



Research Article

A New (E, E)-dioxime with mono nuclear nickel (II) complex containing diazatetrathiodioxa macrobicyclic moieties

Gülsev Dilber^{1*}, Halit Kantekin²¹Macka Vocational School, Karadeniz Technical University, 61750, Macka, Trabzon, Turkey²Department of Chemistry, Karadeniz Technical University, 61080, Trabzon, Turkey**ABSTRACT**

Keywords:
vic-Dioximes,
transition metal,
macrobicyclic compound,
mononuclear complex,
cyanogen-di-N-oxid

In this study, a novel (E, E)-dioxime containing a diazatetrathiodioxa macrobicyclic moieties (19E, 20E)-6,7,14,15,18,21,24,25-oktahidro-13,26-(ethanothioethano-thioethano)dibenzo[14,15:8,9]-[1,4,10,13,7,16]dioxadithiadiazacyclooctadecino[2,3-g]quinoxaline-19,20,27,34-tetrono 19,20-dioxime (H₂L) has been obtained from the reaction of cyanogen-di-N-oxide with 2,3-diamino-6,7,14,15,22,23-hexahidro-8,21-(ethanothioethanothioethano)tribenzo [b,h,n] [1,4,10,13,7,16]dioxadithiadiazacyclooctadecine-25,32-dione (8), which was prepared by the reduction of 2,3-dinitro-6,7,14,15,22,23-hexahidro-8,21-(ethanothioethanothioethano)-tribenzo [b,h,n] [1,4,10,13,7,16] dioxodithiadiazacyclooctadecine-25,32-dione (7). The macrobicyclic (7) was synthesized by the condensation reaction of compound (5) with compound (6) in the presence of the Na₂CO₃ under an argon atmosphere in the refluxing acetonitrile. Mononuclear complex (11) was synthesized with metal:ligand ratio 1:2 of this compound as a result of interaction of the vic-dioxime (H₂L) with NiCl₂.6H₂O. The structures of the new compounds were elucidated by the interpretation of MS spectral data elemental analysis, ¹H- and ¹³C-NMR, IR and MS spectral data.

TR

Diazatetratiyadioksa makrobisiklik grup içeren yeni (E, E) -dioksim ve mono nükleer nikel (II) kompleksi

Ö Z E T

Anahtar Kelimeler:
vic-Dioksim,
geçiş metali,
makrobisiklik bileşik
mononükleer kompleks
siyanojen-di-N-oksit

2,3-dinitro-6,7,14,15,22,23-hegzahidro-8,21-(etanotiyoetanotiyoetano)-tribenzo[b,h,n][1,4,10,13,7,16] dioksoditiyadiazasiklooktadesin-25,32-dion (7) bileşiğinin indirgenmesi ile elde edilen 2,3-diamino-6,7,14,15,22,23-hegzahidro-8,21-(ethanothioethanothioethano)tribenzo[b,h,n][1,4,10,13,7,16]dioksaditiyadiazasiklooktadesin-25,32-dion (8) bileşiği ve siyanojen-di-N-oksit'in reaksiyonundan, diazatetratiyadioksa makrobisiklik grup içeren yeni bir (E,E)-dioksim (19E, 20E)-6,7,14,15,18,21,24,25-oktahidro-13,26-(etanotiyoetanotiyoetano)dibenzo[14,15:8,9][1,4,10,13,7,16] dioksaditiyadiazasiklooktade-sino[2,3-g]kinoksalin- 19,20,27,34-tetrono 19,20-dioksim (H₂L) sentezlendi. Makrobisiklik (7) bileşiği, Na₂CO₃ varlığında, argon atmosferinde riflaks olan asetonitril içerisinde (5) ve (6) bileşiklerinin kondenzasyonu sonucu sentezlendi. vic-Dioksim (H₂L) ve NiCl₂.6H₂O reaksiyonundan, metal:ligand oranı 1:2 olan mononuclear kompleks (11) sentezlendi. Yeni bileşiklerin yapısı elementel analiz, ¹H- and ¹³C-NMR, IR and MS spektral sonuçlar ile aydınlatıldı.

