Inorg. Chem. **2000,** *39,* 712−718

Synthesis and Characterization of Nickel(II) Bis(alkylthio)salen Complexes

D. Scott Bohle,* Abdullah Zafar, Patricia A. Goodson, and David A. Jaeger

Department of Chemistry, University of Wyoming, Laramie, Wyoming 82071-3838

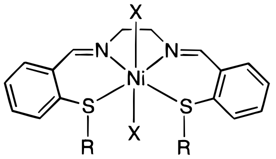
Received August 6, 1999

$NiX_2(2\text{-}RSC_6H_4CH{=}NCH_2CH_2N{=}CHC_6H_4SR\text{-}2)$ (NiX_2L; L = **5**) (**1a**, X = Br, R = C_6H_{13}; **1b**, X = Cl, R = $C_{12}H_{25}$) and $NiX_2(2\text{-}C_6H_{13}SC_6H_4CH_2NHCH_2CH_2NHCH_2C_6H_4SC_6H_{13}\text{-}2)$ (NiX_2L; L = **6**) (**2a**, X = Br; **2b**, X = Cl; **2c**, X = $OClO_3$) were prepared from ligands **5** and **6**, respectively. The 1:2 metal−ligand complex $Ni(OClO_3)_2(2\text{-}RSC_6H_4CH_2NHCH_2CH_2NHCH_2C_6H_4SR\text{-}2)_2$ **3**, was obtained from an EtOH solution of **2c**. The characterization of paramagnetic **1**−**3** included single-crystal X-ray diffraction studies of **1a** and **3**. Complex **2c** converted into **3** in the presence of excess ligand **6** in $CHCl_3$.

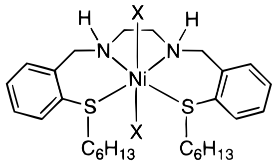
Introduction

There have been numerous reports of transition metal complexes containing thiosalen[1,2] and other ligands[1,2a] with two sulfur and two nitrogen donor atoms but only a few reports of complexes containing related ligands in which both sulfur atoms are alkylated.[1,3,4] In particular, in its thiosalen and similar complexes, Ni(II) typically adopts a four-coordinate square planar geometry.[1,2a−d] Alkylation of the sulfur atoms can give dipositively charged complexes in which Ni(II) remains four-coordinate[3] or neutral octahedral complexes containing coordinated counterions.[1,3,4a−c] In both geometries, the *S*-alkyl groups are in a cisoid relationship. With two functionalized *S*-alkyl chains incorporated into Ni(II) bis(alkylthio)salen and related complexes, one containing a 1,3-diene unit and the other a dienophile unit, their cisoid disposition is appropriate for controlling the regioselectivity of Diels−Alder cycloaddition between them. Namely, the 1,3-diene and dienophile units can interact intramolecularly only in one relative orientation due to the fixed side-by-side alignment of the *S*-alkyl chains. As a result, only one of two possible regioisomeric cycloadducts should be formed, in an application of the coordination template hypothesis.[4d] In related studies,[5] we have used the alignment of functionalized surfactant monomers within their aqueous micelles to control the regioselectivity of Diels−Alder reactions.

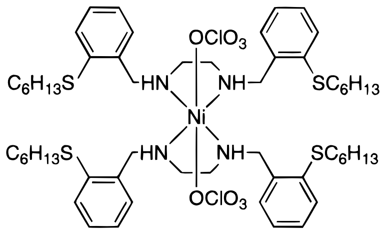
As a part of our evaluation of Ni(II) bis(alkylthio)salen and related complexes as templates for Diels−Alder reactions, we have studied several unfunctionalized complexes. Our interest in such complexes also extends to their potential surfactant character. Surfactant transition metal complexes are anticipated to have a wide range of interesting stereochemical, redox, and physical properties. But there have been only a few reports[6] of the synthesis, isolation, and characterization of surfactant transition metal complexes, in contrast to many reports of the formation and study of such surfactants in solution without isolation.[7] Herein we report the synthesis and characterization of Ni(II) complexes **1** and **2**, which contain several ligands and counterions. Interestingly, **2c** was found to interconvert with 1:2 complex **3**. In contrast to Ni(II) thiosalen and related complexes, **1**−**3** exhibit octahedral coordination with its concomitant paramagnetism.



1a, R = C_6H_{13}; X = Br
1b, R = $C_{12}H_{25}$; X = Cl



2a, X = Br
2b, X = Cl
2c, X = $OClO_3$



3

Experimental Section

General Procedures and Materials. ^1H (400 MHz) and ^{13}C (100.6 MHz) NMR spectra were recorded in $CDCl_3$ unless noted otherwise with Me_4Si and $CHCl_3$ (center line at δ 77.00 relative to Me_4Si) as

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* Corresponding author. Telephone: 307-766-2795. Fax: 307-766-2807. E-mail: Bohle@uwyo.edu.

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10.1021/ic990950p CCC: \$19.00

internal standards, respectively. ^{1}H and ^{13}C NMR spectra recorded in DMSO-d_6 employed $CD_3S(O)CD_2H$ (δ 2.50 relative to Me_4Si) and $CD_3S(O)CD_3$ (δ 39.52 relative to Me_4Si) as internal standards, respectively. J values are in hertz. Vis−NIR spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer with quartz cuvettes (1 cm path length). Magnetic susceptibility was determined on a Johnson Mathey magnetic susceptibility balance (MSB-1). Flash chromatography was performed on silica gel (ICN 02776, 60 Å, 32−63 μm). All melting points were taken in open capillary tubes and are uncorrected. Ratios describing the compositions of solvent mixtures represent relative volumes. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

2-(Hexylthio)benzaldehyde (4a). A modified literature procedure[8] was used. A mixture of 2-nitrobenzaldehyde (Aldrich) (3.00 g, 19.9 mmol), 1-hexanethiol (3.52 g, 29.8 mmol) (Aldrich), K_2CO_3 (3.01 g, 21.8 mmol), and DMF (20 mL) was held at 110 °C for 18 h, cooled to 25 °C, and diluted with Et_2O (125 mL), and the resulting mixture was filtered. Rotary evaporation left a brown oil, which was dried for 15 h (25 °C, 0.001 mmHg) and flash-chromatographed on a 3 cm × 35 cm column of silica gel packed in hexane and eluted with hexane to give **4a** (2.37 g, 54%): ^{1}H NMR ($CDCl_3$) δ 10.39 (s, 1 H, CHO), 7.83 (dd, J = 1.5, 7.7, 1 H, Ar H), 7.51 (m, 1 H, Ar H), 7.41 (m, 1 H, Ar H), 7.29 (dt, J = 0.9, 7.4, 1 H, Ar H), 2.95 (t, J = 7.4, 2 H, SCH_2), 1.66−1.73 (m, 2 H, SCH_2CH_2), 1.45−1.47 (m, 2 H, $SCH_2CH_2CH_2$), 1.28−1.32 (m, 4 H, $(CH_2)_2$), 0.89 (t, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.77, 142.52, 134.15, 134.08, 132.18, 128.31, 125.39, 33.50, 31.55, 28.85, 28.72, 22.71, 14.21. Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16. Found: C, 70.53; H, 8.21.

