J Incl Phenom Macrocycl Chem (2008) 60:235–240
DOI 10.1007/s10847-007-9370-8

ORIGINAL ARTICLE

The synthesis and characterization of a new (E,E)-dioxime containing 20-membered tetraazadioxa macrocyclic moieties and its mononuclear complexes

Zekerıya Biyiklioğlu · Ece Tuğba Güner · Halit Kantekin

Received: 26 April 2007 / Accepted: 21 August 2007 / Published online: 12 September 2007

Abstract A new (E,E)-dioxime, (2*Z*,3*Z*)-9,20-bis[(4-methylphenyl)sulfonyl]-1,4,7,8,9,10,11,12,14,15,17, 18,19, 20,21,22-hexadecahydro-13,16-ethano[1,4,7,11,14,18]dioxatetraazacycloicosino[2,3-*g*] quinoxaline-2,3-dione dioxime (**6**) (H_2L) has been synthesized by reacting cyanogen-di-N-oxide (**5**) with 4,15-bis[(4-methylphenyl)sulfonyl]-2,3,4,5, 6,7,9,10,12,13,14,15,16,17-tetradecahydro-8,11-ethano-1, 18,4,8,11,15-benzodioxatetraazacycloicosine-20,21-diamine (**4**). Mononuclear complexes (**7**) and (**8**) of this ligand have been synthesized by reacting the *vic*-dioxime (H_2L) with $NiCl_2.6H_2O$ and $CoCl_2.6H_2O$ respectively. The BF_2^+ capped Ni(II) and Co(III) complexes (**9**) and (**10**) of the dioxime have been synthesized from (**7**) and (**8**), respectively. The new compounds were characterized by a combination of elemental analysis, ^{1}H- and ^{13}C-NMR, IR. and MS. spectral data.

Keywords (E,E)-Dioxime · Tetraazamacrocycle · BF_2^+-capped complex · Cobalt(III) complex

Introduction

High stability of the complexes prepared with *vic*-dioxime ligands has been extensively used for various purposes in organic, analytical, inorganic, bio, pigment, medical and industrial chemistry [1]. Numerous dioximes and their transition metal complexes have been investigated [2]. The exceptional stability and unique electronic properties of these complexes can be attributed to their planar structure which is stabilized by hydrogen bonding [3].

The polydentate coordination mode of the ligands leads to the formation of homo or heteropolynuclear complexes with cations in the metallo-macrocyclic cavity. This opens the attractive perspective of the design of macrocycle ligands containing additional donor atoms within the N_4, N_2S_2, S_2O_2 or S_4 chain and hydroxyimino nitrogen donor atoms of (E,E)-dioximes. The incorporation of a vic-dioxime unit onto the macrocycle provides an efficient binding site for the transition metal cations by the formation of an MN_4 core with additional two hydrogen bridges [4]. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms causes *vic*-dioximes to be amphoteric ligands which form corrin type square-planar, square-pyramidal and octahedral complexes with transition metal cations such as nickel(II), copper(II) and cobalt(III) as central atoms [5].

The transition metal complexes of polyaza macrocyclic ligands have been subjects of great interest. Another rapidly emerging field of chemical interest, in recent years, is the synthesis of heteronucleating ligands and the coordination chemistry of the heteronuclear complexes that drive such ligands [6].

We have previously synthesized macrocycles containing dioxadithiadiaza macrobicyclic [7], 13-membered dithiadiaza [8] macrocyclic and azacrown [9] moieties. In this paper, we describe the synthesis and characterization of a novel *vic*-dioxime containing a N_4O_2 macrocyclic moiety and some of its complexes.