1. Introduction

Coordination compounds, which include vic-dioxime compounds, have been studied since the last century. The complexes of transition metals and oxime ligands have been discussed in detail in many reviews [1-6]. Oxime ligands are amphoteric because they have an acidic hydroxyl group and slightly basic nitrogen atoms [7]. It is known that dioxime ligands binding metal ions as neutral dioximes [8, 9]. vic-Dioximes have the field of use in various technology areas, such as medicine [10-12], catalysis [13,14], electro optical sensors [15], quid crystals [16], and trace metal analysis [17]. Some oximes are used in technology for different intentions in organic, inorganic, bioinorganic pigment, analytical, dyes and medical chemistry [18, 19]. Because of their numerous advantages, vic-dioxime complexes

of transition metals have attracted much interest [20].

The extraordinary stability and matchless electronic features of these complexes can be ascribed to their planar form, which is strengthened by hydrogen bonding [21].

vic-Dioximes bearing macrobicyclic groups and their alkaline earth metal and transition metal compound have been lately prepared [22]. They have the ability to bind transition metal or alkaline earth metal properties, which is an amazing manner of these complexes [23]. Furthermore, metal complexes of dioxime compounds bearing a great number of macrocycle groups of different size with nitrogen, sulfur and oxygen as donor atom, have been comprehensively researched [24, 25].

We have previously achieved including a dioxadithiadiaz macrobicyclic moiety (H₂L) [26]. In studying, we have worked up a new macrobicyclic vic-dioxime which contains diazatetrathiadiaz macrobicyclic moiety (10).

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Citation: Dilber, G., Kantekin, H., A New (E, E)-dioxime with mono nuclear nickel (II) complex containing diazatetrathiodioxa macrobicyclic moieties (Diazatetratiyadioksa makrobisiklik grup içeren yeni (E, E) -dioksim ve mono nükleer nikel (II) kompleksi), *Karadeniz Chem. Sci. Tech.* 2018, 03, XX-XX.

DOI:
ISSN: 2636-8560

2. Experimental

2.1. General

The IR spectral data were obtained on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. ^1H and ^{13}C -NMR spectral data were obtained on a Varian Mercury 200 MHz spectrometer in CDCl_3 , DMSO, and chemical shifts were measured (δ) relative to Me_4Si as internal standard. Mass spectra were recorded on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analyses were determined by a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer, respectively. Melting points were measured on an electrothermal apparatus and are uncorrected.

2.2. Materials and methods

1,2-Di (o-aminophenoxy) ethanedithiol (1) [27] and 1,2-dinitro-4,5-bis(2-iodoethoxy)benzene (6) [28] was obtained according to given literature. All solvents were dried and purified by traditional methods [29].

2.2.1 Synthesis of compound *N,N'*-[ethane-1,2-diylbis(thio-2,1-phenylene)]bis(2-chloroacetamide) (3)

1,2-Di (o-aminophenoxy) ethanedithiol (1) (3g, 10.86mmol) was dissolved in 51 mL of dichloromethane. A solution of acetylchloride (2) (2.21 mL, 27.17mmol) in 10 mL of dichloromethane was dropped on the prepared solution for 1 h at -5°C under Ar atmosphere. The color that was rose pink reddish before dropping was obtained purple. The reaction content was maintained at room temperature for one day. After then rude product filtered and purple precipitate was achieved, washed with water, ethanol, and diethyl ether and crystallized from ethanol, dried under vacuo. Yield: 2,53g (55 %) mp:170 -171 $^\circ\text{C}$. (Found: C, 50.51; H, 4.34; N, 6.58; S, 14.77; $\text{C}_{18}\text{H}_{18}\text{N}_2\text{O}_2\text{S}_2\text{Cl}_2$ calcd.: C, 50.35; H, 4.23; N, 6.52; S, 14.93 %). MS (EI) (m/z): 429.18 $[\text{M}]^+$. IR (KBr pellet), (cm^{-1}): 3309 (N-H), 3065 (Ar-H), 2957 (Alif.C-H), 1678 (C=O), 1584,1538 (C=C), 1438, 1404, 1308, 1262, 763, 730, ^1H -NMR (DMSO- d_6), (δ : ppm): 9.64 (s, 2H, NH), 8.42 (d, 2H, Ar-H), 7.47 (d, 2H, Ar-H), 7.34(t, 2H, Ar-H), 7.12(t, 2H, Ar-H), 4.20 (s, 4H, O=CCH₂), 2.92 (s, 4H, CH₂-S). ^{13}C -NMR (DMSO- d_6), (δ : ppm): 163.15, 140.34, 130.69, 130.40, 125.04, 120.04, 77.68, 43.41, 34.99.

