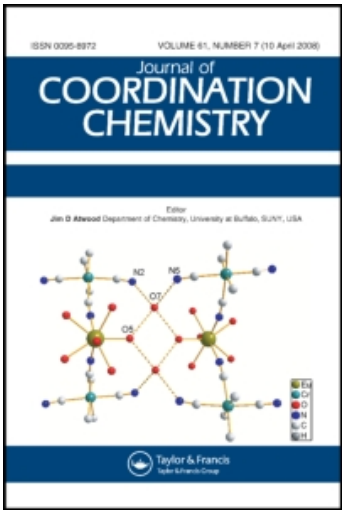

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Highly soluble Ni(II) *vic*-dioxime complexes containing branched thioether with alkyl chains of different lengths: synthesis and characterization

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To cite this Article Atilla, Devrim , Asma, Savaş and Gürek, Ayşe Gül(2009) 'Highly soluble Ni(II) *vic*-dioxime complexes containing branched thioether with alkyl chains of different lengths: synthesis and characterization', Journal of Coordination Chemistry, 62: 18, 3050 — 3059
To link to this Article: DOI: 10.1080/00958970902957097
URL: http://dx.doi.org/10.1080/00958970902957097

Journal of Coordination Chemistry
Vol. 62, No. 18, 20 September 2009, 3050–3059

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Highly soluble Ni(II) *vic*-dioxime complexes containing branched thioether with alkyl chains of different lengths: synthesis and characterization

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(*Received 18 December 2008; in final form 29 January 2009*)

vic-Dioxime ligands (LH_2) containing branched alkylthioether chains of different length have been prepared from (*E*,*E*)-dichloroglyoxime and corresponding thiol derivatives. Mononuclear Ni(II) complexes (**5a–5c**) were synthesized in ethanol by reacting $NiCl_2 \cdot 6H_2O$ with new ligands (**4a–4c**) in the presence of KOH. Branched alkylthioether moieties appended at the periphery of the oxime provide solubility for the *vic*-dioxime complexes in common organic solvents. The compounds have been characterized by elemental analyses, FT-IR and UV-Vis spectroscopy, ^{1}H- and ^{13}C-NMR, and ESI-Mass spectrometry. While **5a** and **5b** are solid at room temperature, **5c** is obtained as an orange viscous liquid. The thermal stabilities of the complexes were determined by thermogravimetric analysis.

Keywords: Oxime; Dioximes; Ni(II) complexes

1. Introduction

Coordination compounds containing *vic*-dioximes have been studied since the beginning of the 90s [1–4]. Vicinal dioximates form a stable N=C–C=N system and have three geometrical isomers of the symmetric *vic*-dioximes, *anti*-(*E*,*E*), *amphi*-(*E*,*Z*), and *syn*-(*Z*,*Z*) forms. The presence of weakly acidic hydroxyl groups and slightly basic nitrogen makes *vic*-dioximes amphoteric ligands, which form square-planar, square-pyramidal, and octahedral complexes with transition metals [5–12]. Their (*E*,*E*)-isomers coordinate transition metals *via* N,N-chelation, however, (*E*,*Z*)-isomers generally coordinate *via* N,O-chelation in tetrahedral geometry [4–8], but can also be bridging ligands *via* coordination of the imino nitrogen and deprotonated oxygen. Oligomer formation results from alternative donor centers at the oxime (N and O), where both have high affinity for metal ions and cannot coordinate simultaneously to the same metal [13–18].

The physical, chemical, and electronic properties of *vic*-dioximes can be improved by addition of functional groups. The reaction of amines or thiols with (*E*,*E*)-dichloroglyoxime or cyanogen-di-*N*-oxide yield various symmetrically substituted

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2009 Taylor & Francis
DOI: 10.1080/00958970902957097

diaminoglyoxime or dithioglyoxime derivatives. In previous papers the synthesis of *vic*-dioxime ligands and their transition metal complexes containing crown ethers [19], monoaza crown ethers [20], ferrocene groups [21], tetrathiamacrocycles [22], or N_2O_2 macrocycles [23] and dendritic groups [24] have been reported.

The low solubility of *vic*-dioxime complexes has hindered study of their structures and reactions. In order to increase solubility or gain liquid crystalline properties, additional groups such as long alkyl chains need to be added to the rigid MN_4 core [25, 26]. Improving solubility of the *vic*-dioximes increases their application potential in catalysis, sensors, and trace metal analysis [25–29].

A limited number of alkyl thia substituted *vic*-dioximes and their complexes have been reported [27–29]. In this work, we have synthesized soluble *vic*-dioximes by substituted branched thioether groups with different length alkyl chains to provide solubility for the *vic*-dioxime complexes (**5a**–**5c**). Thermal stabilities of the complexes were determined by thermogravimetric analysis. The compounds have been characterized by elemental analyses, FT-IR, UV-Vis, ESI-Mass, and ^{1}H- and ^{13}C-NMR spectra.