***N*,*N*′-Bis[(2-(hexylthio)phenyl)methylene]-1,2-ethanediamine (5a).** A solution of **4a** (2.54 g, 11.4 mmol) and ethylenediamine (0.33 g, 5.6 mmol) in C_6H_6 (50 mL) was heated to reflux under a Dean−Stark trap for 2 h and allowed to stand at 25 °C for 12 h over $MgSO_4$. Thereafter the mixture was filtered and rotary-evaporated to give a yellow oil from which ethylenediamine and **4a** were removed by Kugelrohr distillation (ca. 100 °C) to leave **5a** (2.42 g, 93%): ^{1}H NMR ($CDCl_3$) δ 8.87 (s, 2 H, 2 ArC*H*N), 7.91 (dd, J = 1.5, 7.7, 2 H, Ar H), 7.36−7.38 (m, 2 H, Ar H), 7.31 (dt, J = 1.5, 7.3, 2 H, Ar H), 7.21 (br t, J = 7.4, 2 H, Ar H), 4.03 (s, 4 H, NCH_2CH_2N), 2.80 (t, J = 7.3, 4 H, 2 SCH_2), 1.50−1.58 (m, 4 H, 2 SCH_2CH_2), 1.23−1.38 (m, 12 H, 2 $(CH_2)_3$), 0.87 (t, J = 7.1, 6 H, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 161.31, 137.80, 136.20, 130.83, 130.68, 128.16, 126.66, 62.01, 35.16, 31.56, 29.18, 28.67, 22.74, 14.25. Anal. Calcd for $C_{28}H_{40}N_2S_2$: C, 71.74; H, 8.60. Found: C, 71.76; H, 8.58.

[*N*,*N*′-Bis[(2-(hexylthio)phenyl)methylene]-1,2-ethanediamine]nickel(II) Bromide (1a). A modified literature procedure[2a,b] was used for the syntheses of **1a** and the complexes below. To a suspension of anhydrous $NiBr_2$ (0.17 g, 0.78 mmol) in absolute EtOH (20 mL) at 25 °C was added rapidly a solution of **5a** (0.37 g, 0.79 mmol) in EtOH (10 mL). The resulting mixture was heated to reflux ($CaCl_2$ drying tube) for 15 h, concentrated by rotary evaporation to ca. 12 mL, and then held at 5 °C for 15 h. No crystallization occurred until the mixture sat at 25 °C for 30 min. Thereafter the mixture was held at 5 °C for 2 h, followed by filtration to give dark green crystals of **1a** (0.26 g, 48%). After the mother liquor was held at 25 °C for a few weeks, X-ray-quality crystals were obtained: mp 175−177 °C dec; ^{1}H NMR ($CDCl_3$; only broad signals were observed due to **1a**'s paramagnetic character) δ 11.60 (br s), 10.63 (br s), 7.08 (br s), 5.58 (br s), 2.44 (br s), 1.25−1.80 (br m), 0.98 (br s); ^{13}C NMR ($CDCl_3$; only a few signals were observed due to **1a**'s paramagnetic character) δ 159.82, 32.50, 24.25, 12.17. Anal. Calcd for $C_{28}H_{40}N_2S_2NiBr_2$: C, 48.93; H, 5.87. Found: C, 48.95; H, 5.88.

2-(Dodecylthio)benzaldehyde (4b). A mixture of 2-nitrobenzaldehyde (1.00 g, 6.62 mmol), 1-dodecanethiol (2.39 g, 11.9 mmol) (Aldrich), K_2CO_3 (1.00 g, 7.23 mmol), and DMF (5 mL) was held at 110 °C for 24 h under N_2. Then, at 25 °C, it was poured into H_2O (70 mL) and extracted with Et_2O (4 × 25 mL), and the combined extracts were dried over $MgSO_4$. Rotary evaporation left a dark brown amorphous solid, which was chromatographed on a 3 cm × 25 cm column of silica gel packed in hexane and eluted with hexane to give **4b** (0.59 g, 29%): ^{1}H NMR ($CDCl_3$) δ 10.39 (s, 1 H, CHO), 7.83 (dd, J = 1.5, 7.7, 1 H, Ar H), 7.49−7.53 (m, 1 H, Ar H), 7.40−7.42 (m, 1 H, Ar H), 7.29 (dt, J = 0.7, 7.9, 1 H, Ar H), 2.95 (t, J = 7.4, 2 H, SCH_2), 1.66−1.72 (m, 2 H, SCH_2CH_2), 1.43−1.47 (m, 2 H, $SCH_2CH_2CH_2$), 1.26 (m, 16 H, $(CH_2)_8$), 0.88 (t, J = 6.9, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.71, 142.53, 134.13, 134.06, 132.15, 128.29, 125.36, 33.48, 32.11, 29.82, 29.77, 29.67, 29.54, 29.37, 29.17, 28.75, 22.89, 14.32. Anal. Calcd for $C_{19}H_{30}OS$: C, 74.45; H, 9.87. Found: C, 74.49; H, 9.80.

***N*,*N*′-Bis[(2-(dodecylthio)phenyl)methylene]-1,2-ethanediamine (5b).** A solution of **4b** (1.96 g, 6.39 mmol) and ethylenediamine (0.183 g, 3.04 mmol) in C_6H_6 (40 mL) was heated to reflux under a Dean−Stark trap for 6 h and then allowed to stand at 25 °C for 15 h over $MgSO_4$. Thereafter the mixture was filtered and rotary-evaporated to give a yellow solid, which was dried for 2 h (25 °C, 0.001 mmHg) and recrystallized twice from hexane (−20 °C) to give yellow flakes of **5b** (0.86 g, 44%): mp 42−43 °C; ^{1}H NMR ($CDCl_3$) δ 8.87 (s, 2 H, 2 ArC*H*N), 7.91 (dd, J = 1.4, 7.7, 2 H, 2 Ar H), 7.35−7.39 (m, 2 H, 2 Ar H), 7.31 (dt, J = 1.6, 7.5, 2 H, 2 Ar H), 7.21 (br t, J = 7.1, 2 H, 2 Ar H), 4.02 (s, 4 H, NCH_2CH_2N), 2.80 (t, J = 7.4, 4 H, 2 SCH_2), 1.52−1.56 (m, 4 H, 2 SCH_2CH_2), 1.24−1.37 (m, 36 H, 2 $(CH_2)_9$), 0.88 (t, J = 6.8, 6 H, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 161.30, 137.81, 136.20, 130.81, 130.67, 128.17, 126.65, 62.00, 35.15, 32.14, 29.86, 29.82, 29.73, 29.58, 29.39, 29.23, 29.01, 22.91, 14.35. Anal. Calcd for $C_{40}H_{64}N_2S_2$: C, 75.41; H, 10.13. Found: C, 75.60; H, 9.99.

