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Comparative Studies of Mononuclear Nickel(II) Complexes with N_2S_x (x = 2–4) Ligands

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The new ligands 1,12-bis(2-pyridyl)-2,5,8,11-tetrathiadecane (L3) and 1,13-bis(2-pyridyl)-2,5,9,12-tetrathiaundecane (L4) their complexes and those of 1,6-bis(2-pyridyl)-2,5-dithiahexane (L1) and 1,9-bis(2-pyridyl)-2,5,8-trithianonane (L2) have been prepared as their perchlorate and tetrafluoroborate salts. Crystal data are as follows. For triclinic $[Ni(L1)(CH_3CN)_2][ClO_4]_2$: space group $P\bar{1}$; a = 11.269(3), b = 11.889(3), c = 10.624(2) Å; α = 115.25(1), β = 91.25(2), γ = 99.68(2)°; Z = 2; R = 0.057, R_w = 0.048 for 2207 reflections. For triclinic $[Ni(L2)(H_2O)][ClO_4]_2{\cdot}CH_3OH$: space group $P1$; a = 11.515(3), b = 11.869(2), c = 11.466(2) Å; α = 98.72(2), β = 118.22(1), γ = 73.00(2)°; Z = 2; R = 0.050, R_w = 0.043 for 2907 reflections. For monoclinic $[Ni(L3)][ClO_4]_2$: space group $C2/c$; a = 18.126(9), b = 11.599(8), c = 14.506(4) Å; β = 124.42(1)°; Z = 4; R = 0.047, R_w = 0.042 for 1531 reflections. All complexes are pseudooctahedral with coordination sites filled by donor atoms of ligands L1–L4 or solvent. There is no coordination of anions to the metal either in the solids or in solution, but evidence is presented for a second coordination sphere interaction in some cases. Electronic spectroscopic parameters are found to be sensitive to the number and nature of donors in the coordination sphere and to chain length between donor sites. Cyclic voltammetry reveals a sensitivity to anion in some cases but none to chain length, in contrast to the electronic spectroscopic results. Increasing the number of thioether donors increases the positive character of $E_{1/2}$.

Introduction

The relationship between structure and activity at the active sites of metalloenzymes is a matter of continuing interest.[1] Discovery of nickel–sulfur interactions in dehydrogenases and hydrogenases has stimulated interest in nickel enzymes and complexes with sulfur donors, especially since some of the enzymes catalyze difficult reactions like CO_2 reduction to methane and H_2/H^+ exchange under ambient conditions.[2] The active sites in the enzymes must be highly efficient catalysts, and therefore their structure and function relationships are of interest not only for understanding the enzymes on a molecular basis but also as a guide for developing industrial catalysts. The exact structure at the nickel centers in the enzymes remains uncertain, but EXAFS studies indicate an unknown number of sulfur donors with the possibility of nitrogen or oxygen donor ligands, as well, that together provide a pseudooctahedral nickel coordination sphere.[3] Thus, nickel complexes with sulfur–nitrogen ligands are of interest as standards of comparison. In this paper, we report a study of nickel complexes of ligands with the N_2S_x (x = 2–4) donor system (Figure 1) in which properties of the complexes change with the number and type of donor atoms.

Experimental Section

Commercially available reagents were obtained from the Aldrich Chemical Co. Inc. and were used without further purification. Preparations of 1,6-bis(2-pyridyl)-2,5-dithiahexane (ligand L1) and 1,9-bis(2-pyridyl)-2,5,8-trithianonane (ligand L2) have been described previously.[4,5] Spectroscopic data were obtained by using the following instruments: IR, Mattson Polaris FT; UV/vis, Cary Model 5E; NMR, General Electric 300-NB. Magnetic susceptibility data were obtained at room temperature by the Faraday method. Electrochemical measurements were carried out under a nitrogen atmosphere at room temperature by using a Cypress Systems, Inc., CS-1087 computer controlled potentiostat. Solution concentrations were 10^{-3} mol/L in complex and 0.1 mol/L in supporting electrolyte (tetraethylammonium perchlorate). Voltammograms were recorded in acetonitrile by using a glassy carbon working electrode that was prepolished with 0.3-μm Al_2O_3, a platinum counter electrode, and an aqueous saturated calomel reference electrode checked periodically relative to a 1.0 × 10^{-3} mol/L solution of ferrocene in acetonitrile containing 0.1 mol/L tetraethylammonium

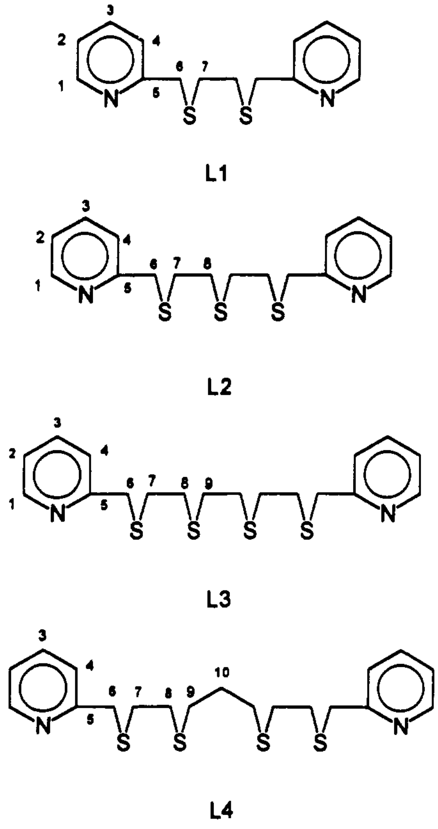

Figure 1. Ligands with site identification.