2. Experimental

2.1. *Measurements*

Elemental analyses were obtained from a Thermo Finnigan Flash 1112 Instrument. FT-IR spectra were recorded on a Bio-Rad FTS 175C FT-IR spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Varian 500 MHz spectrometer using TMS as an internal reference. The mass spectra were recorded on a Bruker Daltonics (Bremen, Germany) MicrOTOF mass spectrometer equipped with electro spray ionization (ESI) source and on a VG Zab Spec GC-MS spectrometer using the liquid secondary ion mass spectrometer (LSIMS). The instrument was operated in positive ion mode using an m/z range of 50–3000. The nebulizer gas flow was 0.4 bar and drying gas flow 4 L min^{-1}. Thermogravimetric analyses were carried out on a Mettler Toledo Star^e thermal analysis system at 10°C min^{-1} in a nitrogen flow (50 mL min^{-1}). Transition temperatures were determined with scan rates of 10°C min^{-1} using Mettler Toledo Star^e Thermal Analysis System/DSC 822^e System differential scanning calorimeter calibrated with indium from 3 to 4 mg samples under nitrogen.

2.2. *Synthesis of alcohol derivatives, 1a–1c*

The 15-hydroxy-13,17-dioxanonacosane **(1a)** was synthesized according to the method(s) provided in [30].

13-Hydroxy-11,15-dioxadecane (1b): Epichlorohydrine (11.5 g, 0.124 mol, 9.72 mL) was added to 100 g (0.63 mol) of *n*-decanol containing 10 g (0.25 mol) of sodium hydroxide under argon. The mixture was heated at 120°C and stirred overnight at this temperature. After cooling to room temperature, 100 mL distilled water was added to reaction mixture and the aqueous phase was extracted with 3×100 mL CH_2Cl_2. The combined organic phase was dried with Na_2SO_4 and evaporated to dryness. Compound **1b** was isolated from the oily residue with vacuum distillation (0.4 Torr, 181°C).

Yield: 35.5 g (77%), m.p.: 41°C. $C_{23}H_{48}O_3$(372). IR (NaCl cell): ν_{max} (cm^{-1}) 3224 (OH), 2924–2858 (CH_3, CH_2), 1377, 1112 (C–O–C). MS (ESI) *m*/*z* (%) : 395 (100) $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.87 (t, 6H, CH_3), 1.20–1.40 (m, 28H, CH2), 1.54–1.56 (m, 4H, CH2), 2.56 (s, 1H, OH), 3.38–3.44 (m, 8H, OCH_2), 3.92–3.96 (m, H, CH). ^{13}C-NMR ($CDCl_3$, APT) δ ppm: 14.30 (CH_3), 22.89–32.12 (CH_2), 69.66 (CH), 71.87 (OCH_2), 71.92 (OCH_2).

9-Hydroxy-7,11-dioxahexane (1c): Compound **1c** was synthesized by the same procedure used for **1b**; **1c** was isolated from the oily residue with vacuum distillation (10^{-1} Torr, 135°C). Yield: 66%, $C_{15}H_{32}O_3$ (260) IR (NaCl cell): ν_{max} (cm^{-1}) 3250 (OH), 2931–2861, (CH_3, CH_2), 1377, 1121 (C–O–C). MS (ESI) *m*/*z* (%): 283 (100) $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.86 (t, 6H, CH_3), 1.22–1.36 (m, 12H, CH_2), 1.58–1.62 (m, 4H, CH_2), 2.63 (s, 1H, OH), 3.38–3.47 (m, 8H, CH_2), 3.90–3.93 (m, 1H, CH). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.46 (CH_3), 22.84 (CH_2), 25.99 (CH_2), 29.79 (CH_2), 31.89 (CH_2), 69.66 (CH), 72.04 (OCH_2), 72.12 (OCH_2).

2.3. *Synthesis of tosyl derivatives, 2a–2c*

The 15-tosyloxy-13,17-dioxanonacosane (**2a**) was synthesized according to the literature method [31].

