

A Coordination Polymer of Nickel(II) Based on a Pentadentate N, S, and O Donor Ligand

Dawn C. Goodman, Patrick J. Farmer,[†] Marcetta Y. Darensbourg,* and Joseph H. Reibenspies

Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255

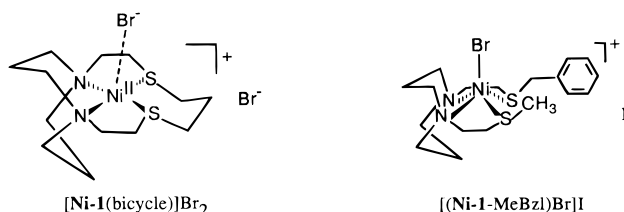
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The synthesis, structural characterization, and electrochemical properties of a Ni^{II} complex derived from the template reaction of *N,N'*-bis(2-mercaptoethyl)-1,5-diazacyclooctane nickel(II), **Ni-1**, with ICH₂CO₂Na are described. Blue *N*-(3-thiabutyl)-*N'*-(3-thiapentanoate)-1,5-diazacyclooctanenickel(II)iodide, [(tbt-p-daco)Ni][I], **[5]I**, contains Ni^{II} in an octahedral environment with N₂S₂O₂ donor atoms; one oxygen is from an adjacent [(tbt-p-daco)Ni] ion and has the same distance to Ni^{II} as the intramolecular oxygen, resulting in a coordination polymer. Complex **[5]I**·H₂O, C₁₃H₂₇N₂O₃S₂NiI, crystallizes in the orthorhombic space group *Pbca* with *a* = 10.898(3), *b* = 18.103(5), *c* = 19.020(5), and *Z* = 8. The extent to which the polymer is retained in solution is counterion dependent, which influences redox properties (accessibility of Ni^I and Ni^{III}).

Introduction

In cases where redox chemistry of metal complexes is involved in catalysis, both the donor type and the structural arrangement of the ligands govern reactivity. In general, π -donor ligands stabilize high metal oxidation states by donating electron density to the metal, and π -acceptor ligands stabilize low oxidation states by delocalizing the metal electron density.¹ The capacity of nickel to bind to both hard and soft donor ligands allows its coordination chemistry to encompass a variety of geometries, coordination numbers, and oxidation states with reactivity ranging from organometallic to biological chemistry. Ligand sets containing hard donor atoms may be utilized for either four- or six-coordination of Ni^{II};² soft donors tend to induce four-coordinate, square planar complexes. Pentacoordination may be achieved with bulky and polydentate ligands which prevent hexacoordination. In soft donor sets such as phosphines and thioethers, 18-electron, organometallic type complexes are known, *i.e.* HNiP₂S₂⁺, P₂S₂NiCN⁺, and P₂S₂-NiR⁺ (R = Me, C(O)Me)^{2e,3} However, attempts to sequentially add axial ligands to square planar Ni^{II} complexes in N₂S₂ (S'

= thioether) mixed donor sets generating square pyramidal complexes have generally been unsuccessful; addition of one axial ligand typically brings about addition of a second one.^{4,5} Crystal structure data implies an apical interaction between the Ni^{II} center and the Br⁻ counterion for **[Ni-1(bicycle)]Br₂**, which finds Ni within the N₂S₂' plane, and \angle S-Ni-Br and \angle N-Ni-Br averaging 90°. Located almost within bonding distance at 2.95 Å,⁷ the Br⁻ is still *ca.* 0.5 Å farther than the average literature values of Ni-Br bond distances (2.41 Å), and the compound is best described as a site specific ion pair. Thus far, the only example of a *bona fide* pentacoordinate N₂S₂ Ni^{II} complex is **[(Ni-1-MeBzl)Br]I** with Ni 0.43 Å above the N₂S₂ plane and a Ni-Br distance of 2.451(3) Å.^{6b}



[†] Current Address: Department of Chemistry, University of California Irvine, Irvine, CA 92717-2025.