2.2.2. Synthesis of compound

9,10,20,21-tetrahydro-5H,12H-dibento[e,q][1,4,10,13,7,16]-tetrathiadiazacyclooctadecine-6,13(7H,14H)-dione (5)

N,N'-[ethane-1,2-diylbis(thio-2,1-phenylene)]bis(2-chloroacetamide) (3) (2g, 4.66mmol) was dissolved in 70 mL of dry acetonitrile and 20 mL of dry DMF. Anhydrous Na_2CO_3 (2.4g, 18.4 mmol) was added to a stirring mixture under nitrogen atmosphere. After a while, etan-1,2-dithiol (2) (0.4g, 4.6mmol) in 10 mL of dry CH_3CN was dropped on the prepared solution for 1h at room conditions. The reaction was continued for 72 h. The white precipitate was filtered. Then it was washed with water ethanol then diethyl ether. It was dried under vacuo. Yield: 1.3g (65%) mp: 284-286 $^\circ\text{C}$. (Found: C, 53.33; H, 4.86; N, 6.35; S, 28.57; $\text{C}_{20}\text{H}_{22}\text{N}_2\text{O}_2\text{S}_4$ calcd.:C, 53.31; H, 4.92; N, 6.22; S, 28.46 %). MS (EI) (m/z): 473 $[\text{M}^+\text{Na}]^+$. IR (KBr pellet), (cm^{-1}): 3263 (N-H), 3030 (Ar-H), 2924 (Alif.C-H), 1681 (C=O), 1577, 1515 (C=C), 1433, 1296, 1162, 760, 596. , ^1H -NMR (DMSO- d_6), (δ : ppm): 9.68 (s, 2H, NH), 7.60 (d, 2H, Ar-H), 7.53(d, 2H, Ar-H), 7.32(t, 2H, Ar-H) , 7.19(t, 2H, Ar-H) , 3.68 (s, 4H, O=CCH₂), 2.98 (s, 4H, CH₂-S), 2.42 (t, 4H, CH₂-S), (t, 4H, CH₂-S). ^{13}C -NMR (DMSO- d_6), (δ : ppm):161.12, 138.30, 134.69, 130.20, 124.04, 119.10, 78.50, 41.44, 32.92, 20.70.

2.2.3. Synthesis of compound *2,3-dinitro-6,7,14,15,22,23-hexahydro-8,21-(ethanothio-ethanothioethano)tribenzo[b,h,n][1,4,10,13,7,16]dioxodithiadiazacyclooctadecine-25,32dione (7)*

9,10,20,21-tetrahydro-5H,12H-dibento[e,q][1,4,10,13,7,16]tetrathiadiazacyclooctadecine-6,13(7H,14H)-dione (5) (1g, 2.21

mmol) was dissolved in dry acetonitrile (100 mL) and dry DMF (60 mL) containing anhydrous Na_2CO_3 (0.24 g, 2.26 mmol) under N_2 atmosphere. After stirring for 30 min, 1, 2-dinitro-4,5-bis(2-iodoethoxy)benzene (6) (1.12 g, 2.21 mmol) in dry acetonitrile (30 mL) was added to the reaction medium. This solution was continued with stirring at 60°C for 168 h. Then, the mixture was filtered and washed with acetonitrile, and reaction solvent was diluted to dryness under reduced pressure. The obtained product was crystallized from EtOH to yield yellow crystals. Yield: 0.9g, (60 %) mp: 295-297 $^\circ\text{C}$. (Found: C, 51.43; H, 4.50; N, 8.07; S, 18.24; $\text{C}_{30}\text{H}_{30}\text{N}_4\text{O}_8\text{S}_4$ calcd.: C, 51.27; H, 4.30; N, 7.97 ; S, 18.25 %). MS (EI), (m/z): 704.83 $[\text{M}^{+2}]^+$. IR (KBr pellet), (cm^{-1}): 3075 (Ar-H), 2994-2917 (C-H), 1670 (C=O), 1519-1320 (Asm. N-O), 1270-1204 (Ar-O-CH₂), 968 (N-O). ^1H -NMR (DMSO- d_6), (δ : ppm): 7.52 (s, 2H, Ar-H), 7.20 (t, 2H, Ar-H), 7.01 (t, 2H, Ar-H), 6.90 (d, 2H, Ar-H), 6.85 (d, 2H, Ar-H), 3.98 (t, 4H, CH₂-N), 3.60 (t, 4H, CH₂-O), 3.25 (s, 4H, CH₂-S), 3.10 (t, 4H, CH₂-S), 2.69 (S, 4H, CH₂-S). ^{13}C -NMR (DMSO- d_6), (δ : ppm): 161.27, 147.86, 142.86, 130.43, 129.25, 126.07, 125.42, 122.72, 115.42, 106.72, 72.42, 51.72, 46.92, 38.08, 34.96.