13-Tosyloxy-11,15-dioxadecane (2b): A solution of **1b** (32.86 g, 0.088 mol) in dry pyridine (118 ml) was cooled to 5°C and then a solution of *p*-toluene sulphonyl chloride (19.11 g, 0.1 mol) in dry pyridine (40 mL) was added with stirring under argon at a rate so that the temperature of the reaction mixture does not exceed 15°C. After stirring for 48 h at room temperature, the reaction mixture was poured into water and ice mixture, and the resulting aqueous solution was extracted with CH_2Cl_2. The organic layer was washed successively with 6 N HCl solution at 0°C and then with water, and dried with Na_2SO_4. After evaporation, oily compound was subjected to purification on a silica gel column (5 : 2/CH_2Cl_2: *n*-hexane) to obtain white solid product, m.p.: 35°C. Yield: 35.44 g (76%). $C_{30}H_{54}O_5S$ (526). IR (KBr pellet): ν_{max} (cm^{-1}) 2927–2857, (CH_3, CH_2), 1368, 1178 (SO_2); 1121 (C–O–C); 554 (C–S). MS (ESI) *m*/*z* (%): 549 (100) $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.89 (t, 6H, CH_3), 1.08–1.37 (m, 28H, CH_2), 1.45–1.60 (m, 4H, CH_2), 2.43 (s, 3H, CH_3), 3.32 (t, 4H, OCH_2), 3.57 (d, 4H, CH_2O), 4.60–4.64 (m, 1H, CH), 7.30 (d, 2H, ArCH), 7.81 (d, 2H, ArCH). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.33(CH_3), 21.82 (CH_3), 22.91–32.14 (CH_2), 69.67 (OCH_2), 71.93 (CH_2O), 80.07 (CH), 128.23 (Ar<u>C</u>–CH_3), 129.73 (ArCH), 134.40 (ArCH), 144.59 (Ar<u>C</u>–SO_2).

9-Tosyloxy-7,11-dioxahexane (2c): Compound **2c** was synthesized by the same procedure as followed for **2b**. The oily compound was subjected to purification on a silica gel column (5/4 CH_2Cl_2/*n*-hexane) to obtain colorless viscous oil. Yield: 68%. $C_{22}H_{38}O_5S$ (414). IR (NaCl cell): ν_{max} (cm^{-1}) 2931–2884 (CH_3, CH_2), 1367, 1178 (SO_2); 1121 (C–O–C); 554 (C–S). MS (ESI) *m*/*z* (%): 414 (100) $[M]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.89 (t, 6H, CH_3), 1.20–1.27 (m, 12H, CH_2), 1.42–1.46 (m, 4H, CH_2), 2.44 (s, 3H, CH_3), 3.33 (t, 4H, OCH_2), 3.57 (d, 4H, CH_2O), 4.65–4.67 (m, 1H, CH), 7.32 (d, 2H, ArCH), 7.82 (d, 2H, ArCH). ^{13}C-NMR ($CDCl_3$) δ ppm : 14.29 (CH_3), 21.84 (CH_3), 22.94–77.55 (CH_2), 80.08 (CH), 128.24 (Ar<u>C</u>–CH_3), 129.79 (ArCH), 134.31 (ArCH), 144.66 (Ar<u>C</u>–SO_2).

2.4. *Synthesis of thiol derivatives, 3a–3c*

15-Thiol-13,17-dioxanonacosane (**3a**) was synthesized according to the literature procedure [31].

13-Thiol-11,15-dioxadecane (3b): 15.1 g (0.028 mol) of **2b** and 2.74 g of thiourea (0.036 mol) were dissolved in anhydrous ethanol (130 mL), the mixture was refluxed for 48 h under stirring and then the solvent was reduced to 60 mL. To the resulting solution, a solution of sodium hydroxide 3.36 g (0.084 mol) in 73 mL of H_2O (degassed with argon) was added. The mixture was refluxed and stirred for an additional 6 h under argon. After 6 h, the reaction mixture was cooled to room temperature and acidified with dilute HCl and then extracted with diethylether (3×100 mL). The ether layers were combined, washed with water, and dried with Na_2SO_4. After evaporation, oily compound was subjected to purification over silica gel (using 5 : 3 CH_2Cl_2: *n*-hexane solvent mixture as eluent) to obtain oily product. Yield: 8.5 g (77%). $C_{23}H_{48}O_2S$ (388). IR (NaCl cell): ν_{max} (cm^{-1}) 2922–2858 (CH_3, CH_2); 2580 (S–H); 1369; 1115(C–O–C). MS (ESI) *m*/*z* (%): 411 (100) $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$) δ pm: 0.88 (t, 6H, CH_3), 1.26–1.40 (m, 28H, CH_2), 1.56–1.60 (m, 4H, CH_2), 1.89 (d, 1H, SH, D-exchangeable), 3.10–3.14 (m, 1H, CH), 3.43 (t, 4H, OCH_2), 3.54 (d, 4H, CH_2O). ^{13}C-NMR ($CDCl_3$) δ pm: 4.32 (CH_3), 22.91–32.14 (CH_2), 39.75 (CH), 71.53 (OCH_2), 72.53 (CH_2O).