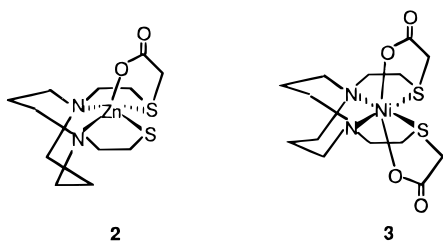
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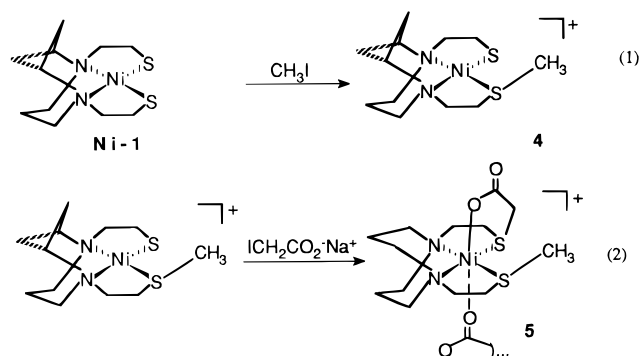
In contrast, a five-coordinate N₂S₂O complex of zinc, **2**, was prepared by the addition of 4 equiv of ClCH₂COOH to [(bme-daco)Zn]₂. It was isolated and characterized by X-ray crystallography.⁸ The diazametallacyclohexane rings in this complex are in a chair/boat conformation. Repeated attempts to prepare the analogous five-coordinate nickel complex led instead to the

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bis(thiapentanoato) complex, (btp-daco)Ni, **3**, even when the synthesis was carried out with a deficiency (*i.e.*, <1 equiv) of ICH₂CO₂Na. This observation suggests that the second thiolate alkylation is as or more rapid than the first.⁸ Such a conclusion contrasts with alkylation by simple alkylhalides such as in eq 1, where the first alkylation severely deactivates the remaining thiolate.



In attempts to produce a pentadentate N₂S₂O ligand, and with it a pentacoordinate Ni^{II} complex, we have utilized complex **4**, [(metb-daco)Ni][I], in which one of the thiolate sulfurs is protected from further reactivity by methylation (eq 1).⁹ Complex **4** was subsequently reacted with ICH₂CO₂Na (eq 2). As will be seen in the results below, nickel's preference to be six-coordinate remains a controlling factor in product geometry.



Experimental Section

General Procedures. Materials were of reagent grade and used as received. Microanalysis was from Galbraith Laboratories, Inc., Knoxville, TN. Instrumentation: infrared spectroscopy, Mattson 6020 spectrometer; conductance, Orion Model 160 conductance meter; magnetic susceptibility, Johnson Matthey Model MK I magnetic susceptibility balance; cyclic voltammetry, Bioanalytical Systems 100A electrochemical analyzer with a glassy-carbon stationary microelectrode and a platinum-wire auxiliary electrode using instrumental *iR* drop correction; UV-vis, Hewlett-Packard 8452A diode array spectrometer. Mass spectral analyses were performed at the Laboratory for Biological Mass Spectroscopy at Texas A&M University. Positive ion fast atom mass spectra were recorded in thioglycerol and nitrobenzyl alcohol (NBA) matrices using a VG-70S spectrometer with a xenon source having a particle energy of 10 keV. Data were collected by a VG11-250J data system.

Syntheses. (*N*-(3-Thiabutyl)-*N'*-(3-thiapentanoate)-1,5-diazacyclooctane)nickel(II) Iodide, [(tbt-p-daco)Ni][I], **[5]I**. One equivalent of ICH₂CO₂Na (0.06 g, 0.029 mmol) was added to [(metb-daco)Ni][I], **4**,⁹ (0.125 g, 0.291 mmol) dissolved in MeOH or MeCN (100 mL) at room temperature with stirring. Over the course of 3 days at room temperature or 1 day at 50–60 °C, the color changed from brown to deep green; upon filtration through Celite and removal of solvent, a sky blue solid was recovered. The blue solid is soluble in water and polar organic solvents; it is insoluble in diethyl ether and hydrocarbons. Blue crystals of **[5]I**·H₂O (H₂O from the hygroscopic Na acetate and from the air) were obtained by Et₂O diffusion into a concentrated MeOH

Table 1. Summary of Crystallographic Data for [(tbt-p-daco)Ni^{II}][I]·H₂O

complex	[(tbt-p-daco)Ni ^{II}][I]·H ₂ O	<i>V</i> (Å ³)	3752(2)
mol formula	C ₁₃ H ₂₇ N ₂ O ₃ S ₂ NiI	<i>Z</i>	8
fw	509.1	ρ (calcd) (g cm ⁻³)	1.802
space group	orthorhombic <i>Pbca</i> (No. 61)	temp (°C)	-80
		λ (Å)	0.71073
<i>a</i> (Å)	10.898(3)	μ (cm ⁻¹)	0.2892
<i>b</i> (Å)	18.103(5)	<i>R</i> (%) ^a	5.3
<i>c</i> (Å)	19.020(5)	<i>R</i> _w (%) ^a	5.5