2.2.4 Synthesis of compound *2,3-diamino-6,7,14,15,22,23-hexahydro-8,21-(ethanothio-ethanothioethano)tribenzo[b,h,n][1,4,10,13,7,16]dioxadithiadiazacyclooctadecine-25,32-dione (8)*

2,3-dinitro-6,7,14,15,22,23-hexahydro-8,21-(ethanothioethanothioethano)tribenzo[b,h,n][1,4,10,13,7,16]dioxodithiadiazacyclooctadecine-25,32dione (7) (0.8 g, 1.24 mmol) was dissolved in dioxane (100 mL) by heating under a nitrogen atmosphere at the reflux temperature. Then the solution was cooled to 30°C . The (10 %) palladium activated charcoal (0,16 g) was added to solution at this at this temperature. Then 0,8 mL of hydrazine hydrate (%100) dropped in one hour. The reaction was continued with stirring at the reflux temperature for 12 h and then filtered from Celite and washed with dioxane. The solvent was removed under reduced pressure. The unprocessed result was crystallized from ethanol. Light yellow yield was obtained after crystallization. Yield 0.5g (70%) mp: 230-232 $^\circ\text{C}$. (Found: C, 56.25; H, 5.57; N, 8.91; S, 20.11; $\text{C}_{30}\text{H}_{34}\text{N}_6\text{O}_4\text{S}_4$ calcd.: C, 56.05; H, 5.33; N, 8.72 ; S, 19.95 %). MS (EI), (m/z): 665.86 $[\text{M}^+\text{Na}]^+$. IR (KBr pellet), (cm^{-1}): 3298 (NH₂), 3092 (Ar-H), 2924-2840 (C-H), 1648 (C=O), 1599, 1512, 1455 (C=C), 1269-1170 (Ar-O-CH₂), 1070. ^1H -NMR (DMSO- d_6), (δ : ppm): 7.35 (s, 2H, Ar-H), 7.16 (t, 2H, Ar-H), 7.06 (t, 2H, Ar-H), 6.90(d, 2H, Ar-H), 6.87 (d, 2H, Ar-H), 5.20 (br, 4H, NH₂), 3.98 (t, 4H, CH₂-O), 3.50 (t, 4H, CH₂-N), 3.25 (s, 4H, CH₂-S), 3.12 (t, 4H, CH₂-S), 2.69(s, 4H, CH₂-S). ^{13}C -NMR (DMSO- d_6), (δ : ppm): 161.40, 147.86, 142.86, 130.43, 129.25, 126.07, 125.42, 122.72, 115.42, 106.72, 72.42, 51.72, 46.92, 38.08, 34.96.