9-Thiol-7,11-dioxahexane (3c): Compound **3c** was synthesized according to the procedure used for **3b**. The oily crude product was subjected to purification over silica gel column (5/3 CH_2Cl_2/*n*-hexane) to obtain oily product. Yield: 46%. $C_{15}H_{32}O_2S$ (276). IR (NaCl cell): ν_{max} (cm^{-1}) 2922–2858 (CH_3, CH_2); 2580 (S–H); 1368; 1116 (C–O–C). MS (ESI) *m*/*z* (%): 299 (100) $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$) δ pm:0.89 (t, 6H, CH_3), 1.20–1.32 (m, 12H, CH_2), 1.56–1.60 (m, 4H, CH_2), 1.89 (d, 1H, SH, D-exchangeable), 3.10–3.15 (m, 1H, CH), 3.43 (t, 4H, OCH_2), 3.53 (d, 4H, CH_2O). ^{13}C-NMR ($CDCl_3$) δ ppm: 4.25 (CH_3), 22.85–31.89 (CH_2), 39.76 (CH), 71.34 (OCH_2), 72.54 (CH_2O).

2.5. *Synthesis of* vic-*dioxime ligands (H_2L), 4a–4c*

The (*E*,*E*)-dichloroglyoxime [32] and cyanogen di-*N*-oxide [33] were prepared according to literature procedure.

Synthesis of *N*,*N*′-*bis*(13,17-dioxadodecyl-15-sulfanyl)glyoxime (4a): A total of 3.20 g (7.21 mmol) of **3a** was dissolved in CH_2Cl_2 (130 mL) under argon and cooled to -30°C. Cooled (*E*,*E*)-dichloroglyoxime (0.83 g, 5.26 mmol) in CH_2Cl_2 (80 mL) and 2.84 g (0.12 mol) Na_2CO_3 in 33 mL of H_2O to -5°C were extracted. The CH_2Cl_2 phase (cyanogen di-*N*-oxide) was added to the solution of **3a** in CH_2Cl_2. The mixture was stirred, first at -30°C for 2 h and then at room temperature overnight. The yellow solution was dried with Na_2SO_4, and then the solvent was removed. The oily crude product was dissolved in *n*-hexane and the white product crystallized at -5°C, m.p. : 39°C. Yield: 1.4 g (40%). $C_{56}H_{112}N_2O_6S_2$ (972). Found (%): C, 64.17; H, 11.30; N, 2.70; requires C, 64.08; H, 11.59; N, 2.88%; IR (KBr pellet): ν_{max} (cm^{-1}) 3252 (OH), 2934–2865 (CH_2, CH_3), 1658 (C=N), 1378, 1121 (C–O–C), 972 (N–O). MS (LSIMS) *m*/*z* (%): 974 (100) $[M+2H]^+$. ^{1}H-NMR ($CDCl_3$) δ pm:0.88 (t, 12H, CH_3), 1.26–1.54 (m, 80H, CH_2), 3.43 (t, 8H, OCH_2), 3.63 (m, 10H, CH_2O, CH), 9.36 (s, 2H, NOH,

D-exchangeable). ^{13}C-NMR ($CDCl_3$) δ pm: 14.10 (CH_3), 22.69–31.94 (CH_2), 44.99 (CH), 69.99 (OCH_2), 71.57 (CH_2O), 148.82 (C=NOH). LSIMS-MS, ^{1}H-, and ^{13}C-NMR spectra have been given as "Supplementary material".

Synthesis of *N,N′-bis*(11,15-dioxadecyl-13-sulfanyl)glyoxime (4b): Compound **4b** was synthesized according to the same procedure used for **4a**. The oily crude product was dissolved in *n*-hexane and the white product was crystallized at −5°C, m.p.: 51°C. Yield: 35%. $C_{48}H_{96}N_2O_6S_2$ (860) Found (%): C, 60.52; H, 11.28; N, 4.35; requires C, 60.34; H, 11.23; N, 4.40%; IR (KBr pellet): ν_{max} (cm^{-1}) 3250 (OH), 2932–2861 (CH_2, CH_3), 1658 (C=N), 1378, 1121 (C–O–C), 970 (N–O). MS (ESI) *m*/*z* (%): 861 (100) $[M+H]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.87 (t, 12H, CH_3), 1.22–1.41 (m, 56H, CH_2), 1.53–1.61 (m, 8H, CH_2), 3.41 (t, 8H, OCH_2), 3.62 (m, 10H, CH_2O, CH), 8.51 (s, 2H, NOH, D-exchangeable). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.32 (CH_3), 22.90–31.13 (CH_2), 45.27 (CH), 70.14 (OCH_2), 71.72 (CH_2O), 148.60 (C=NOH). ESI-MS, ^{1}H-, and ^{13}C-NMR spectra have been given as "Supplementary material".