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Table I. Crystallographic Data[a]

	$[Ni(L1)(CH_3CN)_2][ClO_4]_2$	$[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$	$[Ni(L3)][ClO_4]_2$
chem formula	$C_{18}H_{22}Cl_2N_4NiO_8S_2$	$C_{17}H_{26}Cl_2N_2NiO_{10}S_3$	$C_{18}H_{24}Cl_2N_2NiO_8S_4$
fw	616.12	644.19	654.24
space group (No.)	$P\bar{1}$ (2)	$P\bar{1}$ (2)	$C2/c$ (15)
a (Å)	11.269(3)	11.515(3)	18.126(9)
b (Å)	11.889(3)	11.869(2)	11.599(8)
c (Å)	10.624(2)	11.466(2)	14.506(4)
T (°C)	25	25	25
α (deg)	115.25(1)	98.72(2)	
β (deg)	91.25(2)	118.22(1)	124.42(1)
γ (deg)	99.68(2)	73.00(2)	
μ (cm^{-1})	11.92	12.19	13.53
ρ_{calcd} (g cm^{-3})	1.621	1.620	1.727
V (Å^3)	1262.0(6)	1320.2(5)	2516(1)
Z	2	2	4
λ (Å)	0.710 69	0.710 69	0.710 69
R[b]	0.057	0.050	0.047
R_w[c]	0.048	0.043	0.042

[a] Estimated standard deviations for data here and elsewhere in this paper refer to the least significant figure and are given in parentheses. [b] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

perchlorate for which the ferrocene/ferrocenium reduction potential was 400 mV. The reference electrode was separated from the bulk of the solution by a porous Vycor tube. X-ray diffraction data were collected by using a Rigaku AFC5 diffractometer. Analyses were performed by Canadian Microanalytical Service Ltd.

Preparation of Ligands. 1,12-Bis(2-pyridyl)-2,5,8,11-tetrathiadecane (Ligand L3). Sodium metal (1.84 g, 80.0 mmol) was dissolved in commercial absolute ethanol (300 mL) under a dry nitrogen atmosphere, and 1,4,7,10-tetrathiadecane (4.28 g, 20.0 mmol) was added cautiously. The resulting mixture was heated to reflux, and a solution of 2-picolyl chloride hydrochloride (6.53 g, 40.0 mmol) in absolute ethanol (100 mL) was added dropwise with stirring over 2 h. Refluxing and stirring were continued for an additional 1 h. Volatiles were removed on a rotary evaporator, the residue was extracted with chloroform (100 mL), and the extract was washed with water several times and dried over anhydrous $CaCl_2$. After filtration, chloroform was removed to give a thick liquid, which solidified upon standing at room temperature. The white crystalline solid was washed with a small amount of diethyl ether and dried in air. Yield: 7.15 g (90%). Mp: 34–35 °C. Mass spectrum: m/e = 396, 272, 212, 152, and 124 corresponding to $[C_{18}H_{24}N_2S_4]^+$, $[C_{12}H_{18}NS_3]^+$, $[C_{10}H_{14}NS_2]^+$, $[C_8H_{10}NS]^+$, and $[C_6H_6NS]^+$, respectively. NMR ($CDCl_3$; position identification from Figure 1; ppm from TMS (multiplicity, integrated intensity, assignment, J in Hz)): ^1H 8.5 (d, 2H, C1, 4.1), 7.6 (m, 2H, C3), 7.36 (m, 2H, C4), 7.13 (m, 2H, C2), 3.85 (s, 4H, C6), 2.68 (m, 12H, C7–C9); ^{13}C 158 (C5), 148.8 (C1), 136.5 (C3), 122.7 (C4), 121.7 (C2), 37.46–31.0 (four peaks) (C6–C9).

1,13-Bis(2-pyridyl)-2,5,9,12-tetrathiaundecane (Ligand L4). This preparation is similar except that the product is a thick oil. Yield: 70%. NMR ($CDCl_3$; position identification from Figure 1; ppm from TMS (multiplicity, integrated intensity, assignment, J in Hz)): ^1H 8.5 (m, 2H, C1), 7.6 (m, 2H, C3), 7.38 (m, 2H, C4), 7.16 (m, 2H, C2), 3.86 (s, 4H, C6), 2.68–2.56 (m, 12H, C7–C9), 1.84–1.76 (q, 2H, C10, 7.2); ^{13}C 158.3 (C5), 149 (C1), 136.5 (C3), 122.8 (C4), 121.7 (C2), 37.69–29.02 (C6–C10).

Preparation of Complexes. Preparations of all complexes were similar to that for $[Ni(L1)][ClO_4]_2$.

Caution! *Although we have experienced no problems while handling any of the substances described herein, readers are cautioned to exercise appropriate care when handling perchlorates, which are treacherously prone to explode violently.*

$[Ni(L1)][ClO_4]_2$. A solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.365 g, 1.00 mmol) in methanol (20 mL) was added to a solution of 1,6-bis(2-pyridyl)-2,5-dithiahexane (0.276 g, 1.00 mmol) in methanol (20 mL), and the mixture was stirred for 15 min. A sky blue precipitate was isolated and washed with methanol. Yield: 70%. Mp: >250 °C. Anal. Calcd for $C_{14}H_{16}Cl_2N_2NiO_8S_2$: C, 31.47; H, 2.99; N, 5.25. Found: C, 32.54; H, 2.60; N, 5.49.

$[Ni(L1)][BF_4]_2$. Yield: 65%. Mp: 270 °C dec.

$[Ni(L2)(H_2O)][ClO_4]_2$. Yield: 60%. Mp: 170 °C dec.

$[Ni(L2)(H_2O)][BF_4]_2 \cdot 2H_2O$. Yield: 50%. Mp: 150 °C dec. Anal. Calcd for $C_{16}H_{26}B_2F_8N_2NiO_3S_3$: C, 30.83; H, 4.17; N, 4.50. Found: C, 30.05; H, 3.85; N, 4.30.

$[Ni(L3)][ClO_4]_2$. Yield: 70%. Mp: >250 °C. Anal. Calcd for $C_{18}H_{24}Cl_2N_2NiO_8S_4$: C, 33.02; H, 3.70; N, 4.28. Found: C, 32.99; H, 3.78; N, 4.34.

