropic thermal parameters, but the apparent partial disorders could not be modeled. The *TEXSAN* program suite,[27] utilizing complex atomic scattering factors,[28] was used in all calculations.

Results and Discussion

Synthesis. The pentadentate N$_4$S ligands **Hmmecd** and **Hmmpcd**, having sufficiently flexible pyrazolyl arms, are capable of forming trigonal bipyramidal and square-pyramidal

(25) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van der Hark, T. E. M.; Prick, P. A. J.; Noordik, K. H.; Beurskens, G.; Parthasarathi, V.; Bruins Slot, H. J.; Haltiwanger, R. C.; Strumpel, M.; Smits, J. M. M. *DIRDIF*: *Direct Methods for Difference Structures*; Technical Report 1984/1; Crystallography Laboratory, Toernooiveld: 6525 Ed Nijmegen, The Netherlands.
(26) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.
(27) *TEXSAN*: *Texray Program for Structure Analysis*, version 5.0, Molecular Structure Corp., The Woodlands, TX, 1989.
(28) Cromer, D. T.; Waber, J. T. In *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, 1974; Vol. 4.

Scheme 1

Complex	R	R′
1	H	CH$_3$
2	CH$_3$	CH$_3$
3	CH$_3$	C$_2$H$_5$
4	CH$_3$	C$_3$H$_7$

complexes with zinc(II) and copper(II) ions, respectively, with differing degrees of distortions.[20] The chemistry described here with nickel(II) is altogether different. The metal ion appears to promote the solvolytic cleavage of a C−N single bond of the coordinated N$_4$S ligands in an alcohol solvent in an unprecedented manner (Scheme 1). The products obtained are mononuclear square-planar nickel(II) complexes (**1**−**4**) with a pendant arm that accommodates the alkoxy group provided by the solvent. Use of solvents other than alcohol in this reaction does not proceed to the desired five-coordinated nickel(II) complexes, but only to gummy intractable solids of unknown composition.

When the experimental procedure for **1** was repeated in the presence of excess 3,5-dimethylpyrazole (Me$_2$pz), the only product that could be isolated was **5**. Diffraction-quality crystals could not be grown. However, the product has an almost overlapping IR spectrum to that of the corresponding palladium(II) compound of known molecular structure, established from X-ray crystal structure analysis.[29] By analogy, **5** appears to be a square-planar compound having an N$_3$S chromophore with a free-dangling pyrazolyl arm which stays away from coordination as a result of the *anti* disposition of the pyrazolyl nitrogen N(6) atom (Scheme 1) relative to the metal center (staggered configuration). This observation signifies an inhibitory role of Me$_2$pz and resists the C−N bond cleavage process. Compound **5**, once isolated, is reluctant to undergo the alcoholysis reaction even under refluxing conditions.

The complexes are all air-stable in the solid state and have varying degrees of solubilities in common organic solvents. In solution, the complexes are greenish-brown in color and show signs of decomposition upon prolonged standing in the air. Use of clean solvents which have been freshly dried, distilled, and thoroughly purged with purified dinitrogen can check such decomposition.

IR spectra of the complexes have many characteristic bands of the coordinated N$_4$S ligand framework as described earlier.[20] One such band with a distinctive sharp feature, arising from the ν(CN) stretching mode of the coordinated pyrazolyl group,

(29) Bhattacharyya, S.; Weakley, T. J. R.; Chaudhury, M. Unpublished results.

Table 2. Molar Conductance[a] and Electronic Spectral Data

complex	solvent	Λ/ohm^{-1} cm^2 mol^{-1}	λ_{max}/nm (ϵ/mol^{-1} cm^2)
1	CH$_3$CN	148	599 (115), 400 (6400), 334 (4600)
2	CH$_3$CN	129	618 (85), 403 (6600), 330 (4100)
3	CH$_3$CN	144	615 (70), 400 (7000), 330 (4600)
4	CH$_3$CN	155	590 (85), 402 (10 600), 335 (6600)
5	(CH$_3$)$_2$CO	116	576 (sh), 529 (sh), 398 (6800), 340 (6650)