Synthesis of *N,N′-bis*(7,11-dioxahexyl-9-sulfanyl)glyoxime (4c): Compound **4c** was synthesized according to the procedure used for **4a**. The oily crude product was subjected to purification with preparative thin layer chromatography on silica gel using 5 : 2 CH_2Cl_2/*n*-hexane solvent mixture as eluent to obtain oily product. Yield: 52%. $C_{32}H_{64}N_2O_6S_2$ (636). Found (%): C, 60.17; H, 10.30; N, 4.50; requires C, 60.34; H, 10.13; N, 4.40%; IR (NaCl cell): ν_{max} (cm^{-1}) 3250 (OH), 2922–2852 (CH_2, CH_3), 1650 (C=N), 1377, 1121 (C–O–C), 977 (N–O); MS (ESI) *m*/*z* (%): 637 (100) $[M+H]^+$, 659 (35) $[M+Na]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.89 (t, 12H, CH_3), 1.20–1.38 (m, 24H, CH_2), 1.57–1.63 (m, 8H, CH_2), 3.44 (t, 8H, OCH_2), 3.65 (m, 10H, CH_2O, CH), 8.92 (s, 2H, NOH, D-exchangeable). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.29 (CH_3), 22.87–31.93 (CH_2), 45.20 (CH), 70.18 (OCH_2), 71.44 (CH_2O), 148.47 (C=NOH). ESI-MS, ^{1}H-, and ^{13}C-NMR spectra have been given as "Supplementary material".

2.6. *Synthesis of nickel(II)* vic-*dioxime complexes [Ni(HL)$_2$], 5a–5c*

Synthesis of *bis*[*N,N′-bis*(13,17-dioxadodecyl-15-sulfanyl)glyoximato]-Ni(II) (5a): A solution of $NiCl_2 \cdot 6H_2O$ (274 mg, 0.28 mmol) in 15 mL ethanol was added dropwise to a solution of **4a** (35.64 mg, 0.15 mmol) in 30 mL ethanol with stirring at 60°C for 15 min. A distinct change in color and decrease in pH of the solution were observed. An equivalent of 0.1 M KOH in EtOH was added dropwise to maintain pH at *ca* 6 and the solution was stirred at 60°C for 3 h, then cooled to room temperature. The orange complex precipitated at room temperature, was filtered, washed with water and ethanol, and then dried in vacuum, m.p.: 49°C. Yield: 179 mg (32%). $C_{112}H_{222}N_4O_{12}S_4Ni$ (2003) Found (%): C, 67.25; H, 11.22; N, 2.70; requires C, 67.13; H, 11.17; N, 2.80%; IR (KBr pellet): ν_{max} (cm^{-1}) 3250 (OH), 2933–2862 (CH_2, CH_3), 1765 (O–H–O), 1657 (C = N), 1378, 1121 (C–O–C). MS (LSIMS) *m*/*z* (%): 2004 (100) $[M+H]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.88 (t, 24H, CH_3), 1.26–1.55 (m, 160H, CH_2), 3.42 (t, 16H, OCH_2), 3.59 (d, 16H, CH_2O), 4.41 (m, 4H, CH), 17.72 (s, 2H, OH, D-exchangeable). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.13 (CH_3), 22.71–31.96 (CH_2), 46.06 (CH), 70.47 (OCH_2), 71.55 (CH_2O), 146.27 (C=NOH). LSIMS-MS, ^{1}H-, and ^{13}C-NMR spectra have been given as "Supplementary material".

Synthesis of *bis*[*N*,*N*′-*bis*(11,15-dioxadecyl-13-sulfanyl)glyoximato]-Ni(II) (5b): Compound **5b** was synthesized by the procedure used for **5a**. The reaction mixture was cooled to room temperature and the orange complex was precipitated at 5°C, was filtered, washed with water and ethanol, then dried in vacuum, m.p.: 43°C. Yield: 44%. $C_{96}H_{190}N_4O_{12}S_4Ni$ (1779) Found (%): C, 64.80; H, 10.60; N, 3.10; requires C, 64.79; H, 10.76; N, 3.15%; IR (KBr pellet): ν_{max} (cm^{-1}) 3250 (OH), 2932–2861 (CH_2, CH_3), 1763 (O–H–O), 1658 (C=N), 1377, 1121 (C–O–C). MS (ESI) *m*/*z* (%): 1780 (100) $[M+H]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.86 (t, 24H, CH_3), 1.24–1.54 (m, 128H, CH_2), 3.34 (t, 16H, OCH_2), 3.60 (d, 16H, CH_2O), 4.39 (m, 4H, CH), 17.69 (s, 2H, OH, D-exchangeable). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.32 (CH_3), 22.90–32.14 (CH_2), 46.32 (CH), 70.69 (OCH_2), 71.72 (CH_2O), 146.47 (C=NOH). ESI-MS, ^{1}H-, and ^{13}C-NMR spectra have been given as "Supplementary material".

