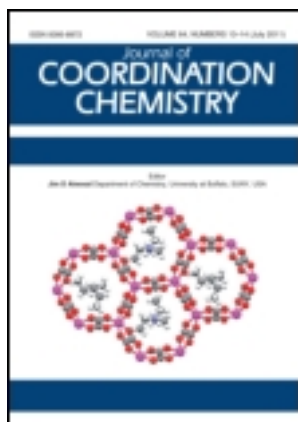


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The synthesis and characterization of a new (E, E)-dioxime, its complex formations of the macrobicyclic group, and conformational analysis of the ligands

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The synthesis and characterization of a new (*E, E*)-dioxime, its complex formations of the macrobicyclic group, and conformational analysis of the ligands

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In this study, 19-nitro-6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo-[b,i,o][1,4,11,14,7,18]tetraoxadiazacycloicosine (**3**) was synthesized using 6,7,8,9,10,11,17,18-octahydro-5H-dibenzo[e,n][1,4]dioxo[8,12]diazacyclopentadesine (**1**) and 4-nitro-1,2-bis(2-iodoethoxy)benzene (**2**) as the starting compounds. Macrobicyclic amine **4** was synthesized by reaction of an aromatic nitro compound with hydrazine hydrate (100%) and palladium (10%)-activated carbon in *n*-butanol. N¹,N²-di-6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo [b,i,o][1,4,11,14,7,18]tetraoxadiazacycloicosin-19-yl-N¹,N²-dihydroxyethane-diimidamide *vic*-dioxime (**6**) was synthesized by reaction of cyanogen-di-N-oxide in CH₂Cl₂, which was obtained from (*E, E*)-dichloroglyoxime and an aqueous solution of Na₂CO₃ (0.1 N) with **4**. Mononuclear Ni(II), Co(III), and Cu(II) complexes, **7**, **9**, and **10**, were synthesized by reaction of *vic*-dioxime with NiCl₂·6H₂O, CoCl₂·6H₂O, and CuCl₂·2H₂O, respectively. BF₂⁺-Capped mononuclear Ni(II) complex **8** was synthesized by reaction of boron-trifluoride diethyl etherate with mononuclear nickel(II) complex **7** in acetonitrile. The structures of new compounds were determined by elemental analysis, ¹H-NMR, ¹³C-NMR, IR, mass spectroscopic data, and thermal methods (TG/DTA). The conformational analysis of the ligands was performed using DFT and AM1 methods.

Keywords: *vic*-Dioxime; Macrobicyclic compound; Mononuclear complex; Host–Guest compounds; BF₂⁺-Capped complex

1. Introduction

Coordination chemistry has seen rapid development due to the possible biological applications of the new compounds [1]. The synthesis of *vic*-dioximes and their derivatives have been a subject of study for a very long period of time. Coordination compounds containing *vic*-dioximes exhibit interesting properties, such as electrochemical [2], optical [3], fluorescent [4], biological activity [5], and thermal and catalytic properties [6]. For photochemical storage of energy or as redox catalysts [7], IR on Langmuir–Blodgett film [8, 9], X-ray crystal structure [10], and kinetic and mechanistic properties [11] have been studied.

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Vicinal dioximates usually form stable N,N-chelated metal complexes containing a conjugated N=C–C=N system [12]. Dioxime ligands are known to coordinate metal ions as neutral dioximes and also monoanionic dioximates *via* dissociation of one oxime proton. They also bridge *via* coordination through oxygen atoms [13]. In addition, they have several geometric isomers in which the environment around the metal varies depending on the particular isomeric structure. Due to use of coordination compounds in medicine [14], electrooptical sensors [15], liquid crystals [16], trace metal analysis [17], and dyes [18], *vic*-dioximes have been of great importance.

Lehn *et al.* [19] developed a range of 3-D macropolycyclic ligand systems and their complexes, which they named cryptands or cryptates. The cryptands form thermodynamically stable complexes with a variety of metal ions [20], where cations are included in the intramolecular cavity of a macropolycyclic ligand [21]. The design, synthesis, and use of macropolycyclic compounds capable of selective recognition of metal cations and other species are of interest in catalysis, separations, extraction, enzyme function, and other areas of chemistry [22].

In this article, we report a new macrobicyclic *vic*-dioxime and its metal complexes which contain macrobicyclic (cryptand) moiety (H₂L).

2. Experimental

All reactions were carried out under dry nitrogen using standard Schlenk techniques. 6,7,8,9,10,11,17,18-Octahydro-5H-dibenzo[e,n][1,4]dioxo[8,12]diazacyclopentadesine (**1**) and 4-nitro-1,2-bis(2-iodoethoxy)benzene (**2**) were prepared according to the literature [23, 24]. All reagents and solvents were of reagent grade; solvents were dried and purified as described by Perrin and Armarego [25]. IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer using KBr pellets. ¹H-NMR and ¹³C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in CDCl₃ or DMSO-d₆ and chemical shifts are reported (δ) relative to Me₄Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analyses were determined by an LECO Elemental Analyser (CHNS O932). DTA curves were recorded with a Seiko II Exstar 6000 TG/DTA. Theoretical conformational analyses of the ligands were performed using DFT and AM1 methods. Melting points were measured on an electrothermal apparatus.

2.1. Synthesis of 19-nitro-6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo [b,i,o][1,4,11,14,7,18]tetraoxadiazacycloicosine (**3**)

6,7,8,9,10,11,17,18-Octahydro-5H-dibenzo[e,n][1,4]dioxo[8,12]diazacyclopentadesine (**1**) (2.5 g, 8.01 mmol) was dissolved in dry acetonitrile (150 mL) and anhydrous K₂CO₃ (3.3 g, 24 mmol) was added to the mixture while stirring at 60°C under N₂. After stirring for 30 min, 4-nitro-1,2-bis(2-iodoethoxy)benzene (**2**) (3.71 g, 8.01 mmol) in dry acetonitrile (40 mL) was added dropwise for 2 h, then the mixture was heated at reflux. The reaction mixture was stirred under N₂ at this temperature for 9 days. During this process, the reaction was monitored by basic TLC using chloroform/acetone (2:0.5). At the end of this period, the reaction mixture was filtered and washed with dry acetonitrile, and then combined solution was evaporated to dryness under reduced