^a Residuals: $R_{\text{int}} = [\sum F^2 - (F_{\text{mean}})^2]/[\sum F^2]$; $R = \sum |F_o - F_c|/\sum F_o$; $R_w = \{[\sum w(F_o - F_c)^2]/[\sum w(F_o)^2]\}^{1/2}$; $S = \{[\sum w(F_o - F_c)^2]/[N_{\text{data}} - N_{\text{parameters}}]\}^{1/2}$.

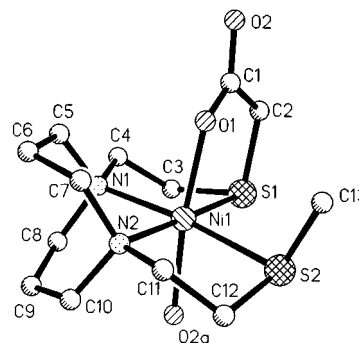


Figure 1. Molecular structure of [(*N*-(3-thiabutyl)-*N'*-(3-thiapentanoate)-1,5-diazacyclooctane)nickel(II)][I]·H₂O, **[5]I**. The water has been omitted.

or MeCN solution. Yield: 0.112 g (79%). IR (KBr): 1580 s, 1378 s (cm⁻¹). UV/vis: λ_{max} [nm] (ϵ) = 592 (100). Anal. Calcd. (found) for C₁₃H₂₇N₂O₃S₂NiI: C, 30.67 (30.76); H, 5.35 (5.33). $\mu_{\text{eff}} = 3.4 \mu_{\text{B}}$.

Ion Exchanges. Complex **[5]I** (84.5 mg, 0.1 mmol) was dissolved in MeOH (75 mL); AgNO₃ (28.2 mg, 0.17 mmol) was added to the blue solution with stirring overnight. To remove the white precipitate, the blue solution was filtered twice through Celite. This solution was subsequently evaporated to concentrate it, and blue crystals of **[5]NO₃** were obtained by Et₂O diffusion. This salt was used for all subsequent ion exchanges. Complex **[5]I** was re-formed by adding NaI (3.0 mg, 0.02 mmol) to **[5]NO₃** (11.2 mg, 0.02 mmol) dissolved in MeOH (10 mL) with stirring overnight. All other attempts at ion exchange were performed in the above manner using **[5]NO₃** (10 mg, 0.02 mmol) and 1 equiv of each of the following: NaBr, NaCl, NaSCH₂CH₃, NaSCH(CH₃)₂, and NaO₂CH. Each combination resulted in a blue solution except that with NaSCH(CH₃)₂ which turned green immediately after addition of the salt. Upon solvent removal via a vacuum, blue powders were isolated for each ionic mixture. The ionic mixtures were analyzed by +FABS-MS at the Laboratory for Biological Mass Spectroscopy at Texas A&M University.

Pressurization with H₂. Complex **[5]I** (0.010 g, 0.02 mmol) was dissolved in MeOD (5 mL). The sample was placed in a Fischer & Porter tube and pressurized to 62 psi with stirring at room temperature. Samples for NMR experiments were extracted daily for 3 days to monitor any increase in MeOH. None was observed.

Results and Discussion

Blue, paramagnetic [*N*-(3-thiabutyl)-*N'*-(3-thiapentanoate)-1,5-diazacyclooctane]nickel(II) iodide–water, [(tbt-p-daco)Ni][I], **[5]I**, was prepared according to the reaction sequence of eqs 1 and 2 in MeOH. Crystals suitable for X-ray analysis were obtained by diethyl ether diffusion into a concentrated methanolic solution of **[5]I**. A summary of the crystallographic collection and refinement data for compound **[5]I** are listed in Table 1. Complex **[5]I** was determined to be in the orthorhombic space group *Pbca*. As seen in Figure 1, the molecular structure shows the nickel center to be in a slightly distorted octahedron with the N₂S₂ unit the same as in the parent compound, **4**, and axial sites occupied by two O donor atoms,

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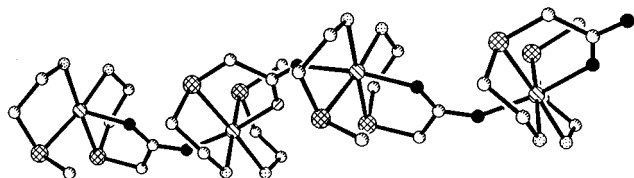


Figure 2. Several units of **5** viewed along the *b* axis.