Experimental

Reagents and apparatus

IR spectra were recorded on a Perkin Elmer 1600 FT-IR spectrophotometer, using KBr pellets or NaCl discs. ^{1}H and

Z. Biyiklioğlu · E. T. Güner · H. Kantekin (✉)
Department of Chemistry, Faculty of Arts and Sciences, Karadeniz Technical University, Trabzon 61080, Turkey
e-mail: halit@ktu.edu.tr

^{13}C-NMR spectra were recorded on a Varian Mercury 200 MHz spectrometer in $CDCl_3$, DMSO, and chemical shifts are reported relative to Me_4Si as internal standard. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS/MS spectrometer. Elemental analyses were determined using a LECO Elemental Analyser (CHNS O932) and Unicam 929 AA spectrophotometer. Melting points were measured on an electrothermal apparatus and are uncorrected. 1,12-Bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ethanododecine [10] **(1)** and 1,2-dinitro-4,5-bis(2-iyodoethoxy)benzene [11] **(2)** were synthesized according to reported procedures. Commercially available solvents were dried and purified by conventional procedures [12].

Preparation of 4,15-bis[(4-methylphenyl)sulfonyl]-20,21-dinitro-2,3,4,5,6,7,9,10,12,13,14, 15,16,17-tetradecahydro-8,11-ethano-1,18,4,8,11,15-benzodioxatetraazacycloicosine (**3**)

1,12-Bis[(4-methyl)sulfonyl]-1,2,3,4,6,7,9,10,11,12-decahydro-5,8-ethanododecine **1** (2 g, 3.93 mmol) and in dry acetonitrile (150 ml) containing finely ground anhydrous Cs_2CO_3 (3.20 g, 9.826 mmol) and purged under argon in a Schlenk system connected to a vacuum-line was heated and stirred under argon until **1** was dissolved. This solution was stirred at 110 °C and a solution of 1,2-dinitro-4,5-bis(2-iyodoethoxy)benzene **2** (1.99 g, 3.93 mmol) in dry acetonitrile (50 ml) was added dropwise over a period of 4 h. The reaction was monitored by TLC using chloroform/petroleum ether/methanol (7:2:1) and was completed in 168 h at the above temperature. At the end of this period, the reaction mixture was filtered and washed with dry acetonitrile and then the combined solution was evaporated to dryness under reduced pressure. The oily product was mixed with water (50 ml) and then extracted with chloroform (3 × 70 ml). The combined extract was washed with water, dried over $MgSO_4$ and then filtered and evaporated to dryness to give clared red solid. This product was chromatographed on silica gel with chloroform:methanol (9.5:0.5) as eluents.Yield: 1.82 g (61%), m.p: 120–122 °C. I.r. (KBr tablet), (cm^{-1}): 3060 (Ar–H), 2925–2854 (C–H), 1597, 1540–1335 (Asm. N–O), 1327–1158 (SO_2), 1284, 1089, 814, 657, 549. ^{1}H-n.m.r. ($CDCl_3$), (δ:ppm): 7.78 (s, 2H, Ar–H), 7.62 (d, 4H, Ar–H), 7.19 (d, 4H, Ar–H), 3.83 (t, 4H, CH_2–O), 3.49 (t, 4H, CH_2–N), 3.22 (t, 4H, CH_2–N), 2.67 (t, 4H, CH_2–N), 2.42 (s, 6H, CH_3), 2.36 (t, 8H, CH_2–CH_2), 1.52 (m, 4H, CH_2). ^{13}C-n.m.r. ($CDCl_3$), (δ:ppm): 146.06, 145.27, 137.25, 136.22, 131.18, 129.86, 101.51, 73.77, 53.27, 52.34, 51.81, 47.29, 29.14, 26.38. (Found: C, 53.9 ; H, 5.5 ; N, 11.3 ; $C_{34}H_{44}N_6O_{10}S_2$ calcd.: C, 53.7; H, 5.8; N, 11.0%). MS (EI), (m/z): 761 $[M + 1]^+$.