pressure. The crude product was dissolved in CHCl_3 (150 mL) and then washed with water (10 mL). The organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated under reduced pressure. Purification of the product was accomplished by column chromatography with aluminum oxide using chloroform/acetone (2:0.5). Yield: 3.08 g (74%) m.p.: 188–190°C. Anal. Calcd for $\text{C}_{29}\text{H}_{33}\text{N}_3\text{O}_6$ (%): C, 67.05; H, 6.36; N, 8.09. Found: C, 67.09; H, 6.30; N, 7.92. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3076 (Ar–H), 2927–2869 (Aliph. C–H), 1599, 1588, 1513–1336 (NO_2), 1493, 1451, 1277, 1241 (Ar–O– CH_2), 1119 (–O– CH_2), 1034, 946 (N–O), 752. $^1\text{H-NMR}$ (200 MHz, CDCl_3) (δ : ppm): 7.84 (dd, $J = 8.8, 2.2$ Hz, 1H, Ar–H), 7.54 (d, $J = 2.2$ Hz, 1H, Ar–H), 7.35–7.19 (m, 4H, Ar–H), 6.97 (t, $J = 8.4$ Hz, 2H, Ar–H), 6.81 (d, $J = 8.4$ Hz, 2H, Ar–H), 6.68 (d, $J = 8.8$ Hz, 1H, Ar–H) 4.30 (s, 4H, $\text{CH}_2\text{--O}$), 4.04–3.98 (dt, $J = 12.4, 4.0$ Hz, 4H, $\text{CH}_2\text{--O}$), 3.70 (s, 4H, $\text{CH}_2\text{--N}$), 3.21–3.20 (bd, $J = 4.0$ Hz, 4H, $\text{CH}_2\text{--N}$), 2.52 (t, $J = 6.8$ Hz, 4H, $\text{CH}_2\text{--N}$), 1.91 (m, 2H, $\text{CH}_2\text{--CH}_2$). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) (δ : ppm): 157.07, 154.99, 148.89, 141.32, 132.39, 132.17, 128.66, 127.98, 120.88, 118.06, 110.63, 107.94, 69.12, 66.12, 54.43, 53.99, 52.35, 51.84. LC-MS/MS (EI), (m/z): 520 $[\text{M} + 1]^+$, 521 $[\text{M} + 2]^+$, 542 $[\text{M} + \text{Na}]^+$.

2.2. Synthesis of 6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo[b,i,o][1,4,11,14,7,18]tetraoxadiazacycloicosin-19-amine (4)

19-Nitro-6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo[b,i,o][1,4,11,14,7,18]tetraoxadiazacycloicosine (3) (3 g, 5.78 mmol) was dissolved in *n*-butanol (140 mL) by heating under nitrogen at reflux. Then the solution was cooled to room temperature and palladium (10%)-activated carbon (0.3 g) was added to the solution. The temperature was gradually increased to 124°C and 4 mL hydrazine hydrate added dropwise during 1 h. The reaction was monitored by TLC using chloroform/methanol (2:1) and was completed in 24 h at the same temperature. Then it was filtered through celite and washed with *n*-butanol, and the combined solution was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel with methanol/chloroform (2:1) as eluent. Yield: 1.75 g (61%), m.p.: 144–146°C. Anal. Calcd for $\text{C}_{29}\text{H}_{35}\text{N}_3\text{O}_4$ (%): C, 71.16; H, 7.15; N, 8.55. Found: C, 71.17; H, 7.03; N, 8.72. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3337–3208 (NH_2), 3060 (Ar–H), 2927–2871 (Aliph. C–H), 1600 (NH_2), 1509, 1493, 1450, 1231 (Ar–O– CH_2), 1123 (–O– CH_2). $^1\text{H-NMR}$ (200 MHz, CDCl_3) (δ : ppm): 7.31–7.19 (m, 4H, Ar–H), 6.96 (t, $J = 8.2$ Hz, 2H, Ar–H), 6.89 (d, $J = 8.2$ Hz, 2H, Ar–H), 6.65 (d, $J = 9$ Hz, 1H, Ar–H), 6.16 (s, 2H, Ar–H), 5.78 (s, 2H, NH_2), 4.34 (s, 4H, $\text{CH}_2\text{--O}$), 3.96 (t, $J = 4.0$ Hz, 4H, $\text{CH}_2\text{--O}$), 3.72 (s, 4H, $\text{CH}_2\text{--N}$), 3.13 (bd, $J = 4.0$ Hz, 4H, $\text{CH}_2\text{--N}$), 2.56 (t, $J = 6.6$ Hz, 4H, $\text{CH}_2\text{--N}$), 1.87 (m, 2H, $\text{CH}_2\text{--CH}_2$). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) (δ : ppm): 156.89, 150.24, 141.11, 132.54, 131.94, 128.43, 120.59, 120.48, 116.35, 110.52, 106.52, 101.91, 68.05, 67.85, 65.86, 53.60, 51.85, 50.22. LC-MS/MS (EI), (m/z): 490 $[\text{M} + 1]^+$, 491 $[\text{M} + 2]^+$.

2.3. Synthesis of N^1, N^2 -di-6,7,15,16,23,24-hexahydro-13H,26H-14,25-propanotribenzo[b,i,o][1,4,11,14,7,18]tetraoxadiazacycloicosin-19-yl- N^1, N^2 -dihydroxyethanediiimide H_2L (6)

Compound 4 (1.7 g, 3.47 mmol) was dissolved in dichloromethane (40 mL) and cooled to -10°C . The solution of cyanogen-di-N-oxide (5) in dichloromethane (25 mL) which

was obtained from dichloroglyoxime (0.27 g, 1.74 mmol) and Na_2CO_3 (1N, 25 mL) was added to this solution at -10°C under N_2 . The reaction was monitored by TLC using ethanol/chloroform (1:1) and continued for 10 h at -10°C . Then the mixture was evaporated to 15 mL under reduced pressure and cooled to -18°C in a refrigerator overnight. The solid product was filtered off, washed with cold ethanol and diethyl ether. Yellow solid product was obtained by recrystallization from ethanol. Yield: 0.96 g (51%), m.p.: 229.7°C (decomposition). Anal. Calcd for $\text{C}_{60}\text{H}_{70}\text{N}_8\text{O}_{10}$ (%): C, 67.77; H, 6.58; N, 10.53. Found: C, 67.74; H, 6.85; N, 10.35. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3378 (N–H), 3230 (O–H), 3060 (Ar–H), 2924–2873 (C–H), 1613 (C=N), 1600 (N–H), 1509, 1489, 1229 (Ar–O–CH₂), 1123 (–O–CH₂), 941 (N–O). ¹H-NMR (200 MHz, DMSO-d₆) (δ : ppm): 10.50 (s, 2H, OH), 9.32 (s, 2H, NH), 7.60 (s, 2H, Ar–H), 7.33–6.81 (m, 20H, Ar–H), 4.28 (s, 8H, CH₂–O), 4.00–3.63 (m, 8H, CH₂–O), 3.35 (m, 8H, CH₂–N), 3.00–2.95 (m, 8H, CH₂–N), 2.60–2.48 (m, 8H, CH₂–N), 2.01 (m, 4H, CH₂–CH₂). ¹³C-NMR (50 MHz, DMSO-d₆) (δ : ppm): 168.40, 167.96, 147.08, 143.89, 142.57, 134.90, 132.54, 131.94, 128.43, 120.59, 120.48, 114.54, 113.01, 106.91, 68.73, 67.85, 54.61, 50.22, 35.74, 25.81. LC-MS/MS (EI), (m/z): 1064 [M + 1]⁺, 1065 [M + 2]⁺.