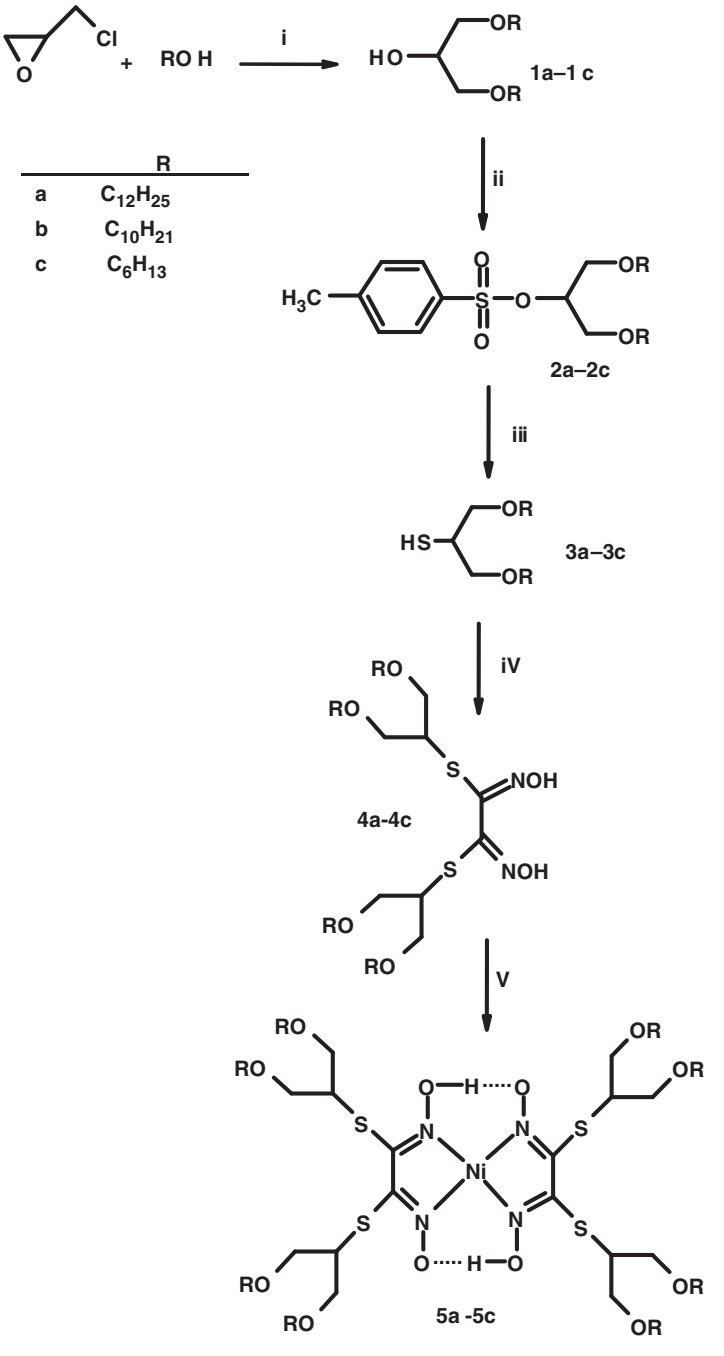
Synthesis of *bis*[*N*,*N*′-*bis*(7,11-dioxahexyl-9-sulfanyl)glyoximato]-Ni(II) (5c): Compound **5c** was synthesized according to the procedure used for **5a**. The orange complex was cooled to −5°C and the ethanol removed by decantation. The oily product was washed with cold water and cold ethanol, and then dried in vacuum. The orange complex is oily at room temperature. Yield: 28%. $C_{64}H_{126}N_4O_{12}S_4Ni$ (1329). Found (%): C, 57.87; H, 9.30; N, 4.10; requires C, 57.77; H, 9.54; N, 4.21%; IR (NaCl): ν_{max} (cm^{-1}) 3250 (OH), 2932–2861 (CH_2, CH_3), 1763 (O–H–O), 1658 (C=N), 1377, 1121 (C–O–C). MS (ESI) *m*/*z* (%): 1330 (100) $[M+H]^+$. ^{1}H-NMR ($CDCl_3$) δ ppm: 0.86 (t, 24H, CH_3), 1.26–1.53 (m, 64H, CH_2), 3.39 (t, 16H, OCH_2), 3.59 (d, 16H, CH_2O), 4.38 (m, 4H, CH), 17.69 (s, 2H, OH, D-exchangeable). ^{13}C-NMR ($CDCl_3$) δ ppm: 14.25 (CH_3), 22.82–31.87 (CH_2), 46.29 (CH), 70.68 (OCH_2), 71.66 (CH_2O), 146.43 (C=NOH). ESI-MS, ^{1}H-, and ^{13}C-NMR spectra have been given as "Supplementary material".