[*N*,*N*′-Bis[(2-(dodecylthio)phenyl)methylene]-1,2-ethanediamine]nickel(II) Chloride (1b). To a solution of $NiCl_2 \cdot 6H_2O$ (0.20 g, 0.82 mmol) in EtOH (15 mL) at 50 °C was added during 4 min a solution of **5b** (0.52 g, 0.82 mmol) in EtOH (10 mL). The mixture was then heated to reflux for 3 h and rotary-evaporated. The resultant crude product was recrystallized from MeOH (25 °C) under a swift current of N_2 to give **1b** (0.15 g, 25%): mp 145−146 °C dec; ^{1}H NMR ($CDCl_3$; broad signals were observed due to **1b**'s paramagnetic character) δ 16.35 (br s), 11.71 (br s), 11.03 (br s), 6.82 (br s), 5.28 (br s), 2.54 (br s), 1.80 (br s), 1.00−1.70 (br m), 0.90 (br m); ^{13}C NMR ($CDCl_3$; only alkyl chain signals were observed due to **1b**'s paramagnetic character) δ 33.18, 32.29, 30.94, 29.39, 28.92, 28.77, 28.40, 21.70, 13.16. Anal. Calcd for $C_{40}H_{64}N_2S_2NiCl_2$: C, 62.66; H, 8.41. Found: C, 62.82; H, 8.43.

***N*,*N*′-Bis[(2-(hexylthio)phenyl)methyl]-1,2-ethanediamine (6).** A solution of $NaBH_4$ (0.117 g, 3.09 mmol) in MeOH (5 mL) was added to a solution of **5a** (0.28 g, 0.60 mmol) in MeOH (5 mL) at 0 °C during 5 min, and the resultant mixture was stirred for 20 min at 0 °C. Another portion of solid $NaBH_4$ (0.050 g, 1.3 mmol) was then added, and the reaction mixture was stirred at 25 °C for 6 h. After the addition of H_2O (30 mL), the resultant mixture was extracted with Et_2O (15 mL). The extract was dried over $MgSO_4$ and rotary-evaporated, and the residue was dried for 12 h (25 °C, 0.001 mmHg) to give **6** as an oil

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(0.25 g, 88%): ^{1}H NMR ($CDCl_3$) δ 7.28−7.33 (m, 4 H, Ar H), 7.20 (dt, J = 1.5, 7.5, 2 H, Ar H), 7.11−7.15 (m, 2 H, Ar H), 3.87 (s, 4 H, $ArCH_2$), 2.89 (t, J = 7.4, 4 H, 2 SCH_2), 2.78 (s, 4 H, NCH_2CH_2N), 1.78 (br s, 2 H, 2 NH), 1.63 (m, J = 7.5, 4 H, 2 SCH_2CH_2), 1.36−1.48 (m, 4 H, 2 $SCH_2CH_2CH_2$), 1.21−1.33 (m, 8 H, 2 $(CH_2)_2$), 0.88 (t, J = 6.9, 6 H, 2 CH_3); ^{13}C NMR ($CDCl_3$) δ 139.68, 136.33, 129.31, 128.40, 127.63, 125.70, 51.98, 48.90, 33.67, 31.59, 29.23, 28.88, 22.76, 14.25. Anal. Calcd for $C_{28}H_{44}N_2S_2$: C, 71.13; H, 9.38. Found: C, 71.09; H, 9.25.

[*N*,*N*′-Bis[(2-(hexylthio)phenyl)methyl]-1,2-ethanediamine]nickel(II) Bromide (2a). To a suspension of anhydrous $NiBr_2$ (0.11 g, 0.50 mmol) in absolute EtOH (10 mL) was added during 5 min a solution of **6** (0.24 g, 0.50 mmol) in EtOH (10 mL) at 50 °C. Then the mixture was heated to reflux for 5 h, concentrated to 10 mL by rotary evaporation, and held at 5 °C for 12 h. The resultant crystals were collected by filtration and dried for 12 h (25 °C, 0.001 mmHg) to give blue **2a** (0.25 g, 73%): mp 163−164 °C dec; ^{1}H NMR (DMSO-d_6; only broad signals were observed due to **2a**'s paramagnetic character) δ 9.77 (br m), 5.64 (br s), 1.69 (br s), 1.07−149 (br m), 0.81 (br s). Anal. Calcd for $C_{28}H_{44}N_2S_2NiBr_2$: C, 48.65; H, 6.42. Found: C, 48.83; H, 6.47.

[*N*,*N*′-Bis[(2-(hexylthio)phenyl)methyl]-1,2-ethanediamine]nickel(II) Chloride (2b). To a solution of $NiCl_2\cdot 6H_2O$ (0.068 g, 0.29 mmol) in EtOH (20 mL) at 25 °C was added during 3 min a solution of **6** (0.136 g, 0.287 mmol) in EtOH (5 mL). The mixture was then heated to reflux for 4 h and rotary-evaporated. The residue was recrystallized from EtOH (25 °C) to give green **2b** (0.075 g, 44%): mp 179−182 °C dec; ^{1}H NMR (DMSO-d_6; only broad signals were observed due to **2b**'s paramagnetic character) δ 9.21−9.86 (br m), 7.72 (br s), 5.75 (br m), 2.01 (br s), 1.67 (br s), 1.16 (br s), 0.76 (br s); ^{13}C NMR (DMSO-d_6; only a few alkyl group signals were observed due to **2b**'s paramagnetic character) δ 30.28, 21.79, 13.38. Anal. Calcd for $C_{28}H_{44}N_2S_2NiCl_2\cdot 0.5H_2O$: C, 55.01; H, 7.42. Found: C, 55.13; H, 7.25. The presence of water was confirmed by IR analysis of **2b** (KBr pellet); an O−H stretch was found (3460 cm^{-1}).

[*N*,*N*′-Bis[(2-(hexylthio)phenyl)methyl]-1,2-ethanediamine]nickel(II) Perchlorate (2c). ***Caution*****!** Perchlorates are potentially explosive. Although we have had no explosions in our work with **2c** or **3** (see below), appropriate precautions should be taken in working with them.