Table 2. A Comparison of Selected Bond Angles (deg) and Distances (Å) of the N₂S₂O₂ Nickel Complexes [**5**]I and **3**

	[5]I	3
Ni–N ₁	2.108(8)	2.094(4)
Ni–N ₂	2.100(8)	2.094(4)
Ni–S ₁	2.402(3)	2.435(2)
Ni–S ₂	2.438(3)	2.435(2)
Ni–O ₁	2.062(6)	2.067(3)
Ni–O ₂	2.096(6)	2.068(3)
O ₁ –C ₁	1.24(1)	1.261(6)
O ₂ –C ₁	1.26(1)	
O ₃ –C ₁		1.254(6)
N ₁ –Ni–S ₁	90.3(2)	88.6(1)
N ₂ –Ni–S ₂	88.8(2)	88.6(1)
N ₁ –Ni–N ₂	85.7(3)	85.7(2)
S ₁ –Ni–S ₂	95.1(1)	98.5(1)
O ₁ –Ni–S ₁	84.4(2)	80.9(1)
O ₂ –Ni–S ₂	80.3(2)	80.9(1)
O ₁ –Ni–S ₂	95.4(2)	93.0(1)
O ₁ –Ni–O ₂	172.5(2)	170.6(2)

one oxygen being from an adjacent molecule. With the exception that in [**5**]I one sulfur is a nonfunctionalized thioether, the structural characteristics of [**5**]I are similar to those of **3**; selected bond angles and distances are compared in Table 2. The Ni–O distances of the intramolecular (2.062(6) Å) and intermolecular (2.096(6) Å) bonds of [**5**]I are statistically indistinguishable, and the C–O distances are the same both within complex [**5**]I and when compared to **3**. Consistently, the position of the two-band C–O vibrations in the solid state IR are similar for **3** (1593 and 1385 cm⁻¹) and [**5**]I (1580 and 1378 cm⁻¹). A noteworthy difference between the complexes is that the O atoms in **3** are H-bonded to water molecules found in the crystal lattice with an O(3) to water O distance of 2.88 Å. The water molecule of hydration of [**5**]I is 8.28 Å away from O(2), well beyond any possibility of interaction. The Ni–S distances, 2.402(3) and 2.438(3) Å, for S–CH₂CO₂ and S–CH₃, respectively, are well within the usual range reported for six-coordinate, Ni^{II}SR₂ complexes (*d*_{av} = 2.42 Å)⁷ and resemble **3** (Ni–S = 2.435(2) Å). As observed for other four- and six-coordinate derivatives of Ni-**1**, the Ni–S and Ni–N bonds in octahedral [**5**]I are *ca.* 0.2 and 0.15 Å longer than those of square planar **4**, respectively. The diazametallacyclohexane rings, formed when the daco backbone binds to a metal center, are in the chair/chair conformation, the usual arrangement for six-coordinate derivatives of Ni-**1**.

A portion of the packing diagram illustrating the polymeric nature of [**5**]I is shown in Figure 2. It may be viewed as a

Table 3. Redox Potentials and Reversibility Data from Cyclic Voltammetry^a and UV–vis Data

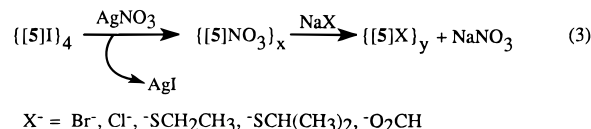
compound ^b	Ni ^{III/II} oxidation			reduction	
	<i>E</i> _{1/2} (V)	Δ <i>E</i> (V)	<i>i</i> _{pa} / <i>i</i> _{pc}	<i>E</i> _{pc} (V)	λ _{max} (nm) ^d
[5]Br ^c	+1.46	0.14	0.23	–1.8	604, 376
[5]I	+1.20	0.08	1.15	–1.6, –1.8	590, 376
[5]NO ₃	+1.19	0.09	1.30	–1.2, –1.5	584, 370
[5]Cl ^c	+1.17	0.06	1.73	–1.7	606, 364
[5]O ₂ CH ^c	+1.17	0.08	2.29	–1.7	604, 366
[5]SCH(CH ₃) ₂ ^c	+1.15	0.07	1.93	–1.6, –1.7	574, 428
[5]SCH ₂ CH ₃ ^c	+1.12	0.06	1.02	–1.6	590, 370
3	+1.19	0.07	0.91		600, 364