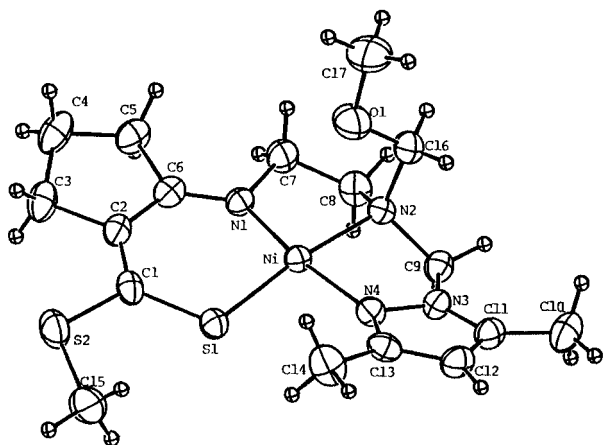[a] Molar conductances were measured with ca. 1.00 mM solutions at 25 °C.

Figure 1. Molecular structure of the cation in [Ni(N$_3$S)-CH$_2$OMe]-ClO$_4$ **1** showing the atom-labeling scheme. The ellipsoids represent a 25% probability.
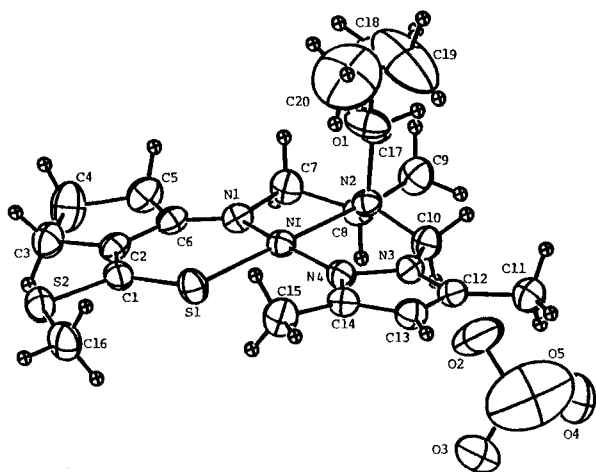

Figure 2. Perspective drawing of [Ni(N$_3$S)′-CH$_2$OPr^n]ClO$_4$ **4** showing the atom-labeling scheme. The ellipsoids represent a 25% probability.

appears at ca. 1550 cm^{-1}. Also, two strong bands at ca. 1100 and 630 cm^{-1} provide evidence for the presence of ionic perchlorate in these molecules.[30] Molar conductivity measurements in acetonitrile (Table 2) find these complexes to be 1:1 electrolyte.[31]

Description of Crystal Structures. Figures 1 and 2 show the perspective views of the complexes **1** and **4,** respectively. Their selected bond distances and angles are given in Table 3. Complex **1** crystallizes in the triclinic space group $P\bar{1}$ with two molecules per unit cell, while **4** has the monoclinic space group $P2_1/n$ with four molecules accommodated in the unit cell. The

observed crystal structures confirm the alcoholysis of the N$_4$S ligands (Scheme 1). In both cases, the ligand structures are altered when one of the pyrazolyl groups of the parent ligand molecule is replaced by the corresponding alkoxy group provided by the solvent. The modified ligand frameworks thus obtained act as tetradentate (N$_3$S) ligands, forming, in each case, a square-planar Ni(II) complex with a pendant arm that includes the ether moiety.

The main features in the structures of **1** and **4** are very similar (Table 3). In both the cases, three Ni–N bond distances are unequal with the Ni–N(2) bond lying trans to the Ni–S(1) direction having the longest bond length of 1.973(3) Å (1.967(4) Å for **4**). The C(1)–S(1) distances 1.719(4) and 1.707(6) Å (for **4**) indicate that the sulfur atoms S(1) have significant thiolate character[9b,13b] in **1** and **4**, a feature typical of these types of ligands containing carbodithioate moiety.[20,21] Of particular interest are the remarkably short Ni–S(1) distances (2.125(1) and 2.114(1) Å observed in **1** and **4**, respectively) as compared to similar Ni–S bonds in octahedral,[13d] square-pyramidal,[16,17] and tetrahedral[32] nickel(II) complexes. This reflects strong Ni–S interaction in these square-planar complexes, capable of exerting an efficient trans-labilizing influence,[33] as evident from the elongation in Ni–N(2) distances. Also in these molecules, the bond angles S(1)–Ni–N(2) and N(1)–Ni–N(4) are quite close to 180°, and the Ni atom is displaced marginally (0.067 Å (0.018 Å for **4**)) from the least-squares plane through S(1), N(1), N(2), and N(4), indicating almost an ideal square-planar geometry around the metal center.