3. Results and discussion

3.1. *Synthesis and characterization*

The routes for the syntheses are summarized in scheme 1. *vic*-Dioxime ligands were synthesized in four steps. The first step is the synthesis of alcohol derivatives (**1a**–**1c**) starting from epichlorohydrine and corresponding alcohols. The tosyl derivatives (**2a**–**2c**) were obtained after tosylation of OH of **1a**–**1c** and these tosyl derivatives were reacted with thiourea to obtain thiol derivatives (**3a**–**3c**). In the fourth step, the ligands (**4a**–**4c**) were synthesized from reaction of corresponding branched thioether (**3a**–**3c**) and cyanogen di-*N*-oxide. The bulky branched alkyl chains of these new ligands as well as hindering interaction of the metal ion increase the lipophilicity of the products, enhancing their solubility in organic solvents such as CH_2Cl_2, THF, ethyl acetate, and *n*-hexane.

The Ni(II) complexes (**5a**–**5c**) were synthesized in ethanol by reacting $NiCl_2 \cdot 6H_2O$ with **4a**–**4c** in the presence of KOH. The melting points of **5a** and **5b** are at 49 and 43°C, respectively, and **5c** is an orange viscous liquid at room temperature. Therefore, we could not obtain single crystals suitable for X-ray crystallographic studies. The phase transition behavior of **5c** was studied by differential scanning calorimetry (DSC) to determine the transition temperature of **5c** from liquid phase to solid phase, but we did



Scheme 1. Synthesis of **1a–1c**, **2a–2c**, **3a–3c**, **4a–4c** and **5a–5c**. (i) NaOH; (ii) dry pyridine, p-toluenesulphonylchloride; (iii) dry ethanol, thiourea; (iv) (*E*,*E*)-dichloroglyoxime, CH_2Cl_2, Na_2CO_3, distilled water; (v) ethanol, $NiCl_2 \cdot 6H_2O$, KOH.

not obtain any peak related to the solid transition from −50 to 50°C, suggesting that **5c** is a liquid in a wide temperature range including −50°C.

Thermal properties of **5a**, **5b**, and **5c** were investigated from 25 to 1000°C with a heating rate of 10°C min^{-1}. The TGA curve of **5b** under a nitrogen atmosphere is provided in "Supplementary material". The complex **5b** shows no mass loss up to 210°C, indicating the absence of water or other adsorptive molecules. The first decomposition stage occurred in the range 210–280°C, assigned to loss of alkyl chains $[(C_5H_{11})_8]$ with a weight loss of 32.76% (calculated 31.94%); the second decomposition occurred from 284 to 358°C, assigned to the loss of $[SCH(CH_2OC_{12}H_{25})_2]$, 84.58% (calculated 87.21%) for **5b**. All the complexes decompose in two steps at similar temperature ranges. When compared with the initial decomposition temperature of the complexes with Ni(II) dimethylglyoxime, thermal stability of Ni(II) dimethylglyoxime is higher than **5a**, **5b**, and **5c** complexes [34].

The new compounds have been characterized by elemental analyses, ESI-Mass spectrometry, UV-Vis, FT-IR, and ^{1}H- and ^{13}C-NMR spectroscopy, and the results are consistent with the structures given in the section 2. ESI-MS and LSIMS-MS, ^{1}H-, and ^{13}C-NMR spectra of compound **4a**–**4c** and **5a**–**5c** are given as "Supplementary material".

The mass spectra of **4a**–**4c** gave clear molecular ion peaks at m/z 974 $[M+H]^+$ for **4a**; at m/z 861 $[M+H]^+$ for **4b**; and at m/z 637 $[M+H]^+$ for **4c**. In the mass spectrum of **4c** the $[M+Na]^+$ peak was observed at m/z 659.

In IR spectra, the oxime derivatives (**4a**–**4c**) showed characteristic stretching vibrations due to O–H, C=N, and N–O stretches at 3250, 1650–1660, and 970–977 cm^{-1} in addition to characteristic aliphatic CH stretches and C–O–C bands of branched thioether substituents. After formation of the oximes, the SH bands around 2580 cm^{-1} disappeared. These results indicate formations of *vic*-dioximes. In the ^{1}H-NMR spectra, deuterium exchangeable protons of C=N–OH show a single chemical shift (at 9.36 ppm for **4a**; at 8.51 ppm for **4b**, and at 8.92 ppm for **4c**), indicating an (*E*,*E*)-structure for the *vic*-dioxime ligands [35]. In ^{13}C-NMR spectra, quaternary carbon signals of the hydroxyimino carbon (C=N–O) appeared around 148 ppm. The other chemical shifts observed in the ^{1}H- and ^{13}C-NMR spectra for **4a**–**4c** were very similar to those found in related thiol derivatives (**3a**–**3c**), as detailed in section 2.