2.4. Synthesis of [Ni(HL)₂] (7)

A solution of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.05 g, 0.21 mmol) in hot EtOH (20 mL) was added to a stirring solution of **6** (0.45 g, 0.42 mmol) in EtOH (40 mL) at 60°C . A distinct change in color to orange and a decrease in pH (pH = 1.98) were observed. Then, the pH of the reaction mixture was adjusted to 4.50 by adding triethylamine (0.1 N) in ethanol. The mixture was stirred at 60°C for 2 h before the solid product was filtered, washed with water, cold EtOH, diethyl ether, and dried *in vacuo* over P_2O_5 . The obtained orange solid was purified by preparative TLC using methanol/acetonitrile (1:1). Yield: 0.24 g (52.2% based on $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$), m.p.: 256.5°C (decomposition). Anal. Calcd for $\text{C}_{120}\text{H}_{138}\text{N}_{16}\text{O}_{20}\text{Ni}$ (%): C, 66.01; H, 6.32; N, 10.25. Found: C, 66.10; H, 6.31; N, 10.39. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3318 (N–H), 3082 (Ar–H), 2920–2857 (C–H), 1661 (O–H...O), 1621(C=N), 1604 (N–H), 1554, 1503, 1264 (Ar–O–CH₂), 1166(–O–CH₂), 1007 (N–O). ¹H-NMR (200 MHz, DMSO-d₆) (δ : ppm): 16.40 (s, 2H, O–H...O), 9.62 (s, 4H, NH), 7.98–6.96 (m, 44H, Ar–H), 4.30 (s, 16H, CH₂–O), 3.90 (m, 16H, CH₂–O), 3.38 (s, 16H, CH₂–N), 2.89 (m, 16H, CH₂–N), 2.46 (m, 16H, CH₂–N), 1.71 (m, 8H, CH₂–CH₂). ¹³C-NMR (50 MHz, DMSO-d₆) (δ : ppm): 168.345, 168.03, 147.02, 143.90, 142.88, 142.54, 141.62, 134.87, 134.15, 130.10, 120.10, 114.50, 106.93, 79.84, 68.77, 67.85, 54.68, 35.75, 35.55. LC-MS/MS (EI), (m/z): 2181 [M – 2]⁺, 2183 [M]⁺, 2185 [M + 2]⁺, 2201 [M + H₂O]⁺, 2206 [M + Na]⁺.

2.5. Synthesis of [Ni(LBF₂)₂] (8)

A suspension of **7** (0.2 g, 0.09 mmol) in freshly distilled dry acetonitrile (50 mL) was brought to reflux under nitrogen. Boron trifluoride diethyl etherate (0.09 mL, 0.36 mmol) was added dropwise for 30 min while the suspension was refluxed and stirred. The resulting reaction mixture was completely dissolved and immediately turned dark red. The reaction was allowed to reflux for 5 h, then the solvent was removed under reduced pressure, and the residue was dissolved in acetonitrile (10 mL), and evaporated to dryness. The last step was repeated, and the residue was dissolved in

ethanol (10 mL) and then cooled in a refrigerator at -5°C overnight. The product was filtered off, washed with cold ethanol, diethyl ether, and dried *in vacuo*. The dark red solid was recrystallized from ethanol. Yield: 0.11 g (55% based on $[\text{Ni}(\text{HL})_2]$ (**7**)), m.p.: $84\text{--}86^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{120}\text{H}_{136}\text{N}_{16}\text{O}_{20}\text{NiB}_2\text{F}_4$ (%): C, 63.23; H, 5.96; N, 9.82. Found: C, 63.37; H, 5.96; N, 9.66. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3392 (N–H), 3032 (Ar–H), 2961–2928 (C–H), 1632(C=N), 1605 (N–H), 1513, 1456, 1245 (Ar–O–CH₂), 1124 (B–O), 1054(B–F), 946 (N–O). $^1\text{H-NMR}$ (200 MHz, CDCl_3) (δ : ppm): 9.48 (s, 4H, NH), 7.01–6.93 (m, 44H, Ar–H), 4.31 (s, 16H, CH₂–O), 4.02–3.98 (m, 16H, CH₂–O), 3.39–3.36 (s, 16H, CH₂–N), 2.96–2.66 (m, 16H, CH₂–N), 2.50 (m, 16H, CH₂–N), 2.08 (m, 8H, CH₂–CH₂). $^{13}\text{C-NMR}$ (50 MHz, CDCl_3) (δ : ppm): 152.77, 152.51, 146.96, 137.59, 134.85, 127.34, 126.26, 125.45, 116.78, 116.33, 112.89, 106.25, 106.09, 61.95, 61.64, 61.35, 51.57, 49.47, 25.85. LC-MS/MS (EI), (m/z): 2278 $[\text{M}]^+$, 2279 $[\text{M} + 1]^+$, 2280 $[\text{M} + 2]^+$, 2281 $[\text{M} + 3]^+$, 2282 $[\text{M} + 4]^+$, 2301 $[\text{M} + \text{Na}]^+$, 2303 $[\text{M} + 2 + \text{Na}]^+$, 2304 $[\text{M} + 3 + \text{Na}]^+$.

2.6. Synthesis of $[\text{Co}(\text{LH})_2\text{pyCl}]$ (**9**)

A solution of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.03 g, 0.12 mmol) in ethanol (15 mL) was added to a hot solution of **6** (0.25 g, 0.24 mmol) in ethanol (40 mL) at 60°C . Pyridine (0.01 mL, 0.12 mmol) in ethanol (2 mL) was added to the above solution while it was being heated. The reaction mixture was heated and stirred at 60°C and a stream of air was bubbled through the solution for 2 h. Then, the solution was concentrated to 25 mL and placed in a refrigerator at -18°C overnight, whereupon a brown solid precipitated from the reaction mixture. The solid product was filtered off, washed with water, cold ethanol, and diethyl ether. The obtained brown solid was purified by preparative TLC using methanol/acetonitrile (1:1). Yield: 0.12 g (44.9% based on $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$), m.p.: $276\text{--}278^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{125}\text{H}_{143}\text{N}_{17}\text{O}_{20}\text{CoCl}$ (%): C, 65.32; H, 6.22; N, 10.35. Found: C, 65.63; H, 6.09; N, 10.22. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3369 (N–H), 3071 (Ar–H), 2925–2879 (C–H), 1697 (O–H...O), 1601 (N–H), 1509, 1493, 1240 (Ar–O–CH₂), 1122(–O–CH₂), 941 (N–O). $^1\text{H-NMR}$ (200 MHz, DMSO-d_6) (δ : ppm): 9.40 (s, 4H, NH), 7.50–6.79 (m, 49H, Ar–H), 4.36–3.95 (m, 32H, CH₂–O), 2.47 (m, 16H, CH₂–N), 2.47 (m, 16H, CH₂–N), 2.23 (m, 16H, CH₂–N), 1.72 (m, 8H, CH₂–CH₂). $^{13}\text{C-NMR}$ (50 MHz, DMSO-d_6) (δ : ppm): 157.61, 157.11, 151.81, 140.11, 131.19, 127.74, 126.42, 121.44, 121.18, 113.36, 112.24, 105.15, 103.14, 80.03, 67.85, 67.23, 51.78, 45.93, 29.38. LC-MS/MS (EI), (m/z): 2296 $[\text{M} - 2]^+$, 2299 $[\text{M} + 1]^+$, 2300 $[\text{M} + 2]^+$, 2321 $[\text{M} + \text{Na}]^+$.