$[Ni(L3)][BF_4]_2$. Yield: 55%. Mp: 235 °C dec.

$[Ni(L4)][ClO_4]_2$. Yield: 50%. Mp: 160 °C dec. Anal. Calcd for $C_{19}H_{26}Cl_2N_2NiO_8S_4$: C, 34.15; H, 3.89; N, 4.19. Found: C, 35.26; H, 4.07; N, 4.61.

$[Ni(L4)][BF_4]_2$. Yield: 45%. Mp: >250 °C. Anal. Calcd for $C_{19}H_{26}B_2F_8N_2NiS_4$: C, 35.47; H, 4.04; N, 4.36. Found: C, 35.92; H, 4.39; N, 4.99.

X-ray Structure Determinations. A summary of crystal data for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$, $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$, and $[Ni(L3)][ClO_4]_2$ is given in Table I. Diffraction intensities were collected at 298 K by using the ω–2θ scan technique to a maximum 2θ values of 45.0° for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$ and 50.0° for $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$ and $[Ni(L3)][ClO_4]_2$. Three standards measured after every 150 reflections showed that, for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$, the intensities declined linearly with time to –62.00% due to loss of solvent (vide infra) but, for the other complexes, there was no indication of significant crystal decay during data collection. The space groups were determined by systematic absences, packing considerations, statistical analyses of intensity distributions, and the successful solution and refinement of the structures. Unit cell parameters were determined by a least-squares refinement of the setting angles of 15 reflections (20.77° < 2θ < 25.68°) for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$, 21 reflections (39.27° < 2θ < 43.03°) for $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$, and 15 reflections (33.37° < 2θ < 42.99°) for $[Ni(L3)][ClO_4]_2$. Lorentz and polarization factors were applied, corrections were made for absorption, and a linear decay correction was applied to the data for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$. The structure was solved by direct methods[6,7] and refined by full-matrix least-squares techniques[8] with counting statistics weights. Non-hydrogen atoms were refined anisotropically (or isotropically in a few cases for $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$) while H atom positions were calculated but their parameters were not refined. The final cycles of refinement were based on 2207 observed reflections ($I > 2.00\sigma(I)$) and 317 variables for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$ and converged, 2907 observed reflections ($I > 3.00\sigma(I)$) and 322 variables for $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$ and converged, and 1531 observed reflections ($I > 2.00\sigma(I)$) and 159 variables for $[Ni(L3)][ClO_4]_2$ and converged. All calculations were performed with the TEXSAN[9] crystallographic software from Molecular Structure Corp., and scattering factors were taken from the usual source.[10]

Results

Two new ligands with thioether and aromatic nitrogen donors and four complex cations of nickel as their tetrafluoroborate and perchlorate salts have been prepared and their properties

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(8) Function minimized: $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/\sigma^2(F_o)^2$, $\sigma^2(F_o^2) = [S^2(C + R^2B) + (pF_o^2)^2]/Lp^2$, S = scan rate, C = total integrated peak count, R = ratio of scan time to background counting time, B = total background count, and Lp = Lorentz–polarization factor.

(9) *TEXSAN-TEXRAY Molecular Structure Package*; Molecular Structure Corp.: The Woodlands, TX, 1985.

(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A.

Table II. Positional Parameters and Equivalent Isotropic Temperature Factors for $[Ni(L1)(CH_3CN)_2][ClO_4]_2$

atom	*x*	*y*	*z*	B_{eq}[a]	atom	*x*	*y*	*z*	B_{eq}[a]
Ni	0.2045(1)	0.3849(1)	0.2462(1)	3.00(4)	C(12)	0.036(1)	0.741(1)	0.263(1)	5.2(5)
S(1)	0.1072(2)	0.3992(2)	0.4510(2)	4.0(1)	C(13)	−0.0279(8)	0.620(1)	0.189(1)	4.5(4)
S(2)	0.3699(2)	0.5499(2)	0.3977(2)	4.2(1)	C(14)	0.0230(8)	0.5215(8)	0.1852(8)	4.0(4)
N(1)	0.2836(6)	0.2492(6)	0.2771(7)	3.2(3)	C(15)	−0.0162(8)	0.1729(8)	0.045(1)	3.7(4)
N(2)	0.1343(6)	0.5391(6)	0.2493(6)	3.1(3)	C(16)	−0.1124(8)	0.0745(8)	−0.055(1)	5.6(4)
N(3)	0.0578(6)	0.2480(6)	0.1196(7)	3.9(3)	C(17)	0.3235(8)	0.3492(8)	−0.032(1)	3.9(4)
N(4)	0.2854(6)	0.3669(7)	0.0703(7)	3.9(3)	C(18)	0.3700(8)	0.3237(9)	−0.1668(9)	5.4(4)
C(1)	0.3748(8)	0.2013(8)	0.2052(8)	3.7(4)	Cl(1)	0.6604(3)	0.3043(3)	0.0192(3)	4.9(1)
C(2)	0.4322(8)	0.1175(8)	0.227(1)	4.5(4)	O(1)	0.6177(8)	0.221(1)	−0.114(1)	15.3(6)
C(3)	0.398(1)	0.0826(8)	0.330(1)	4.9(4)	O(2)	0.5867(7)	0.3818(7)	0.1003(9)	10.5(4)
C(4)	0.3082(9)	0.1319(9)	0.407(1)	4.7(4)	O(3)	0.673(1)	0.231(1)	0.084(1)	20(1)
C(5)	0.2514(8)	0.2133(8)	0.3770(9)	3.7(4)	O(4)	0.768(1)	0.364(1)	0.022(1)	17.6(6)
C(6)	0.1471(9)	0.261(1)	0.457(1)	6.1(5)	Cl(2)	0.7988(3)	0.0181(3)	0.2865(3)	6.0(1)
C(7)	0.206(1)	0.535(1)	0.584(1)	8.7(5)	O(5)	0.776(1)	−0.0617(8)	0.1465(8)	17.1(7)
C(8)	0.329(1)	0.565(1)	0.565(1)	7.7(5)	O(6)	0.874(1)	−0.026(1)	0.350(1)	16.9(8)
C(9)	0.3251(9)	0.6810(8)	0.381(1)	5.4(4)	O(7)	0.6964(8)	0.0187(8)	0.3554(9)	11.5(5)
C(10)	0.1979(8)	0.6585(9)	0.3183(9)	3.8(4)	O(8)	0.8482(8)	0.1423(7)	0.3130(8)	10.9(5)
C(11)	0.149(1)	0.7613(8)	0.329(1)	4.7(4)					

[a] B_{eq} (Å^2) is the mean of the principal axes of the thermal ellipsoid.