Preparation of 4,15-bis[(4-methylphenyl) sulfonyl]-2,3,4,5,6,7,9,10,12,13,14,15,16,17-tetradecahydro-8,11- ethano-1,18,4,8,11,15-benzodioxatetraazacycloicosine-20,21-diamine (**4**)

Compound **3** (1.6 g, 2.10 mmol) was dissolved in dioxane (80 ml) by heating at the reflux temperature. Palladium (10%) /activated carbon (0.51 g) was added to the solution and 9.5 ml of hydrazine hydrate (100%) was then added dropwise during 1 h at 50 °C . The reaction mixture was waited under reflux, stirred for 12 h, and then filtered through Celite and washed with dioxane. The solution was evaporated to dryness under reduced pressure to give orange oily product. This product was purified by using column chromatography [silica gel column (chloroform/petroleum ether)(8:2)]. Yield: 1.0 g (68%). I.r. (KBr tablet), (cm^{-1}): 3339–3197 (NH_2), 3059 (Ar–H), 2926–2855 (C–H), 1598, 1516, 1463, 1328–1157 (SO_2), 1287, 1090, 960, 815, 657, 550 . ^{1}H-n.m.r. ($CDCl_3$), (δ:ppm): 7.73 (d, 4H, Ar–H), 7.31 (d, 4H, Ar–H), 6.28 (s, 2H, Ar–H), 4.21 (br, 4H, NH_2), 3.73 (t, 4H, CH_2–O), 3.59 (t, 4H, CH_2–N), 3.34 (t, 4H, CH_2–N), 2.71 (t, 4H, CH_2–N), 2.43 (s, 6H, CH_3), 2.39 (t, 8H, CH_2–CH_2), 1.61 (m, 4H, CH_2). ^{13}C-n.m.r. ($CDCl_3$), (δ:ppm): 148.67, 144.56, 134.62, 133.792, 131.34, 129.81, 104.46, 73.63, 53.25, 52.46, 51.95, 44.55, 29.93, 27.28. (Found: C, 58.4 ; H, 6.7 ; N, 11.6; $C_{34}H_{48}N_6O_6S_2$ calcd.: C, 58.3; H, 6.9; N, 12.0%). MS (EI), (m/z): 701 $[M + 1]^+$.

Preparation of (2Z,3Z)-9,20-bis[(4-methylphenyl)sulfonyl]-1,4,7,8,9,10,11,12,14,15,17,18, 19,20,21,22-hexadecahydro-13,16-ethano[1,4,7,11,14,18]dioxatetraazacycloicosino[2,3-g] quinoxaline-2,3-dione dioxime (H_2L) (**6**)

A solution of cyanogen-di-N-oxide **5** in CH_2Cl_2 (30 ml), which was prepared from (E,E)-dichloroglyoxime (0.177 g, 1.14 mmol) and an aqueous solution of Na_2CO_3 (30 ml 0.1 N), were added to a cold solution (–10 °C) of **4** (0.8 g, 1.14 mmol) in cold CH_2Cl_2 (50 ml). The reaction was continued for 12 h at –10 °C and then allowed to warm to room temperature. It was then filtered and the brown precipitate so obtained. This product was crystallized from ethanol and washed with Et_2O and dried in vacuo Yield: 0.645 g (72%), m.p: 162–164 °C (decomp.). I.r. (KBr tablet), (cm^{-1}): 3326 (O–H), 3208 (N–H), 3021(Ar–H), 2943- 2879 (C–H), 1637 (C=N), 1593, 1516, 1452, 1331–1156 (SO_2), 1274, 1089, 951 (N–O), 815,657, 550. ^{1}H-n.m.r. (DMSO-d_6), (δ:ppm): 10.15 (s, 2H, D_2O exchangeable OH), 9.38 (s, 2H, D_2O exchangeable NH), 7.63 (d, 4H, Ar–H), 7.34 (d, 4H, Ar–H), 6.50 (s, 2H, Ar–H), 3.92 (t, 4H, CH_2–O), 3.42 (t, 4H, CH_2–N), 3.14 (t, 4H,