2.7. Synthesis of $[\text{Cu}(\text{HL})_2]$ (**10**)

A solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.008 g, 0.01 mmol) in hot EtOH (20 mL) was added to a hot solution of **6** (0.20 g, 0.19 mmol) in EtOH (30 mL) and continuously stirred. A distinct change in color from yellow to black and decrease in pH (pH = 1.78) was observed. The pH of the reaction mixture was adjusted to 4.50 by adding triethylamine (0.1 N) in ethanol. The mixture was stirred efficiently and heated on a water bath at 60°C for 2 h before the solid was filtered, washed with water, cold ethanol, and diethyl ether. The crude product was crystallized from acetonitrile. Yield: 0.086 g (42% based on $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$), m.p.: $273\text{--}275^{\circ}\text{C}$. Anal. Calcd for $\text{C}_{120}\text{H}_{138}\text{N}_{16}\text{O}_{20}\text{Cu}$ (%): C, 65.81; H, 6.30; N, 10.23. Found: C, 65.91; H, 6.25; N, 10.31. IR (KBr tablet) $\nu_{\text{max}}/\text{cm}^{-1}$: 3285

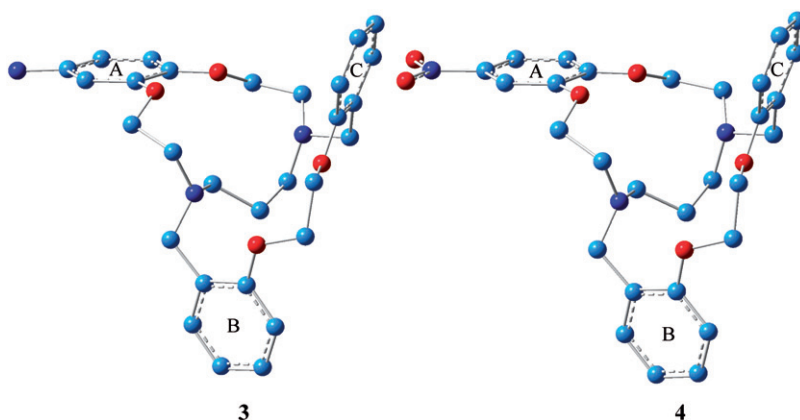


Figure 1. Optimized geometries of **3** and **4** [B3LYP/6-31G(d,p)].

(N–H), 3076 (Ar–H), 2925–2846 (C–H), 1672 (O–H...O), 1613 (C=N), 1602 (N–H), 1547, 1429, 1265 (Ar–O–CH₂), 1139(–O–CH₂). LC-MS/MS (EI), (*m/z*): 2186 [M – 2]⁺, 2190 [M + 2]⁺, 2211 [M + Na]⁺.

2.8. Chemical calculations

The determination of the geometry of **3** and **4** was carried out using the DFT method. Compounds **3** and **4** contain 13-membered and 15-membered macrocyclic rings with three benzene rings bonded to them (figure 1). Each 13- and 15-membered macrocycle includes four heteroatoms (two O's and N's). Conformations of a 3-D ligand are mostly determined through conformations of macrocyclic rings; the conformation of the free ligand is usually different from its conformation in the crystal. Because of the crystal field, the molecule has higher symmetry conformations in the crystal than in the gas phase [26]. Taking all these into consideration, the conformational analyses of **3** and **4** were performed by DFT/B3LYP (density functional theory with B3LYP – the hybrid Becke's three parameter functional and Lee–Yong–Parr exchange-correlation potential) [27, 28] method using the 6-31G (p,d) [29] basis set, and the stable conformations were determined for **3** and **4** (figure 1). Electronic and geometric properties of the most stable conformations of the macrobicyclic compounds were also investigated. The total energies (E_{tot}), dipole moments (μ), frontier molecular orbital energies (ϵ_{HOMO} and ϵ_{LUMO}), values of the distance $\text{N}_{\text{bridgehead}}\text{--N}_{\text{bridgehead}}$ ($R_{\text{Nbri.}\text{--Nbri.}}$), and torsion angles A/B , A/C , and B/C for stable conformation of **3** and **4** were calculated (Supplementary material). In the stable conformation of **3** and **4** (figure 1), the heteroatom takes on a *trans*–*trans* configuration with neighboring heteroatoms in these macrocyclic rings *gauche* relative to each other. In the stable conformation of the compounds benzene rings B and C are almost perpendicular to benzene ring A and also, almost perpendicular to each other.

Conformational analysis of **6** (figure 2) was performed with geometry optimization by using AM1 [30]. The N=C–C=N internal rotation angle (internal rotation angle around the central C–C single bond) (dihedral) (ϕ) for dimer in the stable

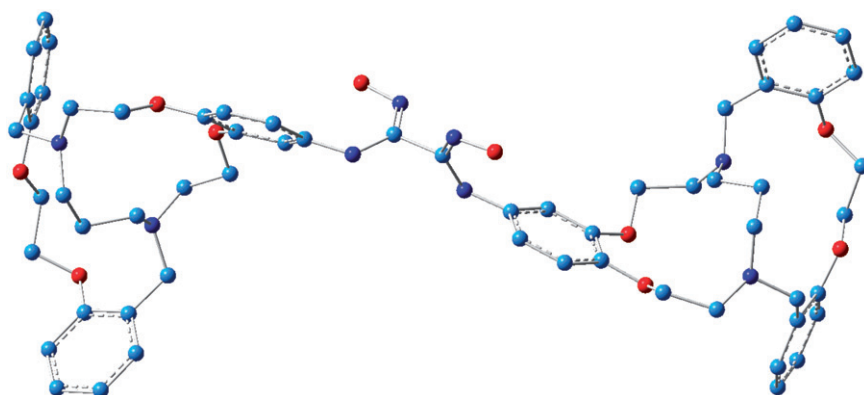


Figure 2. Optimized geometry of **6** (AM1).

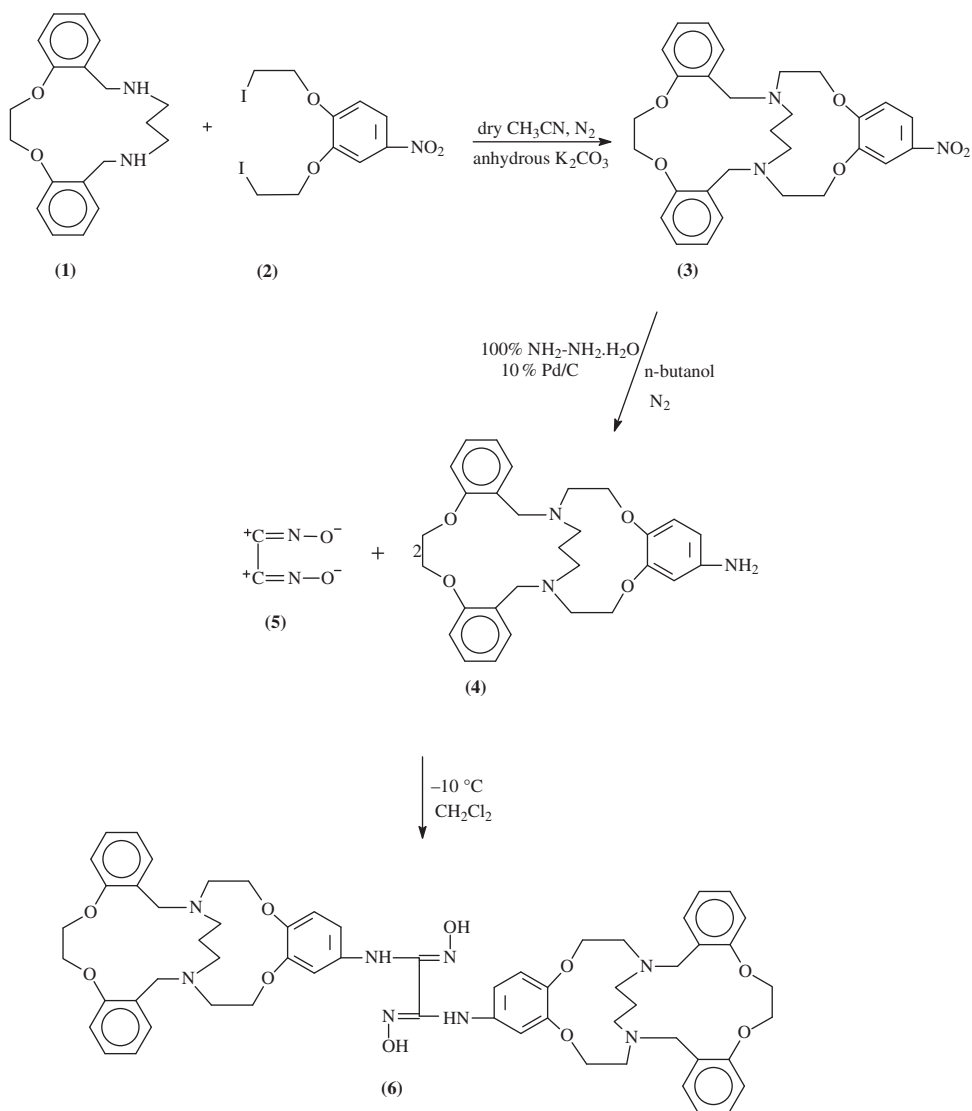
conformations is 108.66° . In other words, a shallow minimum was found at the conformation corresponding to $\phi = 108.66^\circ$. The rotational barriers were $6.708 \text{ kcal mol}^{-1}$ and $8.674 \text{ kcal mol}^{-1}$ for the conversion of the conformation corresponding to the shallow minimum into *trans* and *cis* conformations, respectively.

