3562 *Inorg. Chem.* **1997,** *36,* 3562−3564

Thioether-Coordinated Nickel Oxidation States. A $Ni^{III}S_2N_4$ Family Incorporating Hexadentate Thioether−Azo−Oxime Chelation

Kausikisankar Pramanik, Soma Karmakar,
Suranjan Bhanja Choudhury, and
Animesh Chakravorty*

Department of Inorganic Chemistry, Indian Association for
the Cultivation of Science, Calcutta 700 032, India

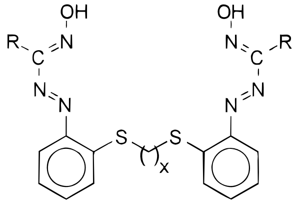
Received January 3, 1997

Introduction

Variable valence nickel thioether chemistry received early attention in this laboratory[1] in the context of nickel hydrogenases.[2] Subsequent research with acyclic[3−5] and macrocyclic[6,7] ligands demonstrated that all oxidation states in the range nickel(I)−nickel(IV) are accessible in solution. Instances of isolation of thioether-ligated complexes other than those of nickel(II) have, however, remained limited to just two examples: one of nickel(III)[8] and the other of nickel(IV).[3] Herein we describe the electrosynthesis and isolation of a family of nickel(III) complexes of coordination type NiS_2N_4, derived from a family of acyclic hexadentate thioether−azo−oxime ligands. Structures, spectra, and reduction potentials of this family are scrutinized.

Results and Discussion

Synthesis and Characterization. We were prompted to use ligands of type **1** (abbreviated H_2R_xL) for possible stabilization of thioether-linked higher nickel oxidation states because of the proven strong-field nature of **1**, which has been shown to induce spin-pairing even in manganese(II) (t_2^5).[9] A strong pseudooctahedral field is expected to promote facile ionization of destabilized e electrons, such as $Ni^{II}(t_2^6e^2) \rightarrow Ni^{III}(t_2^6e^1)$.[10] The 1:1 reaction of H_2R_xL with nickel(II) acetate tetrahydrate in methanol at room temperature afforded paramagnetic (μ_{eff} = 3.05−3.20 μ_B; $S = 1$) pink $Ni^{II}(R_xL)$. The green nickel(III) complexes, $[Ni^{III}(R_xL)]^+$, were electrosynthesized by constant potential coulometry of $Ni(R_xL)$ in an acetonitrile−dichloromethane mixture at 0.7 V vs saturated calomel electrode (SCE). These were isolated in nearly quantitative yields as PF_6^- salts (NH_4PF_6 is the supporting electrolyte). The synthesis is shown in eq 1.



R	x	H_2R_xL
Ph	2	H_2Ph2L
α-Naphthyl	2	H_2Np2L
Ph	3	H_2Ph3L
α-Naphthyl	3	H_2Np3L

1

$$Ni^{2+} \xrightarrow[-2H^+]{H_2R_xL} Ni^{II}R_xL \xrightarrow[0.7\ V,\ -e]{PF_6^-} [Ni^{III}(R_xL)PF_6] \qquad (1)$$

Selected characterization data of the $[Ni(R_xL)]PF_6$ salts are collected in Table 1. These salts absorb strongly in the visible region, are low-spin ($t_2^6e^1$, $S = {}^1/_2$) and EPR-active (*vide infra*), and behave as 1:1 electrolytes in acetonitrile solution. To our knowledge, the only thioether-ligated nickel(III) complex that has been isolated so far in the pure state is the macrocycle $[Ni^{III}(ttc)_2][H_5O_2]_3(ClO_4)_6$ (ttc = 1,4,7-trithiacyclononane) having the NiS_6 coordination sphere.[8] The present work adds four new members, and here, for the first time, the ligand system is acyclic.

The $[Ni(R_xL)]PF_6$ complexes display a quasireversible (ΔE_p = 70−90 mV) one-electron cyclic response near 0.4 V vs SCE (Table 2) due to the couple $[Ni^{III}(R_xL)]^+/Ni^{II}(R_xL)$. Its reduction potential is significantly lower than those of other thioether complexes (usual range 0.6−1.0 V vs SCE),[1,3−5,6a,7] presumably due to stabilization of the higher oxidation state by oximato-*N* coordination.[3,10] The $Ni(R_xL)$ precursors show the same voltammogram (initial scan anodic) as that of $[Ni(R_xL)]^+$ (initial scan cathodic). The two oxidation states can be quantitatively interconverted via constant-potential electrolysis at suitable potentials. Coulometry at 0.7 V has provided the best method for the practical synthesis of $[Ni^{III}(R_xL)]^+$ from $[Ni(R_xL)]$. Chemical oxidants afforded impure products. The complexes also display a second voltammetric response near 1.0 V, which may be due to the nickel(III)−nickel(IV) couple. The nickel(IV) species are, however, unstable and could not be isolated via coulometry.

