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

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ABSTRACT
In this study, a novel (E, E)-dioxime containing a diazatetrathiodioxoa macrobicyclic moieties (19E, 20E)-6,7,14,15,22,25-hexahydro-13,26-(ethanothioethano-thioethano)dibenzo[14,15:8,9]-dioxadithiadiazaacyclooctadecine-25,32-dione (7) has been synthesized from the reaction of cyanogen-di-N-oxide with 2,3-diamino-6,7,14,15,22,25-hexahydro-8,21-(ethanothioethano-thioethano)-tribenzo[h,h,n] [1,4,10,13,17,16]dioxadithiadiazaacyclooctadecine-25,32-dione (8), which was prepared by the reduction of 2,3-dinitro-6,7,14,15,22,25-hexahydro-8,21-(ethanothioethano-thioethano)-tribenzo[h,h,n] [1,4,10,13,17,16]dioxadithiadiazaacyclooctadecine-25,32-dione (19E, 20E)-6,7,14,15,22,25-hexahydro-13,26-(ethanothioethano-thioethano)dibenzo[14,15:8,9]-dioxadithianiazacyclooctadecine-25,32-dione (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 (H2O) 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.

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

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 hydroxy 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 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 dioxadithiadiazao macrobicyclic moiety (H2L) [26]. In studying, we have worked up a new macrobicyclic vic-dioxime which contains diazatetrathiodioxao macrobicyclic moiety (10).
2. Experimental

2.1. General

The IR spectral data were obtained on a Perkin Elmer 1600 FT-IR Spectrophotometer, using KBr pellets. 1H and 13C-NMR spectral data were obtained on a Varian Mercury 200 MHz spectrometer in CDCl3, DMSO, and chemical shifts were measured (δ) relative to MeSi as an 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-aminophenoxo) ethanedithiol (1) [27] and 1,2-dinitro-4,5-bis(2-iodoethoxo)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)

2.2.2 Synthesis of compound 9,10,21-tetrahydro-5H,12H-dibenzo[e,q] [1,4,10,13,7,16]-tetrathiadiazacyclooctadecine-6,13(7H,14H)-dione (4)

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

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

2.2.5 Synthesis of compound [19E,20E]-6,7,14,15,21,22,23-hexahydro-13,26-(ethanothioethanothioethano)tribenzo[b,h,n][1,4,10,13,7,16] dioxadithiodiazacycloocta-deco[2,3-g]quinoline-19,20,27,34-tetron 19,20-dioxime (H_2L), (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), in refigated bath at -10 ºC, was added the solution of cyanogen-di-N-oxide in dichloromethane (25 mL) at the same temperature. The reaction was stirred for 12 h and then filtered from Celite and washed with dichloromethane. The solvent was removed under reduced pressure. The unobtained product was crystallized from ethanol. Light yellow yield was obtained after crystallization. Yield 0.5g (70%) mp: 230-232 ºC. IR (KBr pellet), (cm⁻¹): 3263 (N-H), 3057 (Ar-H), 2924- 2868 (C-H), 1681 (C=O), 1577, 1519 (C=C), 1438, 1404, 1308, 1262, 763, 730.

2.2.5 Synthesis of compound 2,3-dinitro-6,7,14,15,22,23-hexahydro-8,21-(ethanothioethanothioethano)tribenzo[b,h,n][1,4,10,13,7,16] dioxadithiodiazacyclooctadecine-25,32-dione (7)

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) containing anhydrous NaCO₃ 0.5 M, 25 mL in dichloromethane (25mL), in refigated bath at -10 ºC, 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 ºC 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 ºC 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 ºC. IR (KBr pellet), (cm⁻¹): 3268 (O-H), 3276 (N-H), 3087(Ar-H), 2924- 2868 (C-H), 1681 (C=O),
2.2.6. Synthesis of compound [Ni(III)] (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 turned 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; \( \text{C}_{12} \text{H}_{12} \text{N}_{10} \text{O}_{6} \text{S}_{5} \) calc.: 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, 3082 (Ar-H), 2924-2853 (C-H), 1737 (O=H-xx-O), 1648 (C=O), 1614 (C=N), 1264 (Ar-O-CH₃), 950 (N-O). ¹H-NMR (DMSO-d₆), (δ ppm): 17:29 (2s, 2H, OH-xx-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), 2.60s (8H, CH₂-S). ¹³C-NMR (DMSO-d₆), (δ ppm): 168.22, 150.86, 145.86, 134.47, 129.13, 128.67, 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. The 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, CH₂-NH-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 CH₂-NH-S and C=O were monitored at δ = 32.92 and 161.15 ppm respectively. In the IR spectra 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.

Macrobiyclic 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 macrobiyclic compound (7) in moderate yield 60%. In the ¹H-NMR spectrum of (7), the signals of Ar-H and CH₂-NH-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 CH₂-NH-S and C=O at δ = 34.96 and 167.86 and 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 macrobiyclic (7) using 10% palladium-activated charcoal and hydrazine hydrate (100%) in hot ethanol [30] worked out the macrobiyclic compound (8) in yield 70 %. In the ¹H-NMR spectrum of (8), the signal due to Ar-H, NH, and CH₂-NH-S protons were obtained at δ = 7.16, 6.90, 7.68, 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-CH₃, and CH₂-NH-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 NH, 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 CH₂-NH-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 [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, 1618 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 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 diazatetrathidioxa macrobiyclic 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.

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Scheme 1. The synthesis of (E,E)-dioxime (H\textsubscript{L})

Fig. 1. The structure of [Ni(HL)\textsubscript{2}] complex
References