3. Results and discussion

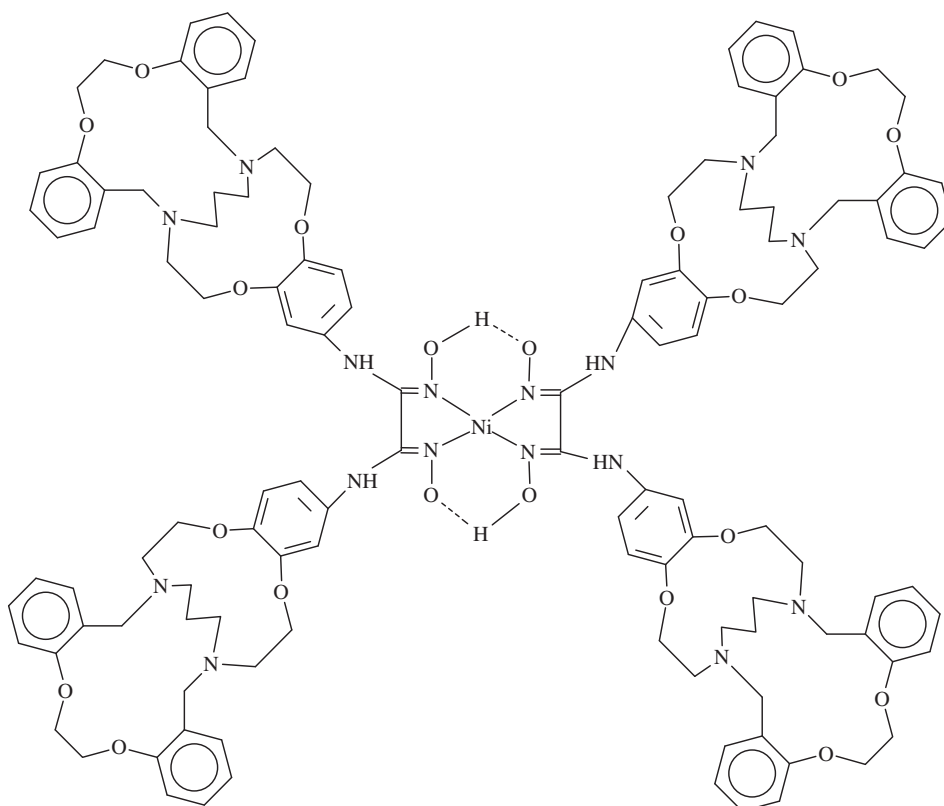
The syntheses of (*E, E*)-dioxime (H_2L) and its mononuclear complexes are summarized in scheme 1 and figures 3–6.

Compound **3** was synthesized by condensation of **1** with **2** in the presence of K_2CO_3 under nitrogen in refluxing acetonitrile; macrobicyclization gave macrobicyclic **3** (74% yield) as a crystalline product. In the IR spectrum of **3**, characteristic stretching vibrations of $-\text{NO}_2$ were observed at $1513\text{--}1336 \text{ cm}^{-1}$. In the $^1\text{H-NMR}$ spectrum of **3** (Supplementary material) chemical shifts of NH of **1** at $\delta = 2.0 \text{ ppm}$ disappeared after condensation. There are three doublets at $\delta = 7.84 \text{ ppm}$, $\delta = 6.68 \text{ ppm}$, and $\delta = 7.54 \text{ ppm}$, suggesting mono-nitro substituted aromatic linkage. The proton-decoupled $^{13}\text{C-NMR}$ and COSY spectral data were in agreement with the formation of **3** (Supplementary material). $^{13}\text{C-NMR}$ of **3** revealed O–C and N–C at $\delta = 68.12$, 66.12 and $\delta = 54.43$, 53.99 , 52.35 , 51.84 ppm , respectively. All aromatics carbons were $\delta = 157.07\text{--}107.94 \text{ ppm}$. $^1\text{H-}^1\text{H}$ correlation for 1,2- and 1,2,3-substituted phenyl rings have been seen at $\delta = 7.31\text{--}5.78 \text{ ppm}$ in the COSY spectrum. $^1\text{H-}^1\text{H}$ correlations were also observed for aliphatic parts of the molecule at $\delta = 4.34\text{--}1.87 \text{ ppm}$. Both the mass spectra (EI) of **3**, which showed molecular ion peaks at $m/z = 520 [\text{M} + 1]^+$, $521 [\text{M} + 2]^+$, $542 [\text{M} + \text{Na}]^+$, and elemental analysis confirmed formation. Calculations indicated that in the macrocyclic rings of the stable conformation of **3** and **4** the neighboring heteroatoms are gauche relative to each other and the benzene rings B and C are almost perpendicular to the benzene ring A and to each other.