Table III. Positional Parameters and Equivalent Isotropic Temperature Factors for $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$

atom	*x*	*y*	*z*	B_{eq}[a]	atom	*x*	*y*	*z*	B_{eq}[a]
Ni(1)	0.17923(8)	0.24285(7)	−0.19119(8)	2.89(4)	C(1)	−0.0614(7)	0.3991(5)	−0.1599(6)	3.8(3)
Cl(1)	0.6246(2)	0.2184(2)	0.5433(2)	5.1(1)	C(2)	−0.1838(8)	0.4812(6)	−0.1942(7)	5.1(4)
Cl(2)	0.8892(2)	0.3020(2)	0.1591(2)	5.4(1)	C(3)	−0.2538(8)	0.5252(6)	−0.3189(8)	5.7(4)
S(1)	0.1635(2)	0.3253(2)	−0.3776(2)	4.5(1)	C(4)	−0.2006(7)	0.4847(6)	−0.4082(7)	4.9(4)
S(2)	0.3874(2)	0.1066(2)	−0.1800(2)	4.1(1)	C(5)	−0.0782(7)	0.4010(5)	−0.3684(6)	3.7(3)
S(3)	0.0662(2)	0.0861(1)	−0.3163(2)	3.34(8)	C(6)	−0.0193(7)	0.3487(6)	−0.4642(6)	4.3(4)
O(1)	0.7258(8)	0.2281(7)	0.656(1)	18.5(6)	C(7)	0.2328(8)	0.1911(6)	−0.4456(7)	5.3(4)
O(2)	0.629(1)	0.2671(6)	0.438(1)	16.5(8)	C(8)	0.3753(8)	0.1316(6)	−0.3390(8)	5.3(4)
O(3)	0.616(1)	0.1047(6)	0.5226(6)	14.4(7)	C(9)	0.3454(7)	−0.0326(5)	−0.2022(7)	4.2(4)
O(4)	0.5116(8)	0.2892(8)	0.5452(9)	16.0(7)	C(10)	0.2042(7)	−0.0385(5)	−0.3101(7)	4.0(3)
O(5)	0.9892(8)	0.2285(6)	0.2608(7)	12.1(5)	C(11)	0.0369(6)	0.0577(5)	−0.1832(6)	3.6(3)
O(6)	0.879(1)	0.4149(5)	0.1995(8)	15.8(6)	C(12)	0.1426(6)	0.0780(5)	−0.0464(6)	3.0(3)
O(7)	0.900(1)	0.2783(9)	0.0498(8)	19(1)	C(13)	0.1744(7)	0.0091(6)	0.0574(7)	4.1(4)
O(8)	0.775(1)	0.271(1)	0.136(1)	18.6(9)	C(14)	0.2589(7)	0.0389(7)	0.1838(7)	4.8(4)
O(9)	0.2758(5)	0.3714(4)	−0.0683(4)	4.8(3)	C(15)	0.3127(7)	0.1320(7)	0.2039(6)	4.6(4)
O(10)	0.4979	0.3546	0.8929	10.2(8)	C(16)	0.2823(6)	0.1939(5)	0.0970(6)	3.6(3)
O(12)	0.4549	0.5499	0.7419	15(2)	C(17)	0.4687	0.6393	0.8521	20(3)
N(1)	−0.0091(5)	0.3596(4)	−0.2455(5)	3.2(3)	C(18)	0.5205	0.4033	0.8056	26(3)
N(2)	0.1983(5)	0.1675(4)	−0.0282(5)	2.8(2)					

[a] B_{eq} (Å^2) is the mean of the principal axes of the thermal ellipsoid.

Table IV. Positional Parameters and Equivalent Isotropic Temperature Factors for $[Ni(L3)][ClO_4]_2$

atom	*x*	*y*	*z*	B_{eq}[a]
Ni(1)	$^1/_2$	0.62601(9)	$^1/_4$	2.25(4)
S(1)	0.5025(1)	0.4743(1)	0.3677(1)	2.73(6)
S(2)	0.3383(1)	0.6234(1)	0.1493(1)	2.98(6)
N(1)	0.4923(3)	0.7453(4)	0.3523(4)	2.7(2)
C(1)	0.5659(4)	0.7889(6)	0.4453(5)	3.7(3)
C(2)	0.5644(4)	0.8471(6)	0.5257(5)	4.0(3)
C(3)	0.4862(4)	0.8618(5)	0.5160(5)	3.4(3)
C(4)	0.4104(4)	0.8208(5)	0.4219(5)	3.6(3)
C(5)	0.4150(4)	0.7655(5)	0.3410(5)	2.9(2)
C(6)	0.3291(4)	0.7325(5)	0.2314(5)	3.7(3)
C(7)	0.3183(4)	0.4925(5)	0.2001(5)	3.3(2)
C(8)	0.3869(4)	0.4685(5)	0.3223(5)	3.3(2)
C(9)	0.5175(4)	0.3449(5)	0.3114(5)	3.5(2)
Cl(1)	0.8057(1)	0.5907(2)	0.1357(1)	3.92(7)
O(1)	0.8187(4)	0.6993(5)	0.1879(5)	8.4(3)
O(2)	0.8450(5)	0.5827(6)	0.0802(6)	11.4(5)
O(3)	0.7134(4)	0.5748(8)	0.0577(6)	12.8(5)
O(4)	0.8304(6)	0.5102(6)	0.2156(6)	13.1(5)

[a] B_{eq} (Å^2) is the mean of the principal axes of the thermal ellipsoid.