Structure and Ground State. The nickel(III) complexes did not afford single crystals suitable for X-ray work, but $Ni^{II}(Ph_3L)$ did. A molecular view is shown in Figure 1, and selected bond parameters are listed in Table 3. The metal center in the distorted octahedral NiS_2N_4 coordination sphere lies on a crystallographic twofold axis. All the five-membered chelate rings are excellently planar (mean deviation ≤ 0.04 Å). In the

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S0020-1669(97)00009-8 CCC: $14.00

Table 1. Molar Conductivity,[a] Magnetic Moments,[b] and Electronic Spectral Data[a] for $[Ni(R_xL)]PF_6$ at 298 K

compound	Λ, Ω^{-1} cm^2 M^{-1}	μ_{eff}, μ_B	UV−vis data, λ_{max}, nm (ϵ, M^{-1} cm^{-1})
$[Ni(Ph_2L)]PF_6$	139	1.88	640 (4230), 550[c] (4270), 440 (14270)
$[Ni(Ph_3L)]PF_6$	142	1.86	660 (2730), 560[c] (4020), 415 (13130)
$[Ni(Np_2L)]PF_6$	132	1.92	620 (3730), 540[c] (4190), 425 (13140)
$[Ni(Np_3L)]PF_6$	135	1.88	650 (3850), 535[c] (5560), 430 (13810)

[a] In acetonitrile. [b] In the solid state. [c] Shoulder.

Table 2. Electrochemical[a] and EPR[b] Data

	$E_{1/2}$, V (ΔE_p,[c] mV)		*g* values		
compound	Ni^{III}/Ni^{II}	Ni^{IV}/Ni^{III}	$g_\perp$	$g_\parallel$	$A_\parallel$, G
$[Ni(Ph_2L)]PF_6$	0.45 (80)	1.03 (90)	2.103	2.040	28
$[Ni(Ph_3L)]PF_6$	0.46 (90)	1.02 (110)	2.109	2.040	28
$[Ni(Np_2L)]PF_6$	0.43 (80)	1.05 (90)	2.106	2.041	27
$[Ni(Np_3L)]PF_6$	0.45 (80)	1.03 (100)	2.103	2.040	27

[a] In acetonitrile at 298K. [b] In acetonitrile-toluene (1:1) glass at 77K. [c] $\Delta Ep = Ep_a - Ep_c$.

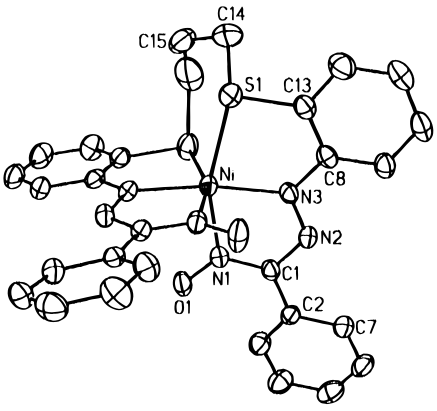

Figure 1. ORTEP plot and atom-labeling scheme for $Ni(Ph_3L)$. All atoms are represented by their 50% thermal probability ellipsoids. H atoms are omitted for clarity.

Table 3. Selected Bond Distances (Å) and Angles (deg) and Their Estimated Standard Deviations for $Ni(Ph_3L)$

	Distances		
Ni−S(1)	2.443(3)	N(2)−C(1)	1.373(4)
Ni−N(1)	2.036(4)	N(2)−N(3)	1.291(5)
Ni−N(3)	1.986(4)	N(3)−C(8)	1.405(4)
N(1)−C(1)	1.351(5)	C(13)−S(1)	1.785(4)
N(1)−O(1)	1.277(4)	C(14)−S(1)	1.828(6)
	Angles		
N(1)−Ni−N(1A)	95.7(2)	S(1)−Ni−N(1)	159.7(1)
N(1)−Ni−N(3)	77.1(1)	S(1)−Ni−N(3)	82.6(1)
N(1)−Ni−S(1A)	87.7(1)	S(1)−Ni−N(3A)	103.5(1)
N(3)−Ni−N(1A)	96.7(1)	S(1)−Ni−S(1A)	96.0(1)
N(3)−Ni−N(3A)	170.9(2)		

six-membered dithiaalkyl ring, the C(15) atom lies 0.64 Å away from the plane of the other five atoms. The Ni−S distance, 2.443(3) Å, is virtually equal to the sum of ionic radii (2.44 Å).[11] Reported Ni(II)−S(thioether) distances usually lie in the range 2.4−2.5 Å.[3−5,6b,7b−f,h,12] The Ni−N(azo) length is shorter than the Ni−N(oxime) length by ~0.05 Å. The lengths within the chelate rings are consistent with the azooxime description −N═N−C═N−O, as is usual in other azooxime complexes.[13]