2.2.5. Synthesis of compound *(19E,20E)-6,7,14,15,18,21,24,25-oktahydro-13,26-(ethanothioethanothioethano)dibenzo [14,15:8,9] [1,4,10,13,7,16]dioxadithiadiazacyclooctadecine-2,3-g]quinoxaline-19,20,27,34-tetrone 19,20-dioxime (H₂L), (10)*

A solution of cyanogen-di-N-oxide in dichloromethane (25 mL) prepared (E, E)-dichloroglyoxime (0.14 g, 0.62 mmol) in dichloromethane (25 mL) with an aqueous solution of Na_2CO_3 0.5 M, 25 mL in dichloromethane (25mL), in refigated bath at -10°C , was added the solution of (8) (0.42 g, 0.62 mmol) in dichloromethane (25 mL) at the same temperature. The reaction was stirred for 12 h at -10°C and the reaction content was left to warm into the room temperature, then the reaction solvent was diluted to 25 mL under reduced pressure. It was cooled down to 15°C in the fridge for one day. Pale brown solid yield was filtered off and washed with cold EtOH. The resulting product was crystallized from EtOH. Yield 0.30 g (65%) mp > 300 $^\circ\text{C}$. (Found: C, 52.59; H, 4.65; N, 11.82; S, 17.73; $\text{C}_{32}\text{H}_{34}\text{N}_6\text{O}_6\text{S}_4$ calcd.: C, 52.88; H, 4.71; N, 11.56 ; S, 17.64 %). MS (EI), (m/z): 727.14 $[\text{M}^{+1}]^+$. IR (KBr pellet), (cm^{-1}): 3368 (O-H), 3276 (N-H), 3087(Ar-H), 2924- 2868 (C-H), 1681 (C=O),

1625 (C=N), 1610 (N-H), 1516, 1456 (C=C), 1228 (Ar-O-CH₂), 941 (N-O). ¹H-NMR (DMSO-d₆), (δ: ppm): 9.88 (s, 2H, OH), 8.65 (s, 2H, NH), 7.75 (s, 2H, Ar-H), 7.30 (t, 2H, Ar-H), 7.23 (t, 2H, Ar-H), 6.93 (d, 2H, Ar-H), 6.87 (d, 2H, Ar-H), 3.95 (t, 4H, CH₂-O), 3.54 (t, 4H, CH₂-N), 3.26 (s, 4H, CH₂-S), 2.77 (t, 4H, CH₂-S), 2.66 (s, 4H, CH₂-S). ¹³C-NMR (DMSO-d₆), (δ: ppm): 161.77, 153.86, 147.6, 135.47, 129.35, 128.37, 124.32, 123.22, 118.49, 107.02, 75.42, 55.42, 46.90, 37.58, 34.46, 32.68.

2.2.6. Synthesis of compound [Ni(HL)₂] (11)

A solution of NiCl₂·6H₂O (0.032 g, 0.13 mmol) in EtOH (10 mL) was added to a solution of (10) (0.2 g, 0.27 mmol) in EtOH (20 mL) with stirring at 60 °C. The color of the solution turn into reddish brown and a decline in pH was monitored. Therefore, the pH of mixture was adjusted about 4.50 by addition of triethylamine (0.1 M) in ethanol. The reaction was resumed with stirring at 60 °C for 2 h. After the reaction mixture was left to warm into the room temperature, the mixture was filtered and the crude product was washed with EtOH and then crystallized from ethanol, dried in vacuo. Yield 0.12g (60%) mp >300 °C. (Found: C, 50.82; H, 4.26; N, 11.40; S, 16.78; C₆₄H₆₆N₁₂O₁₂S₈ calcd.: C, 50.94; H, 4.40; N, 11.13 ; S, 17.00 %). MS (EI), (m/z): 1508.87 [M]⁺. IR (KBr pellet), (cm⁻¹): 3338 (N-H), 3082 (Ar-H), 2924-2853 (C-H), 1737 (O-H×××O), 1648 (C=O), 1614 (C=N), 1264 (Ar-O-CH₂), 950 (N-O). ¹H-NMR (DMSO-d₆), (δ: ppm): 17.29 (s, 2H, O-H×××O), 8.35 (s, 4H, NH), 7.60 (s, 4H, Ar-H), 7.33 (t, 4H, Ar-H), 7.21 (t, 4H, Ar-H), 6.95 (d, 4H, Ar-H), 6.86 (d, 4H, Ar-H), 3.93 (m, 8H, CH₂-O), 3.51 (t, 8H, CH₂-N), 3.24 (s, 8H, CH₂-S), 2.72 (t, 8H, CH₂-S), 2.60 (s, 8H, CH₂-S). ¹³C-NMR (DMSO-d₆), (δ: ppm): 168.22, 150.86, 145.86, 134.47, 129.13, 128.07, 124.32, 123.72, 117.42, 103.36, 74.32, 59.22, 42.92, 36.28, 34.21, 32.68.