Table V. Selected Bond Lengths and Angles in $[Ni(L1)(CH_3CN)_2][ClO_4]_2$

Distances (Å)			
Ni–S(1)	2.411(3)	Ni–N(2)	2.104(6)
Ni–S(2)	2.421(3)	Ni–N(3)	2.078(7)
Ni–N(1)	2.105(6)	Ni–N(4)	2.042(7)
Angles (deg)			
S(1)–Ni–S(2)	88.90(9)	S(2)–Ni–N(4)	92.4(2)
S(1)–Ni–N(1)	83.5(2)	N(1)–Ni–N(2)	170.9(3)
S(1)–Ni–N(2)	90.6(2)	N(1)–Ni–N(3)	92.0(2)
S(1)–Ni–N(3)	89.9(2)	N(1)–Ni–N(4)	95.3(3)
S(1)–Ni–N(4)	178.2(2)	N(2)–Ni–N(3)	94.9(3)
S(2)–Ni–N(1)	89.7(2)	N(2)–Ni–N(4)	90.7(3)
S(2)–Ni–N(2)	83.2(2)	N(3)–Ni–N(4)	88.9(3)
S(2)–Ni–N(3)	177.8(2)		

examined. X-ray structural data for three of the new compounds ($[Ni(L1)(CH_3CN)_2][ClO_4]_2$, $[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$, and $[Ni(L3)][ClO_4]_2$) have been collected, and the results are given in Tables I–VII and Figures 2–4. Conductances, electronic spectra (Table VIII) and magnetic moments and cyclic voltammetry (Table IX) indicate that the compounds are 2:1 electrolytes composed of pseudooctahedral complex cations and the appropriate anions. When the complexes do not contain ligands with sufficient donors to occupy all six coordination sites, the remaining sites are filled by solvent molecules that are bound with varying degrees of strength. The variation in spectral and electrochemical properties with structural parameters such as number and type of donor atoms as well as donor separation within the ligands has been examined. Pertinent observations and data are introduced at appropriate points in the discussion that follows.

Discussion

The new complexes are listed in Table VIII. All are soluble in acetonitrile, nitromethane, *N*,*N*-dimethylformamide, and dimethyl sulfoxide although they are not stable in the latter two solvents. The color of the complexes varies with the ligand but

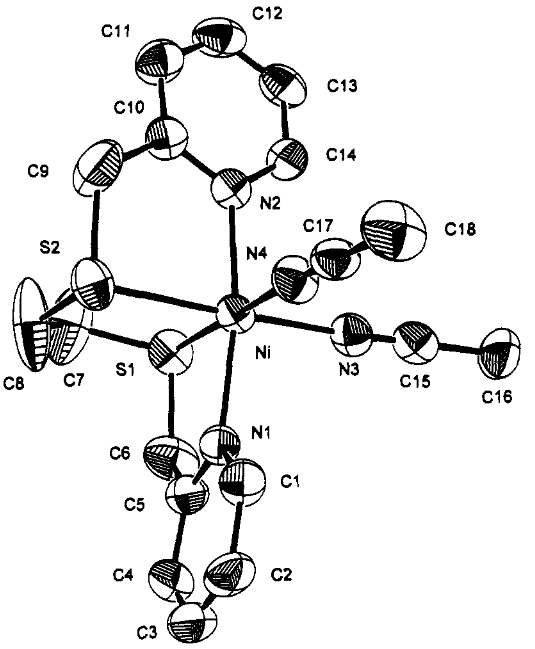

Figure 2. X-ray structure of $[Ni(L1)(CH_3CN)_2][ClO_4]_2$.

Table VI. Selected Bond Lengths and Angles in $[Ni(L2)(H_2O)][ClO_4]_2{\cdot}CH_3OH$

	Distances (Å)		
Ni–S(1)	2.392(2)	Ni–S(2)	2.426(2)
Ni–S(3)	2.460(2)	Ni–O(9)	2.100(4)
Ni–N(1)	2.058(5)	Ni–N(2)	2.084(5)
	Angles (deg)		
S(1)–Ni–S(2)	86.34(7)	S(2)–Ni–N(2)	92.0(1)
S(3)–Ni–O(9)	174.5(1)	S(1)–Ni–S(3)	96.05(7)
S(3)–Ni–N(1)	89.3(1)	S(1)–Ni–O(9)	89.5(1)
S(1)–Ni–N(1)	82.0(1)	S(3)–Ni–N(2)	83.8(1)
S(1)–Ni–N(2)	178.3(1)	O(9)–Ni–N(1)	90.9(2)
S(2)–Ni–S(3)	86.09(6)	O(9)–Ni–N(2)	90.7(2)
S(2)–Ni–O(9)	94.8(1)	N(1)–Ni–N(2)	99.7(2)
S(2)–Ni–N(1)	167.0(1)		