Monoamine substituted macrobicyclic **4** was obtained by reduction of **3** in *n*-butanol using 10% palladium-activated charcoal and hydrazine hydrate (100%) at 124°C [31] in 61% yield. In the IR spectrum of **4**, stretching and bending vibrations of $-\text{NH}_2$ group

Scheme 1. Synthesis of (*E, E*)-dioxime (H_2L).

were observed at $3337\text{--}3208$ and 1600 cm^{-1} , respectively. In the $^1\text{H-NMR}$ spectrum of **4**, the chemical shifts of $-\text{NH}_2$ were at $\delta = 5.78$ ppm. These protons can be easily identified by deuterium exchange. The proton-decoupled $^{13}\text{C-NMR}$ spectrum for **4** was consistent with the proposed structure; proton-decoupled ^{13}C and proton chemical shifts of **4** show an upfield shift to the aromatic protons with respect to the formation of aromatic primary amine instead of nitro. The mass spectrum (EI) of **4** shows peaks at $m/z = 490 [\text{M} + 1]^+$ and $491 [\text{M} + 2]^+$, which support the proposed structure. Elemental analyses confirmed the desired compound. Calculations indicated conformation of **4** is similar to **3** (table S1). All calculated results of **3** and **4** are similar except for dipole

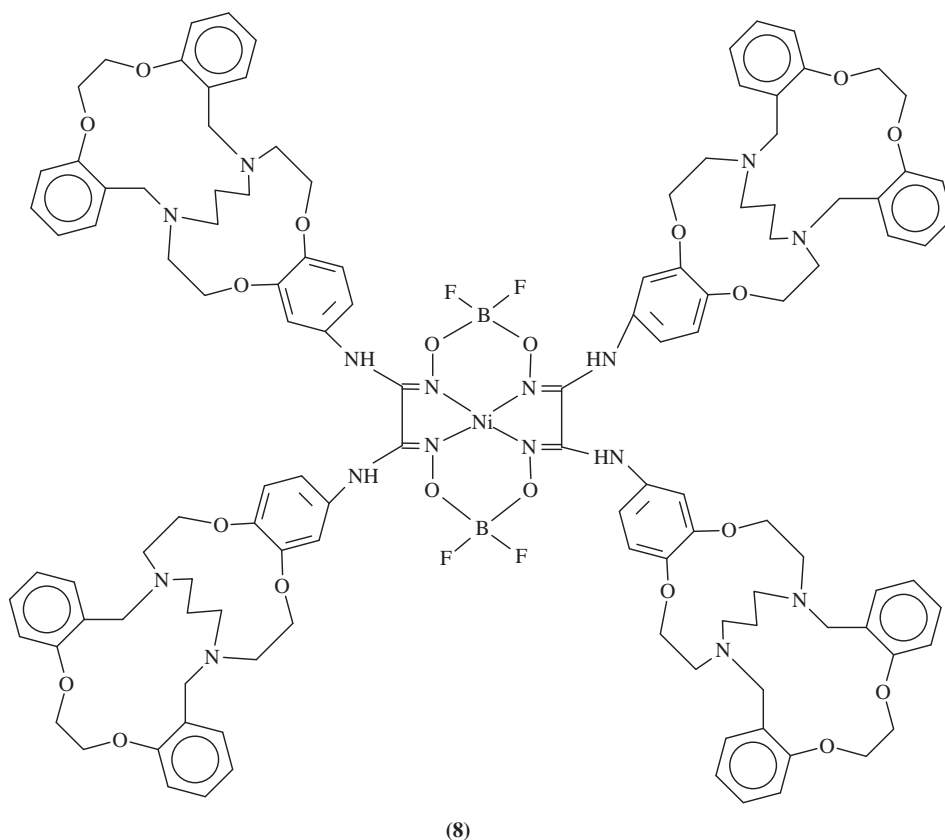


(7)

Figure 3. Structure of $[\text{Ni}(\text{HL})_2]$ (7).

moment (μ), 7.525 D and 0.802 D, respectively. Although their conformations are similar to each other, the strong electron-withdrawing effect of the nitro group is reduced to amine and dipole moment decreases to 0.802 D from 7.525 D. The distance between the two nitrogen atoms in **3** and **4** is almost the same.

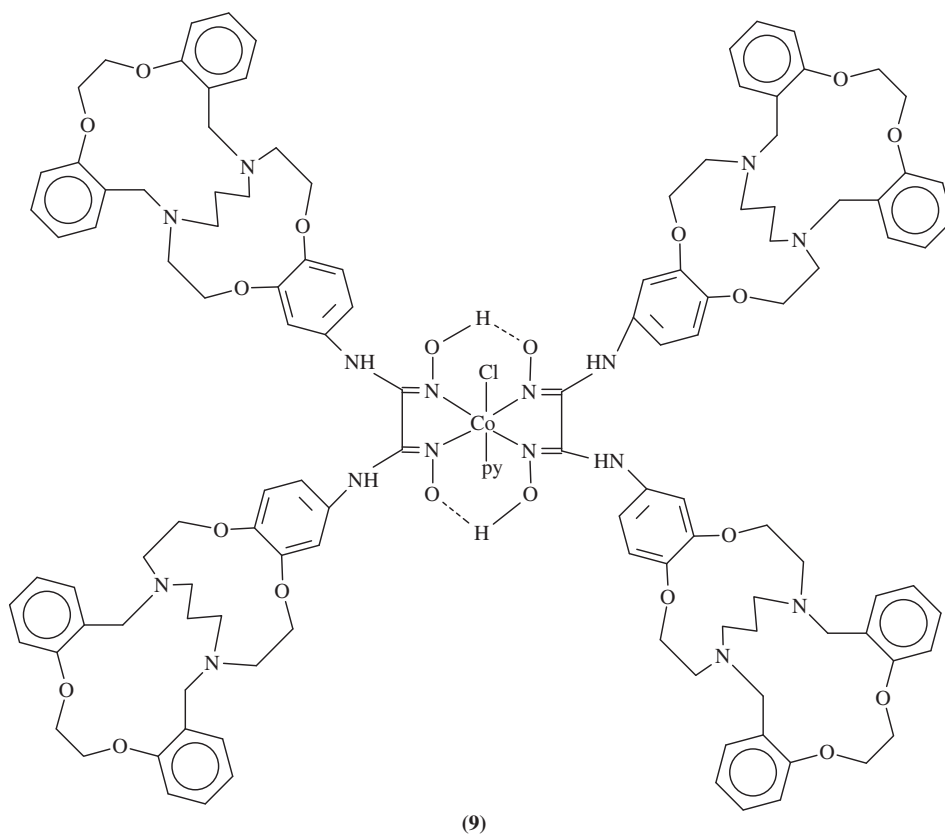
vic-Dioxime (H_2L) **6** was synthesized in moderate yield (51%) by reaction of **4** with cyanogen-di-N-oxide (**5**) in CH_2Cl_2 under nitrogen at -10°C . In this compound, stretching vibrations belonging to NH, OH, C=N and N-O were observed at 3378, 3230, 1613 and 941 cm^{-1} , respectively, in agreement with previously reported values for diaminoglyoxime derivatives [32, 33]. In the $^1\text{H-NMR}$ spectrum of **6**, disappearance of the aromatic primary amine belonging to **4** and the =N-OH and -NH signals at $\delta=10.50\text{ ppm}$ and $\delta=9.52\text{ ppm}$, respectively, support the structure. The deuterium exchange properties of these protons showed formation of the target compound. Single shift for =N-OH protons indicate that oximes are in the (*E, E*)-structure [33]. In the proton-decoupled $^{13}\text{C-NMR}$ spectrum of **6**, the azomethine is at lower field, $\delta=142.57\text{ ppm}$, confirming the (*E, E*)-form of the *vic*-dioxime [34]. The mass spectrum (EI) of **6** shows peaks at $m/z=1064\text{ [M+1]}^+$ and 1065 [M+2]^+ , which support the proposed structure. The DTA curve of **6** was obtained at a heating rate of $10^\circ\text{C min}^{-1}$ in N_2 atmosphere from 30°C to 900°C . Compound **6** has no melting point and

Figure 4. Structure of $[\text{Ni}(\text{LBF}_2)_2]$ (8).

decomposes from 203.6°C to 229.7°C. According to conformational analysis obtained by AM1 calculations, the *E, E*-conformation ($\phi = 108.66^\circ$) of **6** is most stable. Transformation of **6** from *cis* to *trans* does not require much energy and can easily change its conformation during interaction with different metals.