Electronic Spectra. Details of electronic spectra of the nickel(II) complexes are provided in Table 2. In acetonitrile solutions, **1**–**4** display a medium-intensity band (ϵ, 70–115 mol^{-1} cm^2) in the 590–620 nm region due to the spin-allowed $^1A_{1g} \rightarrow {}^1A_{2g}$ transition typical of square-planar d^8 species.[34] For a representative compound **1**, the spectra in the visible region were examined in a number of solvents of varying donor strengths. While this ligand-field band λ/nm (ϵ/mol^{-1} cm^2) remains practically undisturbed in poorly coordinating solvents, viz. acetonitrile, 599(115), acetone, 597(95), and methanol, 597(95), it experiences a noticeable blue shift in strong donor solvents, e.g., DMSO, 586(120) and pyridine, 566(105), thus suggesting axial solvent coordination. No further attempt has been made at this time to follow up on this solvent-dependent phenomenon.

Compound **5** in acetone, however, has two prominent shoulders in the visible region, seemingly associated with d–d transitions. The low-energy band centered at 576 nm is considered to have the same origin as that in **1**–**4** and for the transition at higher energy (at ca. 530 nm), the assignment of $^1A_{1g} \rightarrow {}^1B_{1g}$ appears to be the plausible one.

In all these complexes, the d–d band(s) is followed by an LMCT band (ϵ, 6400–10 600 mol^{-1} cm^2) at ca. 400 nm, attributable to S → Ni charge transfer.[35] The second ligand-field band, $^1A_{1g} \rightarrow {}^1B_{1g}$, expected to appear at higher energy[34] is probably obscured in **1**–**4** by the tail of this LMCT absorption. The remaining UV band appearing at ca. 335 nm is due to a ligand-localized transition.

Electrochemistry and EPR. The redox behavior of **1**–**4** has been examined by cyclic voltammetry (CV) under nitrogen in

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Table 3. Selected Bond Distances (Å) and Angles (deg) of **1** and **4**

	1	4		1	4
Ni−S(1)	2.125(1)	2.114(1)	S(1)−Ni−N(2)	173.1(1)	175.5(1)
Ni−N(1)	1.857(3)	1.861(4)	S(1)−Ni−N(4)	92.0(1)	91.3(1)
Ni−N(2)	1.973(3)	1.967(4)	N(1)−Ni−N(2)	87.3(1)	86.9(2)
Ni−N(4)	1.918(3)	1.922(4)	N(1)−Ni−N(4)	170.5(1)	169.3(2)
S(1)−C(1)	1.719(4)	1.707(6)	N(2)−Ni−N(4)	83.3(1)	84.9(2)
S(2)−C(1)	1.756(4)	1.756(5)	Ni−S(1)−C(1)	111.1(2)	112.0(2)
N(1)−C(6)	1.312(5)	1.310(6)	Ni−N(1)−C(6)	130.5(3)	131.7(4)
C(2)−C(6)	1.420(6)	1.425(7)	Ni−N(1)−C(7)	112.6(2)	112.6(3)
C(1)−C(2)	1.351(6)	1.355(7)	Ni−N(2)−C(8)	104.1(2)	104.7(3)
O(1)−C(16)			Ni−N(2)−C(9)	105.7(2)	107.7(3)
O(1)−C(17)[a]	1.367(5)	1.352(6)	Ni−N(2)−C(16)		
N(2)−C(9)	1.474(5)	1.468(6)	Ni−N(2)−C(17)[a]	112.5(2)	111.5(3)
N(3)−C(9)	1.445(5)	1.447(6)	Ni−N(4)−N(3)	110.8(2)	110.6(3)
N(3)−N(4)	1.376(4)	1.370(3)	S(1)−C(1)−C(2)	126.0(3)	126.4(4)
			C(1)−C(2)−C(6)	125.8(4)	125.5(5)
S(1)−Ni−N(1)	97.3(1)	97.2(1)	N(1)−C(6)-C(2)	127.4(4)	127.0(5)

[a] The carbon atoms viz. C(16) for compound **1** and C(17) for compound **4** are equivalent.