Table VII. Selected Bond Lengths and Angles in $[Ni(L3)][ClO_4]_2$

	Distances (Å)		
Ni–S(1)	2.434(2)	Ni–N(1)	2.091(5)
Ni–S(2)	2.425(2)		
	Angles (deg)		
S(1)–Ni–S(1)	87.41(9)	S(1)–Ni–S(2)	87.15(6)
S(1)–Ni–S(2)	91.82(6)	S(1)–Ni–N(1)	87.9(1)
S(1)–Ni–N(1)	173.8(1)	S(1)–Ni–S(2)	91.82(6)
S(1)–Ni–S(2)	87.15(6)	S(1)–Ni–N(1)	173.8(1)
S(1)–Ni–N(1)	87.9(1)	S(2)–Ni–S(2)	178.58(9)
S(2)–Ni–N(1)	83.9(1)	S(2)–Ni–N(1)	97.1(1)
S(2)–Ni–N(1)	97.1(1)	S(2)–Ni–N(1)	83.9(1)
N(1)–Ni–N(1)	97.1(3)		

not with the anion, which suggests that the anions are not coordinated. This is consistent with the IR spectra, which show strong bands at 1075 and 1050 cm^{-1} that are typical for uncoordinated ClO_4^- and BF_4^-, respectively. Onsager plots[11] of the conductivities at 25 °C for $[Ni(L2)(H_2O)][ClO_4]_2$ and $[Ni(L3)][ClO_4]_2$ indicate that these compounds are 1:2 electrolytes in nitromethane, and electrochemical and spectroscopic data discussed later are indications that the anions are uncoordinated. The complexes bind solvent weakly in open coordination sites. When precipitated from methanol, $[Ni(L1)]^{2+}$ salts exhibit a strong IR band at 3450 cm^{-1}, but after recrystallization from acetonitrile, their color changes to a deeper blue and the IR spectrum develops a strong band at 2300 cm^{-1} as a result of replacement of methanol in the coordination sphere by acetonitrile. As samples age or are dried in vacuum, there is gradual loss of acetonitrile until solvent-free samples are obtained (see analytical data from an aged sample in the Experimental Section) whereas, in freshly precipitated samples, two molecules of solvent are loosely bound to the metal, as detected in the X-ray structural study (Figure 2). Similarly, $[Ni(L2)(H_2O]^{2+}$ has one coordination site occupied by a water molecule, which was detected in the X-ray structure (Figure 3) and in the IR spectrum, where it exhibited a band at 3500 cm^{-1}.

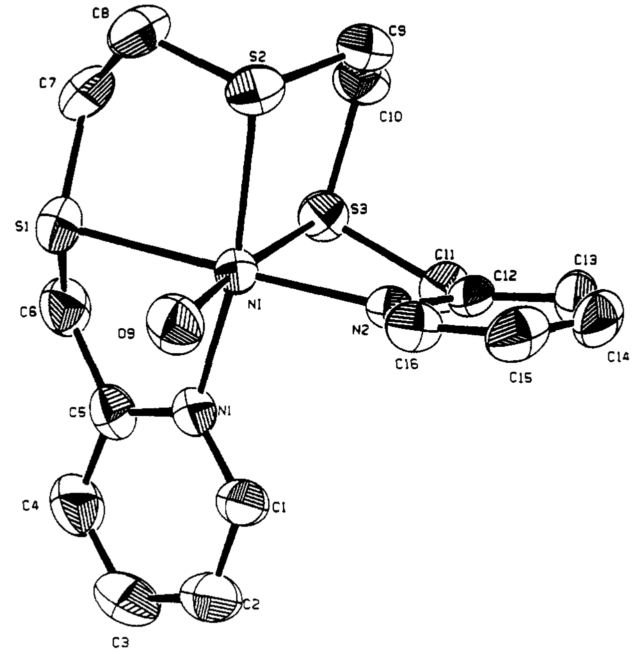

Figure 3. X-ray structure of $[Ni(L2)(H_2O)][ClO_4]_2{\cdot}CH_3OH$.

Crystal Structures. Structures of the Ni complexes and their atomic labeling schemes are shown in Figures 2–4, and fractional atomic coordinates, bond lengths, and bond angles are given in Tables II–VII.

The coordination sphere in $[Ni(L1)(CH_3CN)_2]^{2+}$ is a slightly distorted octahedron in which the nickel atom is coordinated by two thioether sulfurs, two aromatic nitrogens, and two nitrogens from acetonitrile solvent. The Ni–S bond distances (2.411(3) and 2.421(3) Å) are comparable to those in related systems,[12–18] as are the Ni–N(pyridine) distances (2.105(6) and 2.104(6) Å).[15,19,20] The Ni–N(acetonitrile) bond distances (2.078(7) and 2.042(7) Å) are slightly shorter than the Ni–N(pyridine) lengths. They are longer than those involving amine nitrogens in (BME-DACO)Ni (BME-DACO = 1,5-bis(mercaptoethyl)-1,5-diazacyclooctane)[21] (1.985(6) Å) and similar to those in bis(1-thia-4,7-diazacyclononane)nickel(II) nitrate (2.122(2) and 2.108(2) Å).[16] There is no structural evidence to indicate whether the solvent molecules are tightly or weakly bound to nickel although the ease with which they are lost (vide supra) suggests that they are labile. Bond angles in the coordination sphere are close to those expected for an octahedron, with the greatest deviations being found in S(1)–Ni–N(1) (83.5(2)°), S(2)–Ni–N(2) (83.2(2)°), and N(1)–Ni–N(2) (170.9(3)°).

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Table VIII. Electronic Spectral Data

complex	λ_{max}, nm (ϵ, L mol^{-1} cm^{-1})[a]	Δ_0, cm^{-1}	B, cm^{-1}	β
$[Ni(L1)(CH_3OH)_2][ClO_4]_2$	925 (sh), 850 (30), 555 (20)	11 800	728	0.70
$[Ni(L1)(CH_3OH)_2][BF_4]_2$	929 (sh), 852 (30), 556 (15)	11 800	728	0.70
$[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$	985 (sh), 875 (50), 545 (30)	11 400	936	0.90
$[Ni(L2)(H_2O)][BF_4]_2 \cdot 2H_2O$	975 (sh), 885 (45), 550 (35)	11 300	940	0.90
$[Ni(L3)][ClO_4]_2$	1075 (sh), 838 (45), 620 (sh), 540 (25)	11 900	792	0.76
$[Ni(L3)][BF_4]_2$	1038 (sh), 838 (55), 820 (sh), 620 (sh), 541 (30)	11 900	784	0.75
$[Ni(L4)][ClO_4]_2$	1023 (sh), 879 (55), 825 (sh), 625 (sh), 544 (35)	11 400	974	0.94
$[Ni(L4)][BF_4]_2$	1033 (sh), 879 (55), 820 (sh), 623 (sh), 545 (35)	11 400	961	0.92

[a] In CH_3CN.