A mixture of $Ni(ClO_4)_2\cdot 6H_2O$ (0.19 g, 0.51 mmol), **6** (0.24 g, 0.51 mmol), and anhydrous EtOH (16 mL) was heated to reflux for 4 h and rotary-evaporated. The residue was washed with hexane, and CH_2Cl_2 (15 mL) was added. The resultant mixture was filtered, the filtrate was rotary-evaporated, and the residue was dried for 12 h (25 °C, 0.001 mmHg) to give pink **2c** (0.22 g, 60%): mp 222−227 °C dec; ^{1}H NMR ($CDCl_3$; only broad signals were observed due to **2c**'s paramagnetic character) δ 83.37 (br s), 57.79 (br s), 32.34 (br s), 15.67 (br s), 14.13 (br s), 12.77 (br s), 9.67 (br s), 6.77 (br s), 3.07 (br s), 2.76 (br s), 2.49 (br s), 2.00 (br s), 1.70 (br s), 0.89−1.40 (br m); ^{13}C NMR ($CDCl_3$; only a few signals were observed due to **2c**'s paramagnetic character) δ 146.92, 121.49, 35.71, 27.88, 14.98. Anal. Calcd for $C_{28}H_{44}N_2S_2NiCl_2O_8$: C, 46.05; H, 6.07. Found: C, 46.30; H, 6.04.

[Bis[*N*,*N*′-bis[(2-(hexylthio)phenyl)methyl]-1,2-ethanediamine]]nickel(II) Perchlorate (3). Complex **3** was isolated as blue crystals from an EtOH solution of **2c** held at 25 °C for 36 h: mp 119−121 °C dec; ^{1}H NMR ($CDCl_3$; only broad signals were observed due to **3**'s paramagnetic character) δ 10.16−10.29 (br m), 8.11−9.00 (br m), 6.33 (br m), 5.85−6.19 (br m), 3.71 (br s), 0.90−2.11 (br m), 0.75 (br m); ^{13}C NMR ($CDCl_3$) δ 151.05, 150.58, 141.48, 140.93, 140.01, 139.08, 132.76, 132.42, 132.14, 131.27, 37.91, 37.51, 31.64, 31.47, 30.46, 29.03, 22.75, 22.70, 22.61, 14.18, 14.10. Anal. Calcd for $C_{56}H_{88}N_4S_4NiCl_2O_8$: C, 55.90; H, 7.37. Found: C, 55.75; H, 7.18.

Spectrophotometric Titration. A $CHCl_3$ solution of complex **2c** (3.00 mL, 11.63 mM) was placed in a 1 cm quartz cell and its spectrum recorded between 200 and 800 nm against a $CHCl_3$ blank. Then a $CHCl_3$ solution of ligand **6** (85.66 mM) was added in portions. Spectra were recorded after the addition of a total of 0.10, 0.20, 0.30, 0.40, 0.60, and 0.80 mL of the ligand solution. Absorbance was corrected for dilution: $A_{cor} = A_{obs}[(V_i + V_a)/V_i]$, where A_{cor} = corrected absorbance, V_i = initial volume of **2c** solution, and V_a = total volume of **6** solution added.

Table 1. Crystallographic Data and Refinement Parameters

	1a	**3**
empirical formula	$C_{28}H_{40}Br_2N_2NiS_2$	$C_{56}H_{88}Cl_2N_4NiO_8S_4$
mass (g mol^{-1})	687.27	1203.15
a (Å)	21.173(4)	10.377(1)
b (Å)	14.287(3)	11.911(1)
c (Å)	10.053(2)	26.008(3)
α (deg)	90	91.296(7)
β (deg)	98.79(2)	97.868(9)
γ (deg)	90	104.767(9)
V (Å^3)	3005.3(10)	3073.6(6)
space group	$P2_1/c$	$P\bar{1}$
temp (°C)	−100	−50
wavelength (Å)	0.71073	0.71073
ρ_{calcd} (g cm^{-3})	1.519	1.300
abs coeff, μ (mm^{-1})	3.463	0.592
R1^a	0.062	0.065
wR2^b	0.15	0.16

^{a}R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{b} wR2 = $\{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

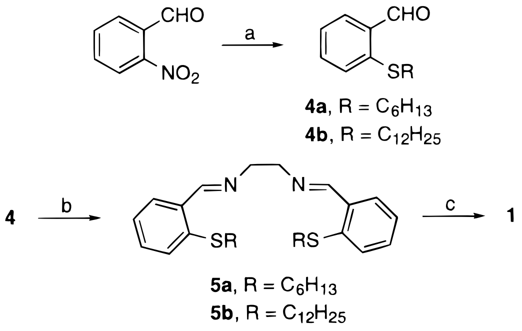
Crystallographic Structure Determinations. X-ray diffraction data were collected for single crystals of complexes **1a** and **3** on a Siemens P4 diffractometer equipped with a molybdenum tube (λ = 0.71073 Å) and a graphite monochromator. In each case, the diffraction data were measured using ω scans. The intensities of three standard reflections monitored every 100 reflections during the respective data collections indicated negligible crystal decomposition.

The structures were solved by direct methods and refined by full-matrix least-squares techniques on F^2 for all data for both **1a** and **3** using structure solution programs from the SHELXTL system.[9] For **1a**, non-hydrogen atoms were refined anisotropically, while all hydrogen atoms were placed in calculated positions (0.96 Å) and refined with fixed isotropic thermal parameters. For **3**, hydrogen atoms on the nitrogen atoms were located in successive Fourier maps and refined isotropically, while all other hydrogen atoms were placed in calculated positions and refined with fixed isotropic thermal parameters set to 1.2 times those of the atoms to which they were attached. The non-hydrogen atoms were refined anisotropically. Crystallographic parameters for **1a** and **3** are collected in Table 1.

Results and Discussion

Syntheses. Complexes **1** were prepared as outlined in Scheme 1. 2-Nitrobenzaldehyde was converted into 2-(alkylthio)benzaldehydes **4** according to a modified literature procedure[8] by reaction with the indicated alkanethiols. The condensation of **4** with ethylenediamine gave ligands **5**, followed by their reactions[2a,b] with NiX_2 to give complexes **1**.

Scheme 1^a



^{a} Key: (a) $C_6H_{13}SH$ or $C_{12}H_{25}SH$, K_2CO_3, DMF, 110 °C; (b) $H_2NCH_2CH_2NH_2$, C_6H_6, Dean−Stark; (c) NiX_2 (X = Br, Cl), EtOH, reflux.

Complexes **2** were prepared as outlined in Scheme 2. The reduction of the carbon−nitrogen double bonds of **5a** gave

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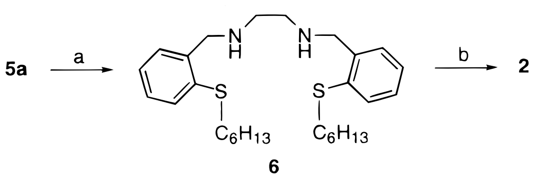
[9] Sheldrick, G. M. *SHELXTL Crystallographic System*, Version 5.03/Iris; Siemens Analytical X-ray Instruments Inc.: Madison, WI, 1994.