3. Result and discussion

The synthesis of (E,E)-dioxime (H₂L) with its mononuclear complex were designed and synthesized as depicted in Scheme 1 and Fig. 1.

Compound (3) was obtained by the reaction of (1) with (2) under a nitrogen atmosphere at -5 °C in a yield (55%). The chemical shift because of NH protons was monitored at δ = 9.64 in the ¹H-NMR spectrum of (3). The deuterium exchange characteristics of NH protons also emerged during the formation of the designed complex. ¹³C-NMR spectral data were confirmed the proposed structures of the compounds (3). The chemical shift for C=O were watched at 163.15 ppm. In the FT-IR spectra of (3), the characteristic signal associated with to NH and C=O groups, were appeared at 3309 and 1672 cm⁻¹, respectively. The mass spectral data of (3) showed a molecular ion peak (EI) at m/z = 429.18 [M]⁺, which confirmed the proposed structure.

Compound (5) was obtained by the reaction of (3) with (4) under N₂ atmosphere in yield 65%. ¹H-NMR spectrum of (5) gave the signal because of NH, CH₂CH₂-S protons at δ = 9.68 and 2.98 ppm, respectively. Also, NH proton signals disappeared after interaction with D₂O. The proton-decoupled ¹³C-NMR displayed compatible spectral data for the structure of the compound (5). The chemical shifts for CH₂CH₂-S and C=O were monitored at δ= 32.92 and 161.15 ppm respectively. In the IR spectrum of (5), the typical stretching vibrations, relating to NH and C=O groups, were watched at 3263 and 1681 cm⁻¹, respectively. The mass spectral data of (5) demonstrated a molecular ion peak (EI) at m/z = 473 [M⁺Na]⁺, which verified the proposed structure.

The macrobicyclic compound (7) was achieved in acetonitrile by the reaction of (5) with (6) in the presence of Na₂CO₃ in a N₂ atmosphere at the reflux temperature. Macrobicyclization gave the macrobicyclic compound (7) in moderate yield 60%. In the ¹H-NMR spectrum of (7), the signals of Ar-H and CH₂CH₂-S protons were emerged at δ=7.52, 7.20, 7.01 and 3.25 ppm, respectively. ¹³C-NMR spectral data of (7) exhibits signals for CH₂CH₂-S and C=O at δ = 34.96 and 167.86 ppm respectively. The data obtained from the ¹H-NMR and ¹³C-NMR spectra of the novel compounds were

provided the characteristic chemical shifts for compounds. In the IR spectrum of compound (7), the typical signal belonging to C=O and NO₂ groups, were watched at 1670 and 1519-1320 cm⁻¹, respectively. The mass spectrum (EI) of (7) exhibits a molecular ion peak (EI) at m/z = 704.83 [M⁺Na]⁺, which confirmed the proposed structure.

Reduction of the dinitro-substituted macrobicyclic (7) using 10% palladium-activated charcoal and hydrazine hydrate (100%) in hot dioxane [30] worked out the macrobicyclic compound (8) in yield 70 %. In the ¹H-NMR spectrum of (8), the signal due to Ar-H, NH₂ and CH₂CH₂-S protons were obtained at δ = 7.16, 6.90, 76.87, 5.20 and 3.25 ppm, respectively. ¹³C-NMR spectral data of 8 were supported the typical chemical shifts for this compound. The signal belonging C=O, O-CH₂ and CH₂CH₂-S were emerged at δ = 161.40, 38.08 and 34.96 ppm respectively. In the FT-IR spectrum of compound (8), the typical signals due to NH₂ and C=O groups were monitored at 3298 and 1648 cm⁻¹, respectively. The mass spectrum (EI) of (8) exhibits a molecular ion peak (EI) at m/z = 665.86 [M⁺Na]⁺, which confirmed structure of the intended compound.