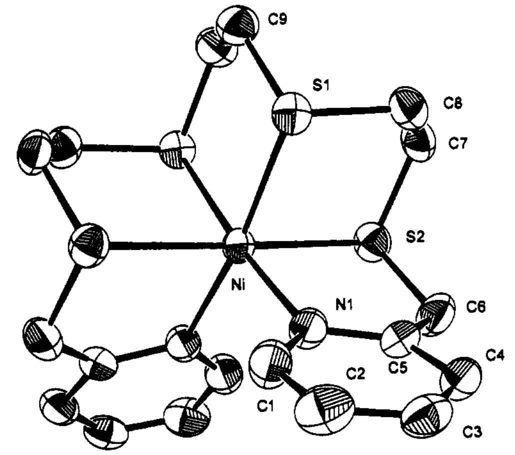

Figure 4. X-ray structure of $[Ni(L3)][ClO_4]_2$.

Table IX. Magnetic Moments and Cyclic Voltammetry Data

complex	μ_{eff}[a]	$E_{1/2}$[b]	ΔE_p[b]
$[Ni(L1)(CH_3OH)_2][ClO_4]_2$	2.97	−784	278
$[Ni(L1)(CH_3OH)_2][BF_4]_2$	2.88	−785	281
$[Ni(L2)(H_2O)][ClO_4]_2 \cdot CH_3OH$	2.75	−642	388
$[Ni(L2)(H_2O)][BF_4]_2 \cdot 2H_2O$	3.10	−603	230
$[Ni(L3)][ClO_4]_2$	3.04	−699 −700[c]	194 118[c]
$[Ni(L3)][BF_4]_2$	2.82	−708	150
$[Ni(L4)][ClO_4]_2$	2.73	−699 −703[c]	194 139[c]
$[Ni(L4)][BF_4]_2$	2.71	−700	164

[a] μ_B at 22 °C. [b] mV vs SCE at 300 mV/s in CH_3CN unless noted otherwise. [c] At 100 mV/s.

The coordination sphere of $[Ni(L2)(H_2O)][ClO_4]_2$ is also a slightly distorted octahedron with the nickel atom coordinated by two aromatic nitrogens, three thioether sulfurs, and a water molecule. The Ni–S bond distances (2.392(2), 2.426(2), and 2.460(2) Å) and Ni–N(pyridine) lengths (2.058(5) and 2.084(5) Å) are not greatly different from those in the L1 complex already discussed although one Ni–S bond is slightly longer and both Ni–N(pyridine) bonds are slightly shorter than those found previously. The Ni–O bond to the coordinated water molecule is 2.100(4) Å and is similar in length to that observed in other octahedral Ni(II) complexes.[22] The bond angles in $[Ni(L2)(H_2O)]^{2+}$ indicate a somewhat greater distortion of the coordination sphere than that in the L1 complex. The distortion involves displacement primarily of N(1) from its expected position to give angles S(2)–Ni–N(1) = 167.0(1)° and N(1)–Ni–N(2) = 99.7(2)° instead of 180 and 90°, respectively.

The pseudooctahedral coordination sphere of nickel in $[Ni(L3)][ClO_4]_2$ consists of four thioether sulfurs and two aromatic nitrogens and is symmetrical about an axis passing through the midpoint of the bond between C(9) and C(9)* and nickel. The Ni–S bond distances (2.425(2) and 2.434(2) Å) and the Ni–N distance (2.091(5) Å) are comparable to those in the other two complexes examined during this study. The largest angular distortions of the coordination sphere involve the aromatic nitrogens. Thus, N(1)–Ni–N(1)* = 97.1(3)°, S(2)–Ni–N(1) = 97.1(1)°, and S(1)–Ni–N(1)* = 173.8(1)°.

Electronic Spectroscopy. The electronic spectra of the complexes and room-temperature magnetic moments (Tables VIII and IX), which vary from 2.71 to 3.10 μ_B, are consistent with pseudooctahedral symmetry. The spectra show two main d–d bands with the third or highest energy band expected for pseudooctahedral Ni(II) complexes, $^3A_2 \rightarrow {}^3T_1(P)$, obscured by a charge-transfer band starting around 400 nm. The Racah parameter, B, calculated from[23]

$$B_{\text{complex}} = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1)$$

the nephelauxetic ratio, β, and the ligand field parameter, Δ_0, are given in Table VIII. It is important to realize while reading Table VIII that the solids dissolved in acetonitrile may not be present in the same form in solution. Evidence presented elsewhere in this paper suggests that complexes of L1 with methanol bound to nickel in the crystal suffer replacement of that methanol by acetonitrile upon dissolving whereas complexes of L2 with water bound to nickel retain their bound H_2O.

Compared to the free-ion value, B = 1038 cm^{-1}, the B values for the complexes are in the range 728–974 cm^{-1}. On changing from ligand L1 to L3, the corresponding B and Δ_0 values change from 728 to an average of 788 cm^{-1} and from 11 800 to 11 900 cm^{-1}, respectively. These are relatively small changes in spite of fairly major structural differences in the complexes. Comparing complexes of ligands L2 and L4, one sees that there is also very little change. It may be noted that similar complexes exhibiting only small structural distortions suffer significant effects upon their spectroscopic characteristics,[16,19] and it is therefore surprising to find such small changes in spectral parameters arising in the present cases from substantial structural changes. It may be that this is the result of effects with opposed consequences nearly canceling each other. For example, replacing harder O- or N-donors with softer S-donors allows delocalization of t_{2g} electron density from the metal into empty low-lying ligand orbitals,[24–26] thereby reducing electron–electron repulsions on the metal. Thus, in the absence of other effects, complexes containing more thioether donors should exhibit a greater nephelauxetic effect. On the other hand, changing the chain length between donor sites may alter the "fit" of the metal ion to the coordination sphere provided by the ligand and decrease the effectiveness of orbital overlap and hence the nephelauxetic effect. Collectively, these effects could nearly cancel each other as, for example, appears to occur when the ligand L2 is replaced by L4. From ligand L2 to L3, the B and Δ_0 values are changed on average from 938 to 788 and from 11 350 to 11 900 cm^{-1}, respectively. These more significant changes are reasonably attributed to replacement of hard donor oxygen by soft donor sulfur. Likewise, significant differences in both parameters are obtained by changing from L3 to L4, and these can be ascribed to a poorer "fit" of nickel into