Scheme 2[a]



[a] Key: (a) $NaBH_4$, MeOH, 25 °C; (b) NiX_2 (X = Br, Cl, ClO_4), EtOH, reflux.

ligand **6**, followed by its reactions[2a,b] with NiX_2 to give complexes **2**. Complex **3** was isolated from an EtOH solution of **2c**.

Characterization. Complexes **1**−**3** were characterized by combustion analyses and ^1H and ^{13}C NMR spectroscopy. Additionally, they were characterized by Vis−NIR spectroscopy, and **1a** and **3** were also characterized by single-crystal X-ray diffraction.

General Characteristics. The complexes were initially determined to be paramagnetic on the basis of their ^1H and ^{13}C NMR spectra. For **1a**, **1b**, **2c**, and **3** in $CDCl_3$ and **2a** and **2b** in DMSO-d_6, large paramagnetic shifts and extensive broadening were observed in their ^1H NMR spectra, and generally only a few signals were observed, mainly for aliphatic carbon atoms, in their ^{13}C NMR spectra. The solid-state magnetic moment of **2a** is 2.91 μ_B at 25 °C, consistent with two unpaired electrons.[10]

Both **1a** and **1b** are insoluble in H_2O and very soluble in organic solvents such as CH_2Cl_2 and $CHCl_3$. They dissociate completely in DMSO, as evidenced by the presence of only sharp signals corresponding to the free ligand **5** in their ^1H NMR spectra; they dissociate partially in MeOH, as indicated by sharp signals corresponding to the free ligand and broad signals corresponding to the paramagnetic complex in their ^1H NMR spectra. Both **1a** and **1b** decompose in aqueous suspensions to give the corresponding 2-(alkylthio)benzaldehydes, as indicated by ^1H NMR. Coordination of the Schiff base nitrogens with Ni(II) activates the carbon−nitrogen double bonds toward hydrolysis.[11]

Complexes **2a**−**c** are insoluble in H_2O and soluble in organic solvents such as CH_2Cl_2 and $CHCl_3$. The colors of the complexes are sensitive to the axial ligands; **2a** is blue, **2b** is green, and **2c** is pink. Complex **2c** exhibits striking solvatochromism and ranges from a very light pink in noncoordinating solvents such as $CHCl_3$ ($\lambda_{max} = 564$ nm, $\epsilon = 16.2$ cm^{-1} M^{-1}) to green in coordinating solvents such as EtOH ($\lambda_{max} = 618$ nm, $\epsilon = 5.62$ cm^{-1} M^{-1}).

Complex **2c** dissociates in coordinating solvents such as DMSO and MeOH/EtOH. The ^1H NMR spectra of **2c** in DMSO-d_6 and CD_3OD display sharp signals for free ligand **6** in addition to broad contact-shifted signals. Presumably, in these coordinating solvents there are multiple equilibria among the 1:1 complex **2c**, the 1:2 complex **3**, the free ligand **6**, and $[Ni(solvent)_n]^{2+}$. Equilibrium constants were unobtainable because the signals in the ^1H NMR spectrum could not be assigned unambiguously.

There are a couple of factors that lead to the formation and isolation of both **2c** and **3**. Presumably, the very low solubility of **3** in EtOH causes its preferential crystallization. The equilibrium between **2c** and **3** in MeOH/EtOH may be associated with the poor coordination properties of ClO_4^-, which result in replacement of the weaker thioether donors in **2c** by the stronger secondary amine donors in **3**. This hypothesis is supported by the facts that **2a** and **2b**, with better coordinating halide ligands, recrystallize from EtOH to give only **2a** and **2b** and that they do not display solvatochromism. Furthermore, by ^1H NMR analysis, **2a** and **2b** do not dissociate in DMSO-d_6.

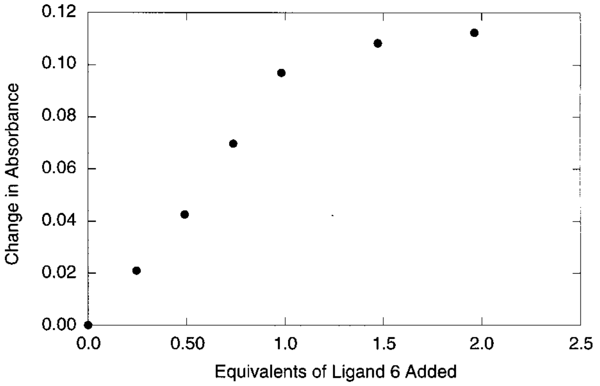


Figure 1. Change in absorbance at 575 nm for a solution of **2c** in $CHCl_3$ upon the addition of ligand **6** in $CHCl_3$. Absorbance was corrected for dilution.

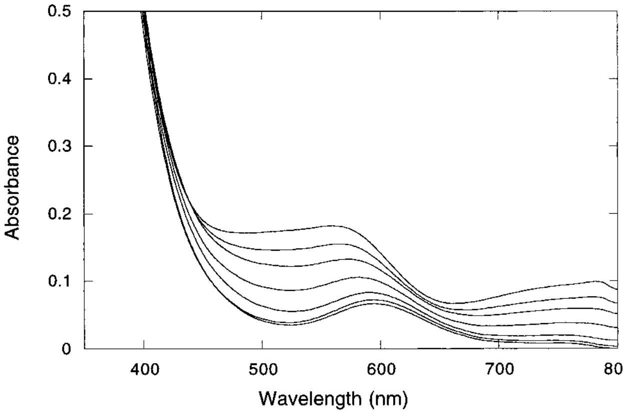


Figure 2. Visible spectra (uncorrected for dilution) obtained in the spectrophotometric titration of **2c** with **6** in $CHCl_3$. From top to bottom, the spectra correspond to the points of Figure 1 on going from 0 to 2.0 equiv of added ligand **6**.

Complex **2c** in $CHCl_3$ converts into complex **3** in the presence of excess ligand **6**. Titration of a solution of **2c** in $CHCl_3$with a concentrated solution of **6** in $CHCl_3$ gave a visual change from pink to green, concomitant with a decrease in absorption. The change in (corrected) absorbance of the system at 575 nm upon the addition of **6** is shown in Figure 1. The absorbance decreased almost linearly upon addition of the first equivalent of **6** and began to level off thereafter, consistent with the conversion of 1:1 complex **2c** into 1:2 complex **3**. The apparent lesser absorbance by the 1:2 complex, as shown in Figure 2, may be due to its higher local symmetry as compared to that of the 1:1 complex.[12] The final (bottom) spectrum of Figure 2 displays λ_{max} at 595 nm, which closely corresponds to that of **3** in $CHCl_3$ ($\lambda_{max} = 597$ nm).