Reaction of **6** with Ni(II) chloride hexahydrate gave $[\text{Ni}(\text{HL})_2]$ (**7**) in 52.2% yield, and its composition was determined by elemental analysis and spectroscopic techniques. In the IR spectrum of **7**, disappearance of O–H stretches and the presence of O–H...O bending vibrations at 1661 cm^{-1} support formation of the desired complex. In the $^1\text{H-NMR}$ spectrum of **7**, a new resonance at $\delta = 16.40\text{ ppm}$ could be assigned to the formation of the hydrogen bridge, easily identified by deuterium exchange [35]. The $^{13}\text{C-NMR}$ spectra of **7** were similar to those of **6**, but shifted slightly as expected. The mass spectra (EI) of **7** showed molecular ion peaks at $m/z = 2181\text{ [M} - 2]^+$, 2183 [M]^+ , $2185\text{ [M} + 2]^+$, $2201\text{ [M} + \text{H}_2\text{O}]^+$ and $2206\text{ [M} + \text{Na}]^+$, confirming formation of the desired compound. Elemental analysis also confirmed the desired compound. The DTA curves of **7** (Supplementary material) were similar to **6**, decomposing from 218.1 to 256.5°C.

The template synthesis of $[\text{Ni}(\text{LBF}_2)_2]$ (**8**) was performed in 55% yield by adding boron trifluoride diethyl etherate to refluxing freshly distilled acetonitrile containing **7**

Figure 5. Structure of $[\text{Co}(\text{LH})_2\text{pyCl}]$.

with hydrogen bridging protons replaced by BF_2^+ . The IR spectrum of **8** exhibits shifts in the stretching vibrations of $\text{C}=\text{N}$ due to the strong electron-withdrawing effect of BF_2^+ incorporated in the macrobicyclic [36]. The broad band at 1661 cm^{-1} of **7** assigned to $\text{O}-\text{H}\cdots\text{O}$ bend disappeared upon insertion of BF_2^+ with simultaneous appearance of peaks at 1124 and 1054 cm^{-1} for $\text{B}-\text{O}$ and $\text{B}-\text{F}$, respectively [37]. In the $^1\text{H-NMR}$ spectrum of **8**, the deuterium exchangeable $\text{O}-\text{H}\cdots\text{O}$ protons disappeared. $^{13}\text{C-NMR}$ spectra of **8** were similar to those of **7**. The mass spectrum (EI) of this complex exhibits molecular ion peaks at $m/z = 2278$ $[\text{M}]^+$, 2279 $[\text{M} + 1]^+$, 2280 $[\text{M} + 2]^+$, 2281 $[\text{M} + 3]^+$, 2282 $[\text{M} + 4]^+$, 2301 $[\text{M} + \text{Na}]^+$, 2303 $[\text{M} + 2 + \text{Na}]^+$, and 2304 $[\text{M} + 3 + \text{Na}]^+$, in agreement with the proposed structure. The results of the elemental analysis also confirmed the desired compound.

The six-coordinate mononuclear $\text{Co}(\text{III})$ complex **9** was obtained when air was bubbled through a suspension of cobalt(II) complex in ethanol in the presence of pyridine in 44.9% yield. Stoichiometric amount of pyridine was necessary because the presence of excess base was reported to yield a complex in which one of the linking protons had been removed and contained axially bound nitrogen base [38]. In the IR spectrum of $[\text{Co}(\text{LH})_2\text{pyCl}]$, the weak deformation vibration assigned to $\text{O}-\text{H}\cdots\text{O}$ bend was at 1697 cm^{-1} . The $^1\text{H-NMR}$ spectrum of the $\text{Co}(\text{III})$ complex is similar to that of **6**; disappearance of the signal at $\delta = 10.50\text{ ppm}$ of $=\text{N}-\text{OH}$ of **6** can be attributed to

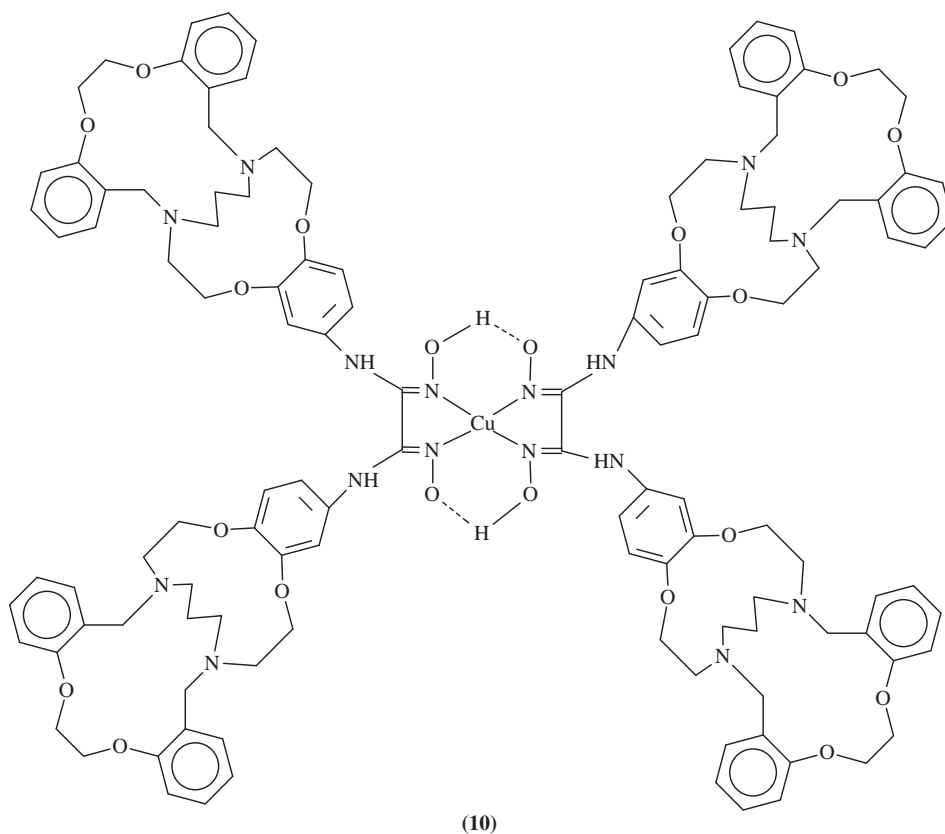


Figure 6. Structure of $[\text{Cu}(\text{HL})_2]$ (**10**).

N–N'-chelation [36]. Upon complexation to Co(III), **6** resonances shift slightly, but the number remains unchanged. Three additional signals due to axially coordinated pyridine were observed. In the proton-decoupled ^{13}C -NMR spectrum of **9**, **6** resonances shift slightly and there are three additional peaks. The mass spectrum (EI) of **9** exhibits molecular ion peaks at $m/z = 2296$ $[\text{M} - 2]^+$, 2299 $[\text{M} + 1]^+$, 2300 $[\text{M} + 2]^+$, and 2321 $[\text{M} + \text{Na}]^+$, confirming formation of the desired compound.