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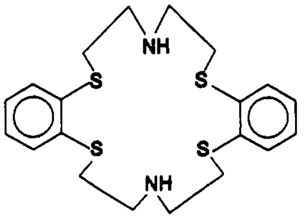
the coordination sphere provided by L4, which differs from L3 in chain length.[12,15,23,27,28]

Electrochemistry. In acetonitrile, all the complexes exhibit electrochemical activity in the potential range +1.9 to −1.2 V vs SCE (Table IX). The ligands display no electrochemical response over this potential range. By coulometry, the processes have been shown to involve one-electron reduction of Ni(II). Similarities in electrochemical behavior of $[Ni(L1)(solvent)_2][ClO_4]_2$ and $[Ni(L1)(solvent)_2][BF_4]_2$ (Table IX) as well as their solution electronic spectra (Table VIII) suggest that the anions are not in the nickel coordination sphere in solution and that the X-ray structure of the L1 complex is a reasonable representation of the cation in solution as well as in the solid state. For the L2 complex salts, there is noticeable dependence of electrochemical parameters on the identity of the anion, which could be interpreted to indicate coordination by the anion. This would be surprising for two reasons. The water molecule, located in the crystal structure (Figure 3), seems firmly bound and is not even displaced during recrystallization from acetonitrile, which is the same solvent used in the electrochemical study. Furthermore, the L1 complex cation has two solvation sites whereas that of L2 has only one. It is difficult to imagine how a cation–anion interaction could occur in the more sterically hindered L2 case but not in the less hindered L1 complex. It may well be, therefore, that the difference in behavior of these pairs of salts is related to events in the second coordination sphere and in particular to differences in the interactions between bound H_2O in the L2 complex and its anions.

Ligands L3 and L4 are similar except for carbon chain length between the central pair of donor atoms. The electrochemistries of their complexes are similar (Table IX) and show no indication of significant influence from the chain length or ion pairing. The complexes of L3 and L4 have a more positive potential (by about 85 mV) than those of L1, consistent with other studies where an increase in the S/N ratio in a coordination sphere has been observed to raise the positive character of the potential.[29]

Potentials of the L2 complexes are more positive than those of others in the series. This may be due simply to the mixed coordination environment, which stabilizes Ni(I),[15,30] or it may be that since Jahn–Teller distortion of all the Ni(I) species can be expected, in the case of the L2 complexes, distortion along the axis on which water is bound could lead to its loss. If H_2O is lost, the reduced L2 complex would be different from those formed by the other ligands. They should not distort along solvation axes and should therefore retain their bidentate and solvent donors in their reduced forms. In this regard, ESR examination of the pale yellow solutions that result upon electrochemical or borohydride reduction of the L2 complex cation revealed no signal. The absence of a signal from formal Ni(I) suggests that this reduced form is not simply the oxidized form with one electron added. Rather, it is a species in which some structural changes have also occurred, such as perhaps dimerization, that preclude ESR activity. Although, this behavior has been noted previously in nickel systems,[15] we have not investigated it further.

It is useful to compare our electrochemical results with those from the macrocylic N_2S_4 ligand.[20]



The Ni(II/I) potential of that system is more negative (−0.864 V vs SCE) than those from our analogous acyclic N_2S_4 systems, ligands L3 and L4, (−0.699 V vs SCE), under similar conditions. The more positive potential for the L3 and L4 complexes may be due to the fact that L3 and L4 are acyclic although there are other differences such as a change from amine to aromatic N-donors between the macrocyclic and acyclic ligands that may also contribute to the potential differences. The complexes of L3 and L4 have no Ni(III/II) wave in their cyclic voltammograms even though the related macrocyclic ligand gives a reversible wave at 1.29 V vs SCE. It seems, therefore, that the macrocyclic ligand stabilizes Ni(III) more effectively than the acyclic ligands. This permits detection of Ni(III/II) redox within the potential range we have examined when the ligand is cyclic but not when it is acyclic. In other words, the acyclic systems are better stabilizers of the lower oxidation state while the macrocyclic system is more effective for the higher oxidation state.

Conclusions

Nickel complexes of N_xS_y ligands have electronic structures that are very sensitive to the number and nature of donor atoms in their coordination spheres and to the "fit" of the metal ion to the coordination sphere provided by the ligand. In some cases, both $E_{1/2}$ and ΔE_p depend on the identity of the anion, and those cases appear to involve second coordination sphere interactions between the anions and a water ligand. There is no electrochemical effect from a change by one carbon atom in chain length between donor atoms, in contrast to a noticeable effect on spectroscopic properties. Increasing the number of thioether donors in the coordination sphere causes an increase in the positive character of $E_{1/2}$, and macrocyclic ligands appear to be better at stabilizing higher oxidation states while analogous acyclic ligands are better at stabilizing lower oxidation states.

Acknowledgment. Financial support from the Natural Sciences and Engineering Research Council of Canada and the Memorial University of Newfoundland is acknowledged. Dr. J. N. Bridson's contribution to the X-ray crystallography is also gratefully acknowledged.

Supplementary Material Available: A description of the X-ray studies and tables giving crystal data and details of the structure determinations, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom locations (32 pages). Ordering information is given on any current masthead page.

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