The insolubility and, in some cases, instability of complexes **1** and **2** in H_2O limit their scope as surfactants. However, it is possible that they aggregate to form reversed micelles[13] in

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[10] Selwood, P. W. *Magnetochemistry*, 2nd ed.; Interscience: New York, 1956; Chapter 10.

[11] (a) Eichhorn, G. L.; Bailar, J. C., Jr. *J. Am. Chem. Soc.* **1953**, *75*, 2905. (b) Eichhorn, G. L.; Trachtenberg, I. M. *J. Am. Chem. Soc.* **1954**, *76*, 5183. (c) Harris, C. M.; Lenzer, S. L.; Martin, R. L. *Aust. J. Chem.* **1961**, *14*, 420. (d) Collman, J. P. In *Transition Metal Chemistry*; Carlin, R. L., Ed.; Marcel Dekker: New York, 1966; Vol. 2, p 1.

[12] Gerloch, M.; Constable, E. C. *Transition Metal Chemistry*; VCH: New York, 1994.

[13] Fendler, J. H. *Membrane Mimetic Chemistry*; Wiley-Interscience: New York, 1982; Chapter 3.

Table 2. Visible Spectral Data for Transitions and Crystal Field Parameters of **1** and **2** in $CHCl_3$

	transitions[a]				crystal field parameters	
complex	$^3T_{2g} \leftarrow {}^3A_{2g}$	$^1E_g \leftarrow {}^3A_{2g}$	$^3T_{1g} \leftarrow {}^3A_{2g}$	$^3T_{1g} \leftarrow {}^3A_{2g}$	B^b (cm^{-1})	$\Delta_o{}^b$ (cm^{-1})
1a	1093, 8.41	961, 6.21	794, 12.0	570,[c] 15.2	584	9068
1b	1044, 7.62	912, 9.06	818, 12.4	594, 14.6	615	9474
2a	1166, 7.89	945, 9.16	844, 13.8	609, 14.9	606	8678
2b	1088, 9.30	906, 12.8	861, 13.7	611, 15.6	629	8925
2c	1204, 3.59	865, 9.83	*d*	564, 16.2	656	8356

[a] λ (nm), ϵ (cm^{-1} M^{-1}). [b] Calculated using the two lowest energy bands. [c] Shoulder observed at ca. 626, 12.12. [d] Unassignable.

relatively nonpolar solvents such as CH_2Cl_2 and $CHCl_3$. In any event, aggregation should not be a requirement for operation of the chain alignment effect noted above for the control of Diels−Alder regioselectivity.

Vis−NIR Absorption Spectroscopy. Visible and near-IR spectra for complexes **1** and **2** were recorded in $CHCl_3$, and their results are summarized in Table 2. All three spin-allowed transitions typical of d^8 high-spin complexes were observed. In addition, a sharp band corresponding to the spin-forbidden transition $^1E_g \leftarrow {}^3A_{2g}$ was observed at ca. 626 nm, which overlapped with the $^3T_{1g} \leftarrow {}^3A_{2g}$ band.

Complexes **1a** and **1b** display interesting trends in the energies of various electronic transitions. The two lower energy transitions undergo a blue shift of 49 nm upon changing the axial ligand from bromide to chloride, as predicted by the spectrochemical series. In contrast, the two higher transitions undergo a red shift of 24 nm with the same change. Presumably, the higher energy states interact more with the larger and more polarizable bromide ligand in **1b** than with the chloride in **1a**. Similar trends were observed with **2a** and **2b**. However, for **2c** the spectrum was more complex and contained at least six bands. Thus the $^3T_{1g} \leftarrow {}^3A_{2g}$ band was not assigned. The crystal field parameters *B* and Δ_o were calculated using the two lowest energy transitions. In general, the Δ_o values are higher for complexes **1** compared to complexes **2** and follow a trend based on the spectrochemical series **1b** > **1a** > **2b** > **2a** > **2c**.

X-ray Diffraction Studies. X-ray-quality crystals of **1a** were obtained from an EtOH solution at 25 °C. The compound crystallized in the monoclinic space group $P2_1/c$ ($Z = 4$). The metal center adopts an octahedral geometry as shown in Figure 3 with the bromides occupying the axial positions with Ni−Br distances of 2.5602(8) and 2.5912(8) Å. The bis(alkylthio)salen ligand chelates the metal center with the donor nitrogen and sulfur atoms occupying the four equatorial positions. The Ni−N distances are 2.035(4) and 2.039(4) Å, longer than the Ni−N distances (1.85 and 1.86 Å) in Ni(thiosalen),[2a] which has a square planar geometry. The origin of these trends can be attributed either to the occupation of the $d_{x^2-y^2}$ orbitals in the paramagnetic complexes or possibly to the distortion of ligand **1a**. Both **1a** and Ni(thiosalen) contain bent N−C−C−N units with dihedral angles of |53.2| and |44|°,[2a] respectively. However, we note that the N−C−C−N dihedral angle is |47.3|° in the crystal structure of a related Cu(I) complex,[4e] and given the similar ligand geometries in these complexes, the differences in the Ni−N bond lengths are most likely due to occupation of the $d_{x^2-y^2}$ orbitals in the paramagnetic derivatives. These trends in metal−ligand bond lengths are also observed for the Ni−S bonds, 2.399(1) and 2.405(1) Å in **1a**, which are in turn significantly longer than the Ni−S bonds (2.14 and 2.17 Å) in Ni(thiosalen).[2a] These values are consistent with general trends for Ni−S bond lengths within Ni−SR and Ni−SR_2 groups; an examination of the Cambridge Crystallographic Database gave a mean value of 2.18 Å for Ni−SR and a bifurcated distribution for Ni−SR_2. Bond lengths in the ranges 2.12−2.28 and 2.32−2.52 Å were observed for diamagnetic and paramagnetic Ni−SR_2 complexes, respectively. Thus, Ni−S bond lengths of 2.39 and 2.40 Å within **1a** are in agreement with those for paramagnetic complexes.