^a Data obtained in 0.1 M [Bu₄N][PF₆]/MeCN with a glassy-carbon working electrode at 200 mV/s; scale referenced to NHE. ^b Except for the I⁻ and NO₃⁻ salts, all contain Na⁺NO₃⁻. ^c Na⁺NO₃⁻ also present in solution. ^d In MeOH.

helical polymer in which the monomeric units are in a left-handed screw winding about the O–Ni–O axis. The iodide counterions are located 4.064 Å from C(13), following the rotation along the screw axis.

Solution Studies. Complex [**5**]I is soluble in water and polar organic solvents producing blue solutions; it is insoluble in hydrocarbons. Solutions of [**5**]I exhibit absorptions in the UV–vis region at 376 and 590 nm; these values are nearly identical to those observed for **3** (364 and 600 nm).⁸ The molecular weight of [**5**]I in MeCN was determined by vapor pressure osmometry to be 1876 amu.¹⁰ Since one unit of [**5**]I has a molecular weight of 491, an aggregation level of approximately 4 accounts for the high molecular weight.

Ion exchanges were performed in attempts to break the intermolecular Ni–O bonds producing pentacoordinate or hexacoordinate monomeric complexes with different axial donors. As depicted in eq 3, the parent species, [**5**]I, was stirred



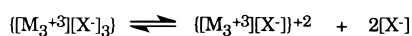
with AgNO₃ in MeOH to yield blue [**5**]NO₃ and AgI; the latter solid was removed by filtration. The methanolic solution of [**5**]NO₃ was then stirred with the following salts: NaBr, NaCl, NaSCH₂CH₃, NaSCH(CH₃)₂, or NaO₂CH. Solvent removal from the clear blue solutions produced blue powders for each of the attempted exchanges. The salts [**5**]I and [**5**]NO₃ which were pure, as well as the ionic mixtures, containing for example, Na⁺, NO₃⁻, [**5**], and X⁻, were examined by UV–vis spectroscopy, mass spectroscopy, and electrochemical analysis.

In CH₃OH solvent, the ionic mixtures exhibit low intensity (ε ~ 100 cm⁻¹ M⁻¹) two-band absorption patterns in the UV–vis spectra indicative of six-coordinate complexes. The position of the absorptions vary somewhat with counterion as shown in Table 3. However, the lack of a rational dependence of band position on the anion's ligand field strength is inconsistent with inner sphere binding of the counterion.

The +FAB mass spectrum of [**5**]I as well as [**5**]NO₃, and the ionic mixtures containing [**5**]O₂CH and [**5**]SCH₂CH₃ showed a parent signal at *m/z* 363, corresponding to one C₁₃H₂₅N₂–NiO₂S₂ unit. In contrast, [**5**]Br displayed an *M* + 2 signal at *m/z* equal to 445, indicating an N₂S₂OBr donor set about the Ni^{II} center. Another important fragment common to each of the spectra was found at *m/z* 307 and is assigned to complex **4**. From this, one may conclude that the aggregation found in the

(10) Vapor pressure osmometry performed by Galbraith Laboratories, Inc., Knoxville, TN.

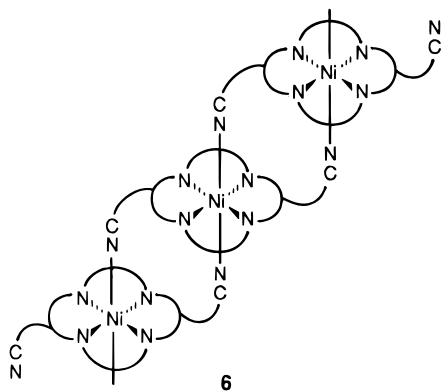
Scheme 1



solid state structure and solutions of [5]I is broken under the conditions of the mass spectroscopy experiment and that the counterions, with the exception of bromide, are not bound to the Ni^{II} center.