Table 4. Summary of Electrochemical Data[a]

complex	Ni(II)/Ni(I)			Ni(II)/Ni(III)
	$E_{1/2}{}^{b}$/mV	$\Delta E_{p}{}^{c}$/mV	n^{d}	$E_{pa}{}^{b}$/mV
1	−1005	87	0.98	1085
2	−1002	68	1.03	1098
3	−1027	66	0.85	1090
4	−1065	69	0.90	1095

[a] Solvent: acetonitrile. Supporting electrolyte: TEAP (0.1 M). Solute concentration ca. 10^{-3} M. Working electrode: platinum. Temperature: 25 °C. [b] Potentials are vs Ag/AgCl and estimated by cyclic voltammetry at a scan rate of 100 mV s^{-1}. $E_{1/2} = 0.5(E_{pc} + E_{pa})$. [c] $\Delta E_{p} = E_{pc} - E_{pa}$. [d] Number of electrons/molecule determined by controlled-potential coulometry.

acetonitrile solutions (0.1 M TEAP). The results are listed in Table 4. The CVs are well-behaved in the cathodic range (0 to −2.0 V vs Ag/AgCl), displaying a one-electron reduction with $E_{1/2}$ close to −1.0 V throughout this series. The peak-to-peak separations (ΔE_{p}) are all in a narrow range (66−87 mV at a scan rate of 100 mVs^{-1}) with i_{pc}/i_{pa} approaching unity (0.97−1.06);[36] the process can be regarded as nearly reversible in the electrochemical sense.[37] A representative voltammogram (**2**) is shown in Figure 3. The metal-centered nature of the reduction process is established by the coulometric ($n = 1.0 \pm 0.15$) generation of Ni(I) instead of a metal-stabilized ligand radical as supported by EPR spectroscopy (see later text). In the anodic span (0 to +1.5 V), an irreversible oxidation is observed with $E_{pa} \approx 1.1$ V. Failure to observe any cathodic response even at a very high scan rate (500 mV s^{-1}) indicates instability of the oxidized species, sufficient to vitiate coulometric evaluation of electron stoichiometry for this process. However, a metal-centered Ni(II)/Ni(III) one-electron transfer is proposed from an estimation of current height data (at E_{pa}) which are comparable to those of the reduction process (Figure 3). Also, an approximate 2 V separation between the reduction and oxidation events in this case is indicative of both the processes being based on metal.[38−40] The electrochemical results thus revealed a 3-membered electron-transfer series comprising Ni(III)/Ni(II)/Ni(I) oxidation states (eq 1).

Figure 3. Cyclic voltammogram of [Ni(N$_3$S)′-CH$_2$OMe]ClO$_4$ **2** in 0.1 M TEAP/CH$_3$CN at a platinum electrode (100 mV s^{-1} scan rate).

$$[\text{Ni}^{I}(\text{N}_3\text{S})]^0 \underset{E_{1/2} = -1.0 \text{ V}}{\overset{+e^-}{\rightleftharpoons}} [\text{Ni}^{II}(\text{N}_3\text{S})]^+ \overset{-e^-}{\underset{E_{pa} = 1.1 \text{ V}}{\longrightarrow}} [\text{Ni}^{III}(\text{N}_3\text{S})]^{2+} \quad \text{.....(1)}$$
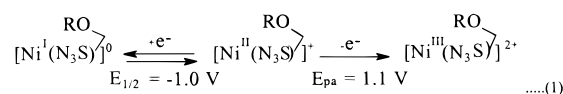
Noteworthy here is the one-electron reduction of the square-planar Ni(II) complexes (**1**−**4**) with a directly associated, fully developed oxidation response ($i_{pa}/i_{pc} \approx 1.0$) observed in the reverse scan (Figure 3). Few examples,[38−49] mostly with the macrocyclic ligands,[40,44−49] are known to date of such a

(36) At 25 °C complex **3** displays a reversible reduction with $E_{1/2} = 1027$ mV which, unlike the other members of this series, has a current height ratio slightly less than unity ($i_{pc}/i_{pa} \approx 0.85$) due to some ECE reaction. However, the current heights become almost identical in the CV at 0 °C, with the corresponding $E_{1/2}$ being 1035 mV.