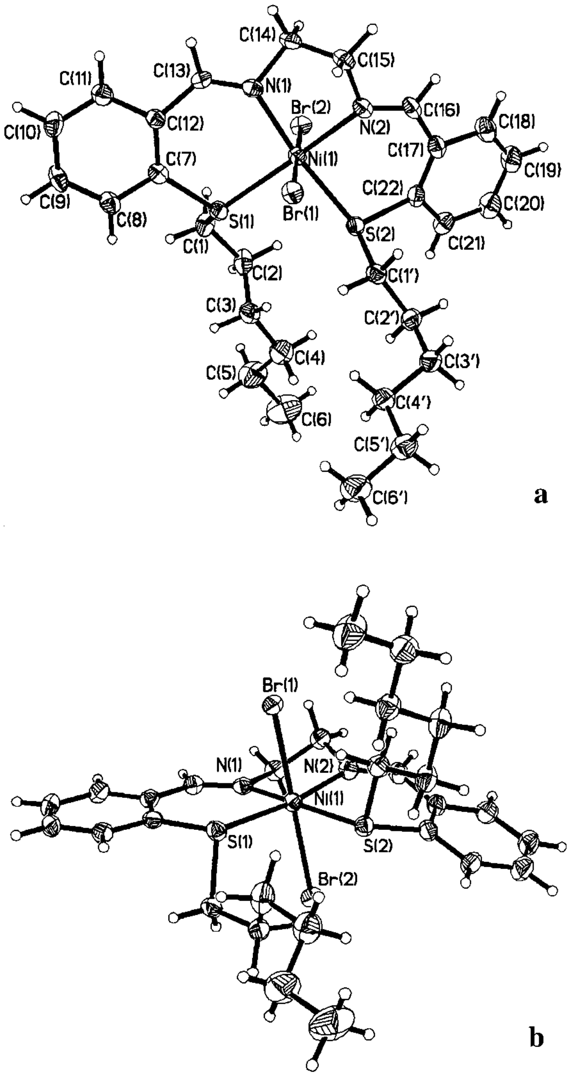


Figure 3. X-ray crystal structure of **1a**: (a) view showing octahedral geometry around Ni; (b) view illustrating opposed orientation of the alkyl side chains. Important metric parameters: Ni(1)−Br(1) 2.5602(8), Ni(1)−Br(2) 2.5912(8), Ni(1)−N(1) 2.039(4), Ni(1)−N(2) 2.035(4), Ni(1)−S(1) 2.3987(13), Ni(1)−S(2) 2.4045(13) Å; Br(1)−Ni(1)−Br(2) 178.69(3), S(1)−Ni(1)−S(2) 93.00(4), N(1)−Ni(1)−N(2) 83.8(2), N(1)−Ni(1)−S(1) 92.85(11), N(2)−Ni(1)−S(2) 90.84(12)°.

Another interesting feature of **1a**'s crystal structure is that both sulfur atoms have the same configuration (*R* in Figure 3). As a result, the two hexyl chains extend in opposite directions, thereby precluding the possibility of intramolecular hydrophobic interaction between them in the solid state; see Figure 3b. Also note that the hexyl chains are not in a fully extended all-trans conformation.

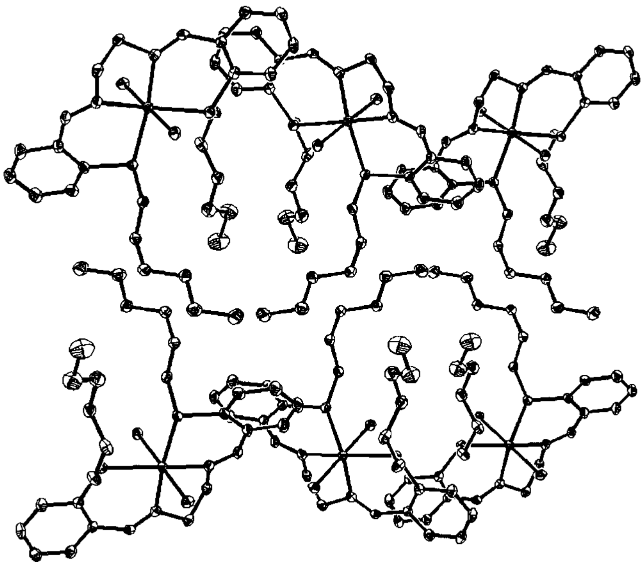
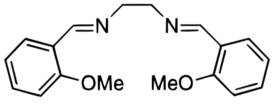


Figure 4. X-ray crystal structure of **1a** showing the bilayer packing arrangement (hydrogen atoms not shown).

Figure 4 shows the bilayer packing arrangement for **1a**, which is typical for solid-state surfactants.[14] Molecules are packed in a zigzag manner with the benzene ring of one molecule partially stacked over the benzene ring and associated aldimino carbon of another molecule. The shortest face-to-face stacking distance between the two π-systems is 3.5 Å. Another interesting feature is the presence of a weak hydrogen-bonding interaction between Br(2) of one molecule and H at C(8) of the adjacent stacked benzene ring; the Br$\cdots$H$_{Ar}$ distance is 2.73 Å. Weakly acidic protons are known to engage in hydrogen bonding with electronegative atoms such as oxygen and the halogens.[15] For example, this type of intermolecular hydrogen bonding is observed for acetic acid between a hydrogen of the methyl group and the carbonyl oxygen (CH$\cdots$OC; 2.4 Å).[15b]

It is interesting to compare the solid-state structure of **1a** with that of the Ni(II) complex of ligand **7**,[16] in which both oxygens



7

are alkylated. In the latter complex, the oxygen atoms do not coordinate with Ni(II); thus **7** behaves as a bidentate ligand utilizing only its nitrogen atoms.

X-ray-quality crystals of **3** were grown from an EtOH solution of **2c**; the crystal structure of **3** is shown in Figure 5. The compound crystallized in the centrosymmetric triclinic space group $P\bar{1}$ ($Z = 2$) with two independent half-molecules in the asymmetric unit. One occupies the center of the unit cell, and the other occupies a corner. Within each molecule, Ni lies on a crystallographic inversion center. The molecules have octahedral geometry at Ni with two chelated ligands in a trans relationship; the chelate rings have a λ,δ-configuration. Within one molecule, N(1) and N(2) have opposite configurations, which invert on going to N(1A) and N(2A), respectively; within the other molecule, the nitrogen atoms have analogous configurations. In the final refinement, there were no correlation coefficients greater than 0.1. The Ni−N bond lengths range from 2.121(4) to 2.140(5) Å, which are longer than those of **1a**. A weaker Ni−N interaction for secondary amine ligands relative to Schiff base ligands is typical. The two axial positions are occupied by two perchlorate counterions with Ni−O distances of 2.157(4) and 2.124(4) Å for the center and the corner molecules, respectively. The oxygen atoms on the perchlorate ions of the corner molecules are disordered.