The conductivity of [5]I measured in anhydrous acetonitrile over a concentration range of 8.6×10^{-6} M to 1.6×10^{-4} M yielded Λ_M values between 234 and 238 with Λ_M at infinite dilution extrapolated to 239 S/cm²mol. For [5]Br, Λ_M data obtained in acetonitrile over a concentration range of 7.6×10^{-6} M to 1.0×10^{-4} M extrapolated to a value of Λ_M at infinite dilution equal to 260 S/cm²mol, the average value of a di-univalent electrolyte.¹¹ Both values for Λ_M at infinite dilution lie within the accepted range for di-univalent electrolytes in acetonitrile.¹¹ Since the monomeric forms of [5]I and [5]Br are uni-univalent electrolytes, the large Λ_M is evidence for aggregation, at minimum $[M_2^{+2}][X^-]_2$. Other possible species that would accommodate a diunivalent electrolyte are presented in Scheme 1. The maximum aggregation level, M_4X_4 , is consistent with the solution molecular weight determination.

Another six-coordinate Ni^{II} coordination polymer, **6**, was recently reported as its PF₆⁻ salt.¹² This Ni^{II} is encased in an N₆ donor set; four of the N donors are secondary amines from a macrocycle and two are nitrile group substituents on neighboring macrocyclic ligands. In contrast to [5]I, the axial nitrile ligands of **6** are labile in polar solvents. Thus, the coordination



polymer is not retained in solution. Conductivity data places this complex in the range of a uniunivalent electrolyte.¹¹ Unfortunately, the electrochemistry for this complex was not reported.

Electrochemistry. As reported earlier, complex **3** displays a quasi-reversible reversible oxidation wave at +1.19 V assigned to a Ni^{II/III} couple and no reduction wave when scanned to -2.0 V (vs. NHE).⁸ That is, the Ni^{I-III} redox range is over 3 V. In contrast, the square planar, thioether derivatives of Ni-**1** have both electrochemically reversible Ni^{II/I} (ca. -0.5 V) and quasi-reversible Ni^{II/III} (ca. 1.6 V) couples, *i.e.*, separated by ca. 2 V.^{6,9} Cyclic voltammograms were obtained for all of the ionic mixtures of [5] reported here; the redox potential data are presented in Table 3.

Figure 3 shows overlaying cyclic voltammograms representative of the salts of [5]. The simpler cyclic voltammogram for [5]SCH₂CH₃ (··· in Figure 3) illustrates a broad quasi-reversible

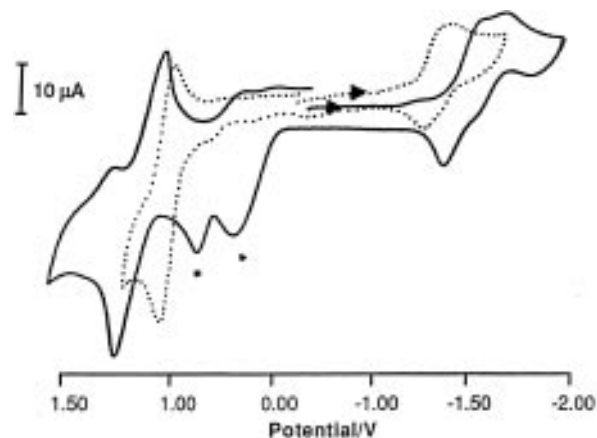
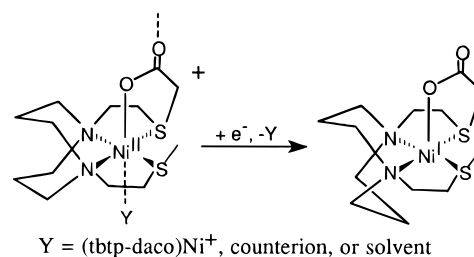


Figure 3. Cyclic voltammograms of [5]I (—) and [5]SCH₂CH₃ (···) obtained in a solution of 0.1 M [Bu₄N][PF₆] in MeCN with a glassy carbon electrode at 200 mV/s, with the scale referenced to NHE. An asterisk denotes oxidation of I⁻.

(scan rate dependent) reduction event at -1.6 V and a well defined, reversible oxidation event at 1.1 V. A slightly more complicated cyclic voltammogram is observed for [5]I (— in Figure 3). Oxidation features for the iodide counterion are starred in the figure and the quasi-reversible oxidation, assigned to Ni^{II/III}, is ca. 80 mV higher (less accessible) than that of [5]-SCH₂CH₃. The reduction events differ for the two salts in both position and shape. The cathodic reduction feature (assigned to Ni^{II/I})⁹ at ca. -1 V appears to have two broad overlapping waves for the [5]I salt. However, this becomes a single broad wave for [5]SCH₂CH₃.