(E, E)-dioxime (10) successfully achieved the reaction of the aromatic diamine compound (8) and cyanogen-di-N-oxide (9) in dichloromethane and N₂ media at -10 °C with 65 % yield. In the ¹H-NMR spectrum of this ligand, the chemical shifts due to OH, NH and CH₂CH₂-S protons were observed at δ = 9.88, 8.65 and 2.90 ppm, respectively. Also, OH and NH proton signals disappeared after interaction with D₂O. The chemical shifts due to =N-OH protons were maintained in the ¹H-NMR spectral data. The equal chemical shifts because of hydroxyimino groups verify the (E, E)-form of vic-dioxime [31-33]. In the ¹³C-NMR spectrum, two signal due to carbonyl and azomethine groups are showed at δ= 161.77 and 147.86 ppm, respectively. The signal belonging the azomethine group carbon atom at δ= 147.86 is the most prominent feature for oxime ligands and support the (E, E)-form of the vic-dioxime [34]. In the FT-IR spectra of compound (10), the signal due to OH, NH, C=O and C=N groups appeared at 3368, 3276, 1681 and 1625 cm⁻¹, respectively. The mass spectrum (EI) of oxime ligand (10) exhibited a molecular ion peak at m/z = 727.14 [M⁺]⁺, which supported the proposed structure.

vic-Dioxime Ni(II) complex was accomplished in 60 % yield by the addition of a solution of Ni (II) salt, triethylamine in ethanol and oxime ligand dissolved in hot ethanol. In the ¹H-NMR spectrum data of (11), the signal due to OH protons belonging H₂L ligand vanished after the formation of (E, E)-dioxime Ni (II) complex. On the other hand, a new signal appeared at δ=17.29 can be ascribed to the formation of the hydrogen bridge [35, 36]. The data observed from the ¹³C-NMR spectra of the novel compounds were supported the characteristic chemical shifts for compounds (11), as expected. The novel signal belonging O-H...O groups emerged at 1737 cm⁻¹ in the FT-IR spectrum of complex (11) which provides the structure of (H₂L) Ni (II) complex. The fast atom bombardment mass spectra of (11) exhibited a molecular ion peaks at m/z = 1508.87 [M]⁺, which supported the aimed structure.