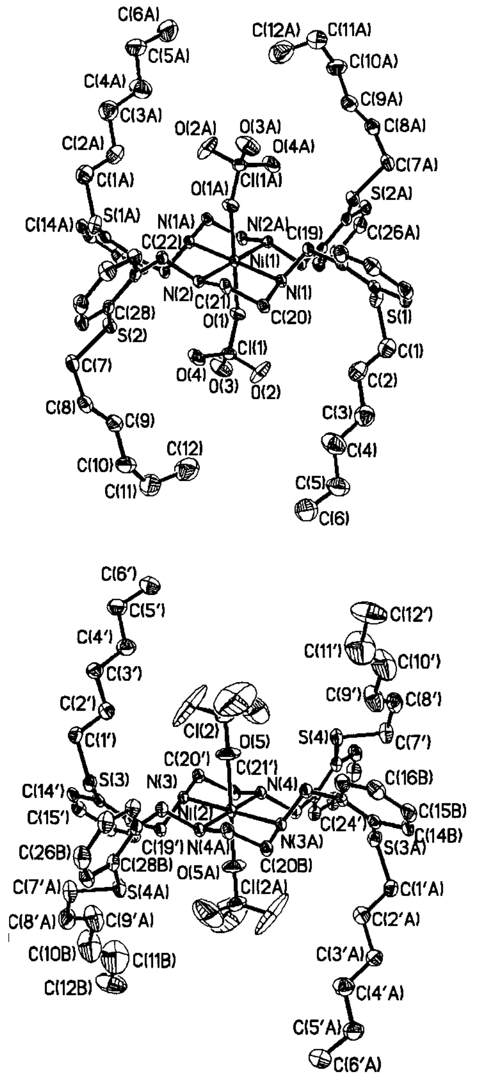


Figure 5. X-ray crystal structure of **3** showing the two independent molecules. Important metric parameters: Ni(1)−N(1) 2.131(4), Ni(1)−N(2) 2.131(4), Ni(1)−O(1) 2.157(4), Ni(2)−N(3) 2.140(5), Ni(2)−N(4) 2.121(4), Ni(2)−O(5) 2.124(4) Å; N(1)−Ni(1)−N(2) 83.9(2), N(1)−Ni(1)−N(2A) 96.1(2), N(1)−Ni(1)−O(1) 87.9(2), N(3)−Ni(2)−N(4) 83.4(2), N(3)−Ni(2)−N(4A) 96.6(2), N(3)−Ni(2)−O(5) 88.3(2)°.

Figure 6 shows the two-dimensional packing of **3**'s crystal lattice. The molecules form linear arrays with hydrophobic carbon−carbon contacts (shortest 3.59 Å) between the benzene ring edge of one molecule and the ethylene group of the ethylenediamine unit of another molecule. Every molecule makes such contacts on either side to form a linear array. The linear arrays pack together in a bilayer arrangement presumably stabilized by hydrophobic interactions between the hexyl chains. The interacting chains run antiparallel to each other with a distance of 4.0−4.2 Å between intermolecular carbon atoms. Every molecule uses two of its four hexyl chains, one on each

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(14) For example, see: Pascher, I.; Lundmark, M.; Nyholm, P.-G.; Sundell, S. *Biochim. Biophys. Acta* **1992**, *1113*, 339 and references therein.

(15) (a) Desiraju, G. R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2311. (b) Jönsson, P.-G. *Acta Crystallogr., Sect. B* **1971**, *27*, 893. (c) Mehta, G.; Uma, R. *J. Chem. Soc., Chem. Commun.* **1998**, 1735. (d) Zafar, A. Ph.D. Dissertation, University of Pittsburgh, 1997.

(16) Sacconi, L.; Bertini, I. *Inorg. Chem.* **1968**, *7*, 1178.

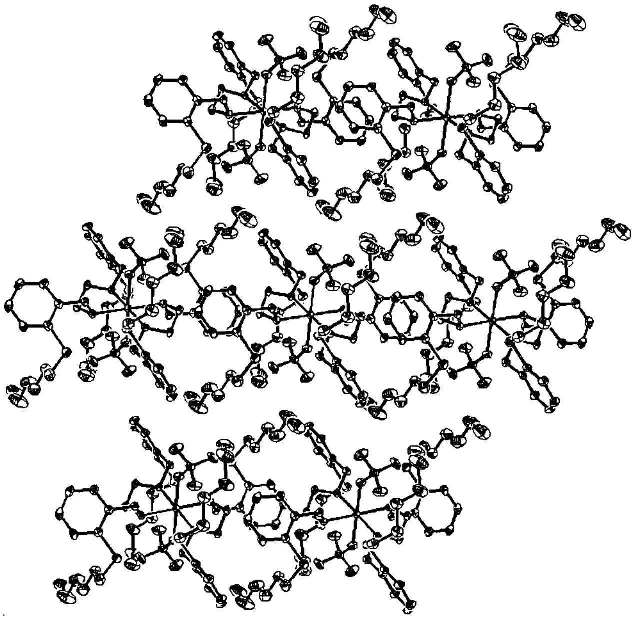

Figure 6. X-ray crystal structure of **3** showing the packing of linear arrays.

side, to pack into linear arrays, while the other two chains are disposed above and below the plane of the linear bilayer array to form a three-dimensional lattice. As with **1a**, the hexyl chains are not in an all-trans conformation. The most striking feature of the crystal structure is the absence of any binding interaction between Ni and the thioether groups. Uncoordinated donor groups such as OH, OR_2, and pyridyl have been observed in the X-ray crystal structures of related octahedral Ni(II) complexes.[17]

Summary

Paramagnetic bis(alkylthio)salen complexes **1** and **2** were prepared from NiX_2 and ligands **5** and **6**, respectively. Complexes **1** are soluble and stable in solvents such as CH_2Cl_2 and $CHCl_3$ but are unstable in coordinating solvents. Complexes **2** are also soluble and stable in solvents such as CH_2Cl_2 and $CHCl_3$; **2a** and **2b** are stable in coordinating solvents, but **2c** is unstable. Complex **3** crystallized from a solution of **2c** in EtOH. The transformation in $CHCl_3$ of **2c** into **3** in the presence of excess ligand **6** was investigated. The X-ray crystal structure of **1a** displays quadridentate binding of Ni by ligand **5a** and a bilayer packing arrangement that is typical of surfactants. The X-ray crystal structure of **3** shows an octahedral geometry at Ni with two trans ethylenediamine chelates, uncoordinated thioether groups, and a bilayer packing arrangement.

Acknowledgment. D.S.B. and D.A.J. acknowledge the Department of Energy (Contract DE-FC02-91ER) and the National Science Foundation (Grant CHE-9526188), respectively, for the support of this research.

Supporting Information Available: Tables of positional parameters, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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[17] (a) Brooker, S.; McKee, V. *J. Chem. Soc., Dalton Trans*. **1990**, 3183. (b) Bailey, N. A.; Fenton, D. E.; Kitchen, S. J.; Lilley, T. H.; Williams, M. G.; Tasker, P. A.; Leong, A. J.; Lindoy, L. F. *J. Chem. Soc., Dalton Trans.* **1991**, 627.