The cyclic voltammograms of the other salts are either similar to [5]I ([5]SCH(CH₃)₂ and [5]NO₃) or [5]SCH₂CH₃ ([5]Cl, [5]Br, and [5]O₂CH). The sharpest reduction wave is found in the voltammogram of [5]Br and becomes extremely broad for the ⁻O₂CH species. For all of the counterions used, the reverse scan anodic peak is more sharply defined than the cathodic peak. Such electrochemical responses are suggestive of electron transfer followed by, or concurrent with, a slower chemical rearrangement.¹³ A reasonable possibility is that reduction is coupled with the loss of an axial ligand, either a bound counterion, a second (tbt-p-daco)Ni⁺ unit, or a trapped solvent molecule (eq 4).



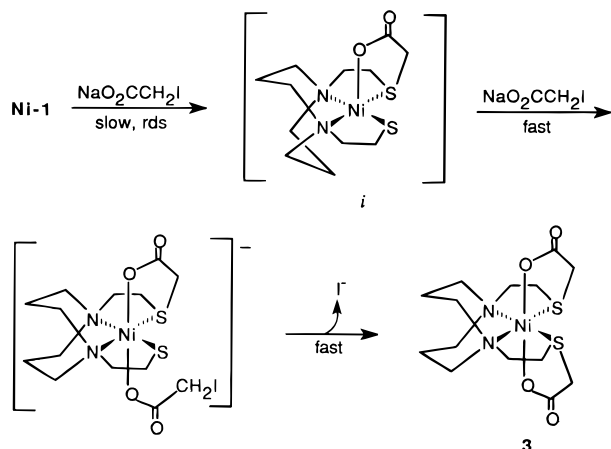
The potential of the quasi-reversible Ni^{II/III} redox couple varies little with counterion; with the exception of bromide (all of the halides exhibit irreversible oxidations between 0.5 and 1 V). The Ni^{II/III} redox potential for the bromide complex is ca. 0.3 V less accessible than the other ion exchange products. This indicates that at millimolar concentrations Br⁻ may bind to the Ni center and that it decreases the Ni^{III} accessibility as compared to the original O donors. We conclude that the borderline hard/soft bromide ion in the mixed donor set utilized here possesses the optimal size and electronic character to bind to a Ni^{II} center.

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Scheme 2



This is consistent with the fact that Br^- is the only counterion shown to interact with the Ni^{II} center in $[\text{Ni-1}(\text{bicycle})]$, *vide supra*.⁹ It is also noteworthy that the thiolate ions lead to the most accessible oxidation potentials. The Ni^{III} accessibility dependence on counterions in this donor set is as follows: $\text{Br}^- < \text{I}^- < ^-\text{O}_2\text{CH} \cong \text{Cl}^- < \text{RS}^-$.

Comments

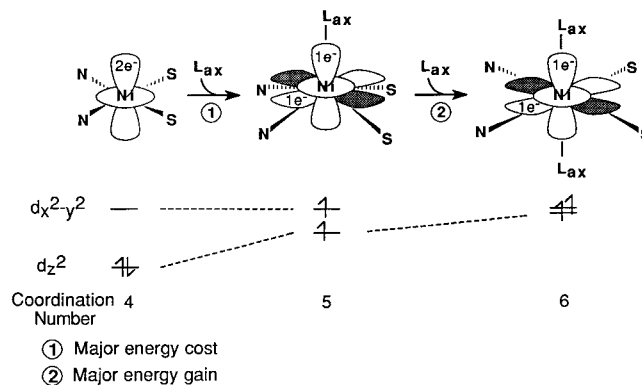
Our strategy for preparing and isolating pentacoordinate Ni in an $\text{N}_2\text{S}'_2\text{O}$ environment was unsuccessful due to the great propensity for Ni^{II} with a hard axial donor to attract a second hard axial ligand. Given the ubiquity of this diaxial ligation phenomena,^{4-6,8,14} it is likely that such is operative in the mechanism of formation of complex **3**; this is explored below.

Ongoing kinetic studies have shown that the first alkylation with MeI of **Ni-1** is $\sim 10^3$ times faster than the second because the remaining thiolate sulfur of the mono-alkylated cationic complex is deactivated or less nucleophilic relative to the first. This accounts for our ability to isolate complex **4**, eq 1. The difference between **4** and the product of single alkylation by $\text{NaO}_2\text{CCH}_2\text{I}$, *i.e.*, the intermediate, *i*, shown in Scheme 2, clearly lies in the axial ligation. The first S-alkylation and axial binding of the carboxylate oxygen to the Ni^{II} center is expected to rapidly induce the binding of another acetate to complete the octahedral coordination sphere of Ni^{II} . The dangling alkyl halide group is then positioned for nucleophilic attack by sulfur. Thus, the formation of the second thioether is facilitated by such preorganization.