In frozen acetonitrile−toluene glass (77 K) the $[Ni(R_xL)]PF_6$ complexes display axial EPR spectra with $g_\perp \approx 2.10$ and $g_\parallel \approx 2.04$. A representative spectrum is shown in Figure 2, and spectral parameters are listed in Table 2. For a NiS_2N_4 coordination sphere, the geometry would have only rhombic symmetry, but in practice the splitting of $g_\perp$ is smaller than the line width. The $g_\perp > g_\parallel$ relationship corresponds to d_{z^2} ground state.[10a,14] The five-line superhyperfine structure ($A_\parallel \approx 28$ G) in the $g_\parallel$ region is assigned to the σ-coupling between the metal d_{z^2} and the two coordinated azo−^{14}N($I = 1$) atoms lying in mutually trans positions (z-axis). It cannot involve coupling with azo-π^* orbitals because the coupling constant would then be very small.[13b,c,15]

Figure 2. X-band EPR spectrum of $[Ni(Ph_3L)]PF_6$ in frozen 1:1 acetonitrile−toluene solution at 77 K.

Concluding Remarks. The present work demonstrates that facile isolation of thioether-ligated unusual oxidation states (here 3+) of nickel is possible, once suitable ligands are designed. In $[Ni(R_xL)]PF_6$, we have the first examples of Ni^{III}−S(thioether) species incorporating acyclic ligands. The complexes, synthesized electrochemically from nickel(II) precursors, are characterized by d_{z^2} ground state and relatively low metal reduction potentials, oximato coordination being a controlling factor.

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Experimental Section

Physical Measurements. A Hitachi 330 spectrophotometer was used to record UV−vis spectra. EPR spectra were studied with a Varian E-109C spectrometer fitted with a quartz dewar. Room temperature magnetic susceptibilities were measured with Model 155 PAR vibrating sample magnetometer fitted with a Walker Scientific L75FBAL magnet. A Perkin-Elmer 240C elemental analyzer was used to collect microanalytical data (CHN). Electrochemical measurements were performed under nitrogen atmosphere on a PAR 370-4 electrochemistry system as before:[16] working electrode, platinum disk; reference electrode, saturated calomel electrode (SCE); auxiliary electrode, platinum wire; supporting electrolyte, Et_4NClO_4 (0.1 M); scan rate, 50 mV s^{-1}; solute concentration, 10^{-3} M. Solution electrical conductivities were measured with the help of a Philips PR 9500 bridge, the solute concentration being $\sim 10^{-3}$ M.

Synthesis of Ligands and Complexes. The ligands were synthesized as previously described.[9] All the complexes were synthesized by the same general method. Details are given below for $[Ni(Ph_3L)]PF_6$.

Propane-1,3-diylbis[α-[(*o*-thiophenylene)azo]benzaldoximato]nickel(III) hexafluorophosphate, $[Ni(Ph_3L)]PF_6$. This complex was synthesized by constant potential electrochemical oxidation of the corresponding nickel(II) precursor. The nickel(II) precursor $Ni(Ph_3L)$ was synthesized as follows. To a hot solution (15 mL) of H_2Ph_3L (0.22 g, 0.40 mmol) in methanol was added a solution (5 mL) of nickel(II) acetate tetrahydrate (0.1 g, 0.40 mmol) in the same solvent. The mixture was stirred at room temperature for 0.5 h, and then the deposited dark crystalline solid was filtered off, washed with methanol, and dried *in vacuo* over P_4O_{10}. Yield: 0.18 g (75%).