Ni(II) complexes **5a**–**5c** gave molecular ion peaks, $[M+H]^+$, at m/z 2004 for **5a**; at m/z 1780 for **5b**; and at 1330 m/z for **5c**. All the complexes have similar IR spectra with broad and weak OH bands around 3250 cm^{-1} and a weak band around 1765 cm^{-1} attributed to intramolecular hydrogen bonding [36]. C=N and N–O stretches of *vic*-dioximes were also observed. In the ^{1}H-NMR spectra of **5a**–**5c** the chemical shifts of free OH (around 9 ppm) were not observed, however, resonances of intramolecular OH···O protons were observed around 17.70 ppm and disappeared with D_2O exchange. In the ^{13}C-NMR spectra, quaternary carbon signals of the hydroxyimino carbon (C=N–O) appeared at 146 ppm. In the FT-IR, ^{1}H-NMR, and ^{13}C-NMR spectra, signals of branched thioether substituents were observed at expected locations (section 2).

The electronic absorption of **4a**–**4c** and **5a**–**5c** obtained in chloroform are given in table 1. The electronic absorption spectra of **4a** and **5a** are depicted in figure 1. UV-Vis spectra of the complexes showed four absorption peaks between 242 and 418 nm, due to both the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition of C=N and charge-transfer

Table 1. Electronic spectral data of the *vic*-dioximes and their Ni(II) complexes in chloroform.

Compound	λ_{max}(nm) [$\varepsilon(10^{-4}\,dm^3\,mol^{-1}\,cm^{-1})$]
4a	253 (0.67), 278 (1.18), 325 (0.52)
4b	253 (0.69), 279 (1.19), 324 (0.62)
4c	254 (0.72), 278 (1.21), 366 (0.58)
5a	242 (2.18), 275 (2.34), 375 (1.02), 418 (1.04)
5b	241 (2.210), 276 (2.350), 374 (1.030), 418 (1.06)
5c	242 (2.13), 275 (2.40), 374 (1.06), 417 (1.09)

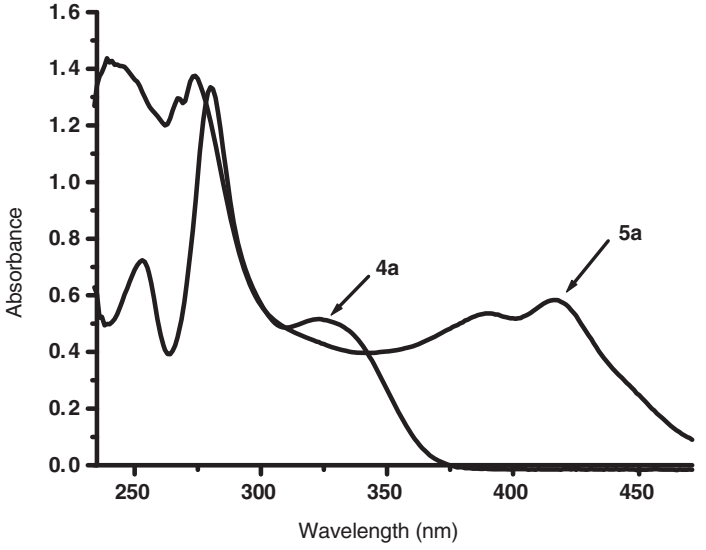


Figure 1. Absorption spectra of **4a** and **5a** in chloroform.

transition arising from π electron interactions from metal to ligand or ligand to metal [27, 37]. The absorption bands at 242 and 275 nm can be attributed to $\pi \rightarrow \pi^*$ transitions in the azomethine (–C=N) group of the oxime. The band at 375 is probably $n \rightarrow \pi^*$ transition. The absorption bands at around 418 nm are assigned to $M \rightarrow L$ charge transfer (MLCT) or $L \rightarrow M$ charge transfer (LMCT). On complex formation, the electronic spectra of **5a** exhibited significantly different absorption bands compared to the ligand **4a**. No peak belonging to d–d transitions can be observed.

4. Conclusions

We have prepared new vicinal dioximes (LH_2) and their mononuclear complexes. Spectroscopic studies confirmed the structure of $[Ni(LH)_2]$. Addition of alkyl groups to the oxime core decreases melting point and improves solubility of the complexes. All the complexes are soluble in common organic solvents. Compound **4c** and its Ni(II) complex, **5c**, are liquids in a wide temperature range, while other oxime derivatives and their complexes are solid at room temperature. Thermal results show that **5a**–**5c** are stable up to 210°C.

Acknowledgements

This work was supported by the Research Fund of Gebze Institute of Technology (Project No. 2007-A-02). The authors thank Dr Fatma Yüksel for fruitful discussions.

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