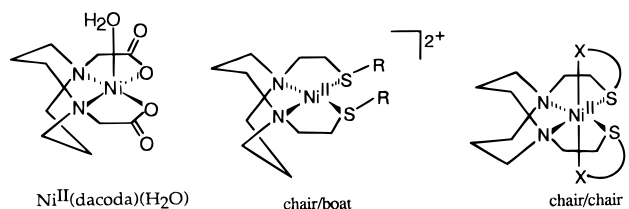
An alternate rationale for the facile formation of **3** and inability to isolate *i* is based on the S-nucleophilic character of *i* resulting from binding of the π -donor, anionic $\text{O}_2\text{C-R}$ ligand. One thiolate donor has been changed in essence to a neutral thioether, and an anionic acetate oxygen donor, *cis* to the remaining thiolate, has been added. The effect of this exchange, diminishing or enhancing the nucleophilicity of the remaining S-thiolate, is not known. Whether sulfur nucleophilicity or nickel-anion interactions control the kinetics of alkylation depends on a myriad of factors, even in simple RX alkylations.¹⁵ Certainly the predilection for axial ligation shown in complex **5** supports the mechanism of Scheme 2 for the unique alkyl halide $\text{NaO}_2\text{CCH}_2\text{I}$.

The factors which govern pentacoordination of Ni^{II} in hard or mixed hard/soft donor sets are still being defined. An example for pentacoordination in a hard donor environment has

Scheme 3



been established with the isolation of green (daco-diacetate)- $(\text{H}_2\text{O})\text{Ni}^{\text{II}}$, $\text{Ni}^{\text{II}}\text{daco}$.¹⁶ In this compound, the β -methylene protons of the daco ring in the chair/boat configuration are positioned to sterically block the open coordination site on the nickel center. The influence of this "steric block" is however, questioned as several derivatives of **Ni-1** exhibit chair/chair configurations for the metalladiazacyclohexane rings. Typically, the diazametallacyclohexane rings have been found to be in the boat/chair conformation whenever the $\text{N}_2\text{S}_2\text{Ni}$ complex is four-coordinate; however the chair/chair conformation prevails for six-coordinate complexes.^{17,18} That is, the expected steric block of one coordination site of the metal by the β -methylene protons in the boat configuration is readily overcome when ligands with strong binding abilities are employed, thereby forming six-coordinate complexes.^{6,8}



The current study gives two examples of Ni^{II} in an $\text{N}_2\text{S}'_2\text{O}_2$ donor set and further establishes the difficulty of synthesizing pentacoordinate nickel with an N_2S_2 basal plane environment. The difficulty in isolating pentacoordinate intermediates may be accounted for as follows. A change from square planar to square pyramidal geometry results in destabilization of the d_{z^2} orbital. The energy gained from adding a single new bond barely counterbalances this effect. However, this binding of an axial ligand induces a spin state change producing a more reactive frontier orbital.^{4,19} Thus, the major energy cost is in the first ligation; addition of the second axial ligand is both

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(20) One might consider this analogous to the hypervalent ClF , ClF_2 , and ClF_3 complexes. The binuclear ClF species is known, but ClF_2 never forms because the energy lost from unpairing the lone pair is not regained by adding a single bond. Yet, when two bonds are added, as is the case with ClF_3 , the second bond contributes enough stabilization that the 3-center, 4-electron bond is formed, and ClF_3 is isolated.

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thermodynamically and kinetically favored. That is, the ultimate electron rearrangement in the z direction is already accomplished by the first axial ligation; the second axial ligation then represents a major energy gain (Scheme 3).^{20,21}

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Supporting Information Available: Text giving a summary of structure determination and solution refinement, tables summarizing crystallographic data for *N*-(3-thiabutyl)-*N'*-(3-thiapentanoate)-1,5-diazacyclooctanenickel(II)-iodide, [5]I, including atomic coordinates and isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, H-atom coordinates and isotropic displacement parameters, torsion angles less those to hydrogen atoms, and figures showing the crystal structure with thermal ellipsoids and a packing diagram for [5]I (11 pages).

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