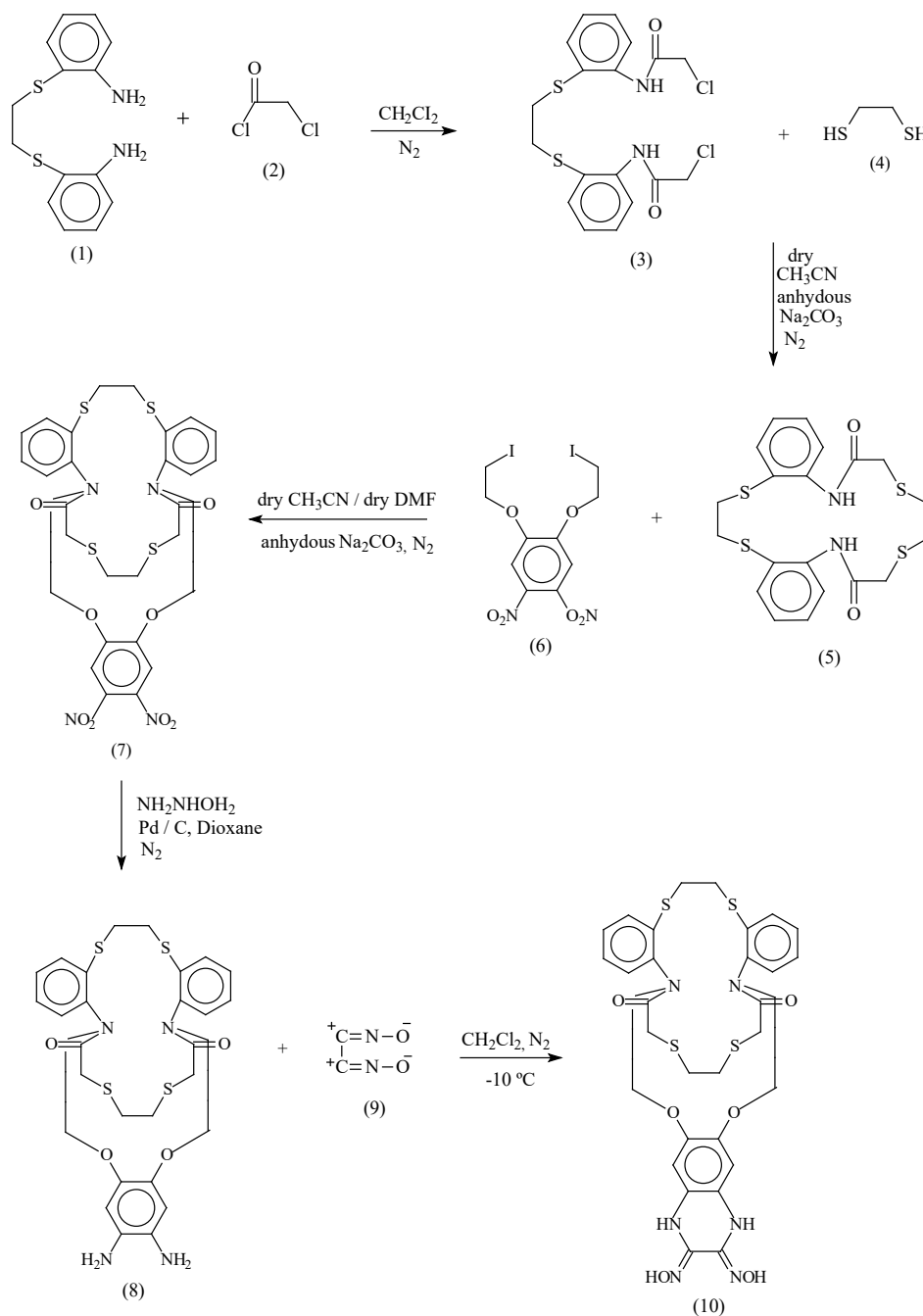
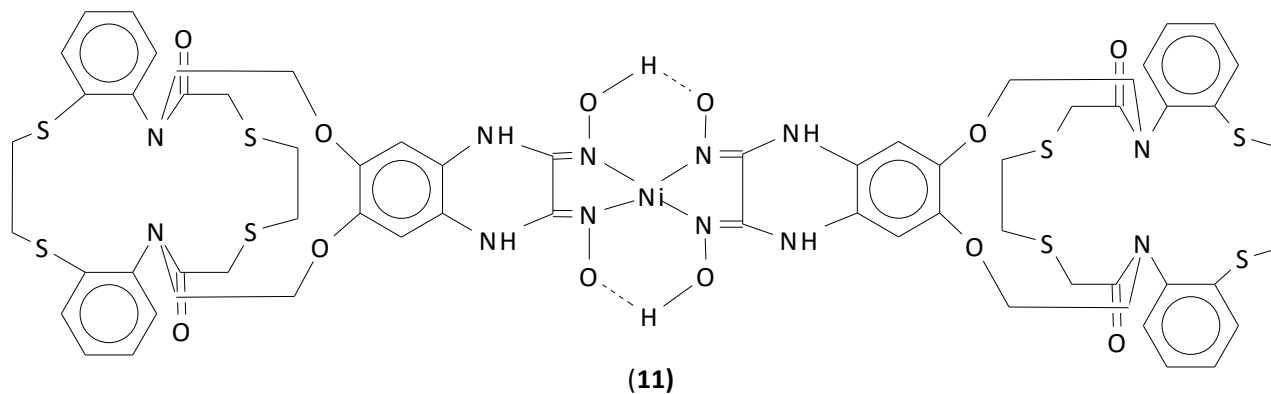
The obtained elemental analyses data for all compounds were supported of the corresponding compound structure.

4. Conclusions

In this work, a new (E, E)-dioxime with mono nuclear nickel (II) complex containing diazatetradithioxa macrobicyclic moieties. The structures of all new compounds were clarified by elemental analysis and different spectroscopic techniques such as FT-IR, UV-vis, ¹H NMR, ¹³C-NMR and MALDI-TOF. Examination of the analysis results revealed that the metal ligand ratio was 1: 2.

Acknowledgements

This study was supported by the Research Fund of Karadeniz Technical University, project no: 2006.111.02.1, (Trabzon-Turkey).

Scheme 1. The synthesis of (E,E)-dioxime (H_2L)Fig. 1. The structure of $[\text{Ni}(\text{HL})_2]$ complex

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