$[\text{Cu}(\text{HL})_2]$ (**10**) was prepared by reaction of **6** with a stoichiometric amount of Cu(II) chloride dihydrate in 42% yield. The IR spectrum of **10** exhibited C=N stretching vibrations at 1613 cm^{-1} and does not show O–H stretches of **6**. The O–H \cdots O observed at 1672 cm^{-1} upon complexation supports formation of **10**. Mass spectra (EI) of **10**, with molecular ion peaks at $m/z = 2186$ $[\text{M} - 2]^+$, 2190 $[\text{M} + 2]^+$, and 2211 $[\text{M} + \text{Na}]^+$, and elemental analysis confirmed formation of the desired compound.

4. Conclusion

In this study, an (*E, E*)-dioxime (H_2L) containing cryptand **7**, **9**, and **10** was synthesized and characterized by ^1H -NMR, ^{13}C -NMR, IR, mass spectroscopic data, and thermal

methods (TG/DTA). BF_2^+ -capped mononuclear Ni(II) complex **8** was synthesized by the reaction of boron-trifluoride diethyl etherate with **7** in acetonitrile. These complexes have a metal:ligand ratio of 1:2 according to elemental analyses. Conformational analysis of the ligands was performed by the DFT and AM1 methods.

Macrobicyclic groups containing nitrogen and oxygen donors bonded to E, E-dioxime (**3**) might have selective ion-binding properties and can be used for remediation of heavy metal pollution or recovery of precious metals from heavy metal wastes.

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References

- [1] M. Kurtoğlu, E. İspir, N. Kurtoğlu, S. Serin. *Dyes Pigm.*, **77**, 75 (2008).
- [2] A. Coşkun, F. Yılmaz, E.G. Akgemci. *J. Inclusion Phenom. Macrocyclic Chem.*, **60**, 393 (2008).
- [3] W.D. Cheng, D.S. Wu, J. Shen, S.P. Huang, Z. Xie, H. Zhang, Y.J. Gong. *Chem. Eur. J.*, **13**, 5151 (2007).
- [4] M. Özer, M. Kandaz, A.R. Özkaya, M. Bulut, O. Güney. *Dyes Pigm.*, **76**, 125 (2008).
- [5] M. Kurtoğlu, M. Dağdelen. *Transition Met. Chem.*, **31**, 382 (2006).
- [6] A. Kilic, F. Durap, M. Aydemir, A. Baysal, E. Taş. *J. Organomet. Chem.*, **693**, 2835 (2008).
- [7] M. Murali, M. Palaniandavar. *Polyhedron*, **26**, 3980 (2007).
- [8] M. Civan, C. Topaçlı, A. Topaçlı, I. Gürol, V. Ahsen. *J. Mol. Struct.*, **834-836**, 482 (2007).
- [9] A. Topaçlı, B. Teşneli, T. Richardson, G. Gümüş, V. Ahsen. *Vib. Spectrosc.*, **40**, 20 (2006).
- [10] Z.A. Savel'eva, R.F. Klevtsova, L.A. Glinskaya, V.N. Ikorskii, S.N. Bizyaev, A.V. Tkachev, S.V. Larionov. *Russ. J. Coord. Chem.*, **32**, 723 (2006).
- [11] T. Das, B.K. Bera, A.K. Datta, A.K. Ghosh. *Transition Met. Chem.*, **34**, 247 (2009).
- [12] M. Kurtoğlu, F. Purtaş, S. Toroğlu. *Transition Met. Chem.*, **33**, 705 (2008).
- [13] B. Burdinski, F. Birkelbach, T. Weyhermüller, U. Florke, H.J. Lengen. *Inorg. Chem.*, **37**, 1009 (1998).
- [14] I.H. Hall, K.F. Bastow, A.E. Warren. *Appl. Organomet. Chem.*, **13**, 819 (1999).
- [15] A. Yari, S. Azizi, A. Kakanejadifard. *Sensors Actuators B: Chemical*, **119**, 167 (2006).
- [16] K. Ohta, R. Higashi, M.I. Kejima, I. Yamamoto, N. Kobayashi. *J. Mater. Chem.*, **8**, 1979 (1998).
- [17] S. Kumar, R. Singh, H. Singh. *J. Chem. Soc., Perkin Trans.*, **1**, 3049 (1992).
- [18] H. Kocaokutgen, S. Özkınalı. *Dyes Pigm.*, **63**, 83 (2004).
- [19] B. Dietrich, J.M. Lehn, J.P. Sauvage, J. Blanzat. *Tetrahedron*, **29**, 1629 (1973).
- [20] R.M. Izatt, J.S. Bradshaw, S.A. Nielsen, J.D. Lamp, J.J. Christensen, D. Sen. *Chem. Rev.*, **85**, 271 (1985).
- [21] P. Meakin, J.P. Jesson. *J. Am. Chem. Soc.*, **96**, 5751 (1974).
- [22] H. An, J.S. Bradshaw, K.E. Krakowiak, C. Zhu, N.K. Dalley, R.M. Izatt. *J. Org. Chem.*, **57**, 4998 (1992).
- [23] P.G. Grimsley, L.F. Lindoy, H.C. Lip, R.J. Smith, J.T. Baker. *Aust. J. Chem.*, **30**, 2095 (1977).
- [24] Y. Gök, Ü. Ocak, H.B. Şentürk. *New J. Chem.*, **25**, 364 (2001).
- [25] D.D. Perrin, W.L.F. Armarego. *Purification of Laboratory Chemicals*, 2nd Edn, Pergamon, Oxford (1989).
- [26] J. Bernstein, A.T.J. Hagler. *J. Am. Chem. Soc.*, **100**, 673 (1978).
- [27] C. Lee, W. Yang, R.G. Parr. *Phys. Rev.*, **37**, 785 (1988).
- [28] A.D. Becke. *J. Chem. Phys.*, **98**, 5648 (1993).
- [29] R. Krishnan, J.S. Binkley, R. Seeger. *J. Chem. Phys.*, **72**, 650 (1980).
- [30] M.J. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart. *J. Am. Chem. Soc.*, **107**, 3902 (1985).
- [31] Z. Biyıklıoğlu, G. Dilber, H. Kantekin. *Transition Met. Chem.*, **31**, 979 (2006).
- [32] H. Kantekin, G. Dilber, Y. Gök, Ü. Ocak, R. Abbasoğlu. *Transition Met. Chem.*, **28**, 51 (2003).
- [33] A. Bilgin, B. Ertem, Y. Gök, G. Dilber, M. Kılıçarslan. *J. Coord. Chem.*, **57**, 883 (2004).

- [34] Y. Gök, H. Kantekin. *New J. Chem.*, **19**, 461 (1995).
- [35] K.A. Lance, K.A. Goldsby, D.H. Busch. *Inorg. Chem.*, **29**, 4537 (1990).
- [36] H. Kantekin, Ü. Ocak, Y. Gök, İ. Acar. *J. Inclusion Phenom. Macrocyclic Chem.*, **48**, 95 (2004).
- [37] M.S. Hussain, H.M. Almohdhar, A. Alarfaj. *J. Coord. Chem.*, **18**, 339 (1988).
- [38] G.N. Schrauzer. *Inorg. Synth.*, **11**, 61 (1968).