$Ni(Ph_3L)$ (0.07 g, 0.114 mmol) was dissolved in 20 mL of dichloromethane, and to it was added ammonium hexafluorophosphate (0.03 g, 0.180 mmol in 5 mL of acetonitrile). The mixture was stirred at room temperature for 0.25 h and then subjected to coulometric oxidation at 0.7 V vs SCE under nitrogen. The oxidation was stopped when the solution had changed from pink to green and the coulomb count corresponded to one-electron oxidation. The solution was filtered and the solvent evaporated *in vacuo* to obtain a dark solid, which was washed several times with water and then dried in air over fused $CaCl_2$. The solid thus obtained was recrystallized from a dichloromethane−hexane mixture to obtain pure crystalline $[Ni(Ph_3L)]PF_6$. Yield: 0.064 g (74%). Anal. Calcd for $C_{29}H_{24}N_6O_2S_2PF_6Ni$: C, 46.05; H, 3.18; N, 11.12. Found: C, 46.10; H, 3.22; N, 11.10. Anal. Calcd for $[Ni(Ph_2L)]PF_6$, $C_{28}H_{22}N_6O_2S_2PF_6Ni$: C, 45.30; H, 2.97; N, 11.33. Found: C, 45.32; H, 2.94; N, 11.38. Anal. Calcd for $[Ni(Np_3L)]PF_6$, $C_{37}H_{28}N_6O_2S_2PF_6Ni$: C, 51.89; H, 3.27; N, 9.82. Found: C, 51.94; H, 3.30; N, 9.78. Anal. Calcd for $[Ni(Np_2L)]PF_6$, $C_{36}H_{26}N_6O_2S_2PF_6Ni$: C, 51.32; H, 3.09; N, 9.98. Found: C, 51.34; H, 3.04; N, 10.04. Results of elemental analyses (CHN) for the nickel(II) precursors follow. Anal. Calcd for $Ni(Ph_3L)$, $C_{29}H_{24}N_6O_2S_2Ni$: C, 56.98; H, 3.93; N, 13.75. Found: C, 56.94; H, 3.96; N, 13.72. Anal. Calcd for $Ni(Ph_2L)$, $C_{28}H_{22}N_6O_2S_2Ni$: C, 56.31; H, 3.69; N, 14.08. Found: C, 56.37; H, 3.67; N, 14.09. Anal. Calcd for $Ni(Np_3L)$, $C_{37}H_{28}N_6O_2S_2Ni$: C, 62.47; H, 3.94; N, 11.82. Found: C, 62.50; H, 3.99; N, 11.80. Anal. Calcd for $Ni(Np_2L)$, $C_{36}H_{26}N_6O_2S_2Ni$: C, 62.01; H, 3.73; N, 12.06. Found: C, 61.98; H, 3.70; N, 12.11. UV−vis (CH_2Cl_2), λ_{max} in nm (ϵ in M^{-1} cm^{-1}): 540 (14470), 360 (sh, 12940) for $Ni(Ph_3L)$; 540 (14540), 370 (sh, 12950) for $Ni(Ph_2L)$; 545 (13620), 370 (sh, 11140) for $Ni(Np_3L)$; 520 (12340), 360 (sh, 14750) for $Ni(Np_2L)$.

Table 4. Crystallographic Data for $Ni(Ph_3L)$

chem formula	$C_{29}H_{24}N_6O_2S_2Ni$
fw	611.4
space group	*C*2/*c* (No. 15)
a, Å	16.272(7)
b, Å	8.528(3)
c, Å	20.355(12)
β, deg	110.49(4)
V, Å^3	2645(2)
Z	4
T, °C	23
λ, Å	0.71073
ρ_{obsd}, g cm^{-3}	1.539
ρ_{calcd}, g cm^{-3}	1.541
μ, cm^{-1}	9.36
R,[a] %	4.80
R_w,[b] %	5.65

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w^{-1} = \sigma^2(|F_o|) + g|F_c|^2$; $g = 0.0003$ for $Ni(Ph_3L)$.

X-ray Structure Determination. Single crystals of $Ni(Ph_3L)$ (crystal used, 0.48 × 0.42 × 0.12 mm^3) having parallelpiped habit were grown by slow diffusion of hexane into dichloromethane solution. The unit cell parameters were determined by the least-squares fit of 30 machine-centered reflections having 2θ values in the range 15−30°. Data were collected at 296 K by the ω-scan method over the 2θ range 2−55° on a Nicolet R3m/V diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Two check reflections measured after every 98 reflections showed no significant intensity reduction during 31 h of exposure to X-rays. All data were corrected for Lorentz-polarization effects. An empirical absorption correction was done on the basis of azimuthal scans.[17] Of the 3050 unique reflections, 1911 satisfying $I > 3.0\sigma(I)$ were used for structure solution (direct methods). Refinement was done by full-matrix least-squares procedures, making all non-hydrogen atoms anisotropic. Hydrogen atoms were included in calculated positions with fixed U (= 0.08 Å^2). The highest residual was 0.58 eÅ^{-3}. Significant crystal data are listed in Table 4. Computations were carried out on a MicroVAX II computer using the SHELXTL-PLUS program package,[18] and crystal structure plots were drawn using ORTEP.[19]

Acknowledgment. Support received from the Indian National Science Academy, New Delhi, the Department of Science and Technology, New Delhi, and the Council of Scientific and Industrial Research, New Delhi, is acknowledged. Affiliation with the Jawaharlal Nehru Centre for Advanced Scientific Research, Bangalore, India, is acknowledged.

Supporting Information Available: Tables of complete crystallographic data, atomic coordinates, bond distances and angles, anisotropic thermal parameters, and hydrogen atom positional parameters for $Ni(Ph_3L)$ (4 pages). Ordering information is given on any current masthead page.

IC970009A

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