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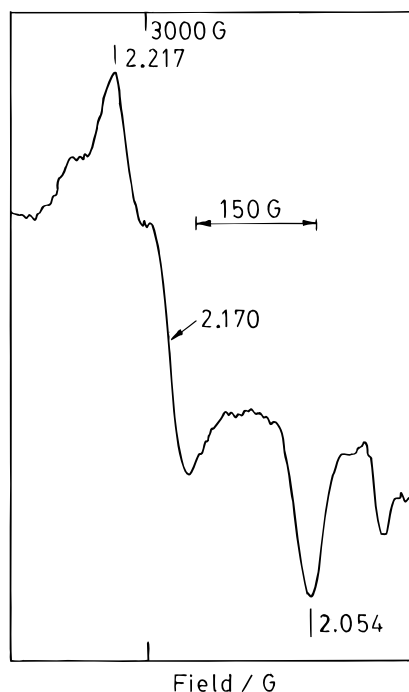(48) Dietrich-Buchecker, C. O.; Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1985**, 760.

Figure 4. X-Band frozen solution (CH$_3$CN, 77 K) EPR spectrum of [Ni^I(N$_3$S)'-CH$_2$OMe], generated electrochemically from **2** by coulometric reduction.

complete reversibility of Ni(II)/Ni(I) electron transfer entailed in square-planar geometry. This, obviously, is because of the conflicting type of coordination environments needed to stabilize these odd oxidation states.[50] Macrocyclic ligands have a balancing role to play in this situation because of their remarkable ability to stabilize unusual oxidation states.[47]

For a representative compound, **2**, the product obtained in the cathodic event was monitored further by EPR spectroscopy. An extremely unstable yellow catholyte solution (CH$_3$CN),

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generated by coulometric experiment ($E_w = -1.2$ V vs Ag/AgCl) at -40 °C under dinitrogen, was immediately transferred to an EPR tube and then frozen at -196 °C. The spectrum, as displayed in Figure 4, has a rhombic feature with $g_1 = 2.217$, $g_2 = 2.170$, and $g_3 = 2.054$. This indicates that a Ni(I) species is being generated during the course of electrolysis.[9a, 14]

Concluding Remarks

Chemistry of the pentadentate N$_4$S ligands with nickel(II), as described here, is really unique in involving an unprecedented alcoholysis of a saturated C−N bond linkage, possibly due to its activation by the coordinated metal ion. The products obtained are square-planar mononuclear nickel(II) complexes with a pendant arm that accommodates the alkoxy group provided by the solvent. This observation clearly indicates the inherent reluctance shown by nickel(II) to attain pentacoordination when subjected to hard/soft donor environments.[39] These square-planar complexes (**1**−**4**) in acyclic ligand environments have interesting redox behavior as monitored by cyclic voltammetry, involving three nickel oxidation states Ni(III)/Ni(II)/Ni(I) of which the Ni(II)/Ni(I) electron transfer is nearly reversible. The difference in potential between the Ni(III)/Ni(II) and Ni(II)/Ni(I) couples is ca. 2.0 V as compared to a few hundred milivolts observed in [NiFe] hydrogenase.[2a] The reduced nickel(I) species displays a rhombic EPR spectrum at 77 K with features g_1, $g_2 > g_3 \approx 2.0$, which is consistent with the odd electron occupying the metal d$_{z^2}$ orbital.[9a]

Supporting Information Available: Atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for **1** and **4**. Two X-ray crystallographic files, in CIF format, are available on the Internet only. Ordering and access information is given on any current masthead page.

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