CH_2–N), 2.68 (t, 4H, CH_2–N), 2.40 (s, 6H, CH_3), 2.33 (t, 8H, CH_2–CH_2), 1.58 (m, 4H, CH_2). ^{13}C-n.m.r. (DMSO-d_6), (δ:ppm): 149.32, 143.11, 142.47, 136.04, 129.72, 126.80, 101.49, 73.95, 54.52, 52.26, 51.87, 46.25, 27.91, 27.14. (Found: C, 55.4 ; H, 6.0 ; N, 14.0; $C_{36}H_{48}N_8O_8S_2$ calcd.: C, 55.1; H, 6.2; N, 14.3%). MS (EI), (m/z): 785 $[M]^+$.

Preparation of $[Ni(HL)_2]$ (**7**)

A solution of $NiCl_2.6H_2O$ (0.045g, 0.19 mmol) in EtOH (10 ml) was added to a solution of H_2L (0.30 g, 0.38 mmol) in EtOH (25 ml) with stirring at 60 °C. After the addition, a distinct change in color from pale to dark brown and a decrease in the pH of the solution to 2.36 was observed. A solution of KOH (0.056 g, 1 mmol) in EtOH (10 ml) was added to this solution at 60 °C. An increase in the pH of the solution to 4.70 was observed. The reaction mixture was stirred for 2 h at 60 °C. After cooling to room temperature, the mixture was filtered and the residue was washed with water, EtOH and Et_2O and then dried in vacuo to give a dark brown solid. Yield: 0.21 g (69%), m.p: >300 °C I.r. (KBr tablet), (cm^{-1}): 3368 (N–H), 3058 (Ar–H), 2925–2846 (C–H), 1716 (O–H···O), 1619 (C=N), 1593, 1558, 1493, 1329–1156 (SO_2), 1086, 952 (N–O). ^{1}H-n.m.r. (DMSO-d_6), (δ:ppm): 16.32 (s, 2H, O–H···O), 8.12 (br, 4H, N–H), 7.61 (d, 8H, Ar–H), 7.33 (d, 8H, Ar–H), 6.75 (s, 4H, Ar–H), 3.95 (t, 8H, CH_2–O), 3.48 (t, 8H, CH_2–N), 3.17 (t, 8H, CH_2–N), 2.71 (t, 8H, CH_2–N), 2.43 (s, 12H, CH_3), 2.37 (t, 16H, CH_2–CH_2), 1.63 (m, 8H, CH_2). ^{13}C-n.m.r. (DMSO-d_6), (δ:ppm): 148.12, 143.82, 143.23, 133.76, 130.82, 128.19, 126.48, 100.65, 76.44, 53.55, 52.39, 48.73, 23.11, 22.57. (Found: C, 53.4 ; H, 5.9 ; N, 13.7 ; Ni, 3.7 ; $C_{72}H_{94}N_{16}O_{16}S_4Ni$ calcd.: C, 53.2; H, 5.8; N, 13.8; Ni, 3.6%). MS (FAB), (m/z): 1624 $[M]^+$.

Preparation of $[Co(HL)_2pyCl]$ (**8**)

A solution of $CoCl_2.6H_2O$ (0.044 g, 0.19 mmol) in EtOH (5 ml) was added to a hot solution of H_2L (0.3 g, 0.38 mmol) in EtOH (20 ml). Pyridine (0.002 g, 0.66 mmol) in EtOH (1 ml) was added to the above solution while heating. The reaction mixture was heated and stirred for 45 minutes at 60 °C then cooled to room temperature and a stream of air was bubbled through the solution for 2 h. The mixture was filtered and the brown precipitate was washed with cold EtOH and Et_2O and then dried in vacuo. Yield: 0.240 g (72%), m.p: >300 °C. I.r. (KBr tablet), (cm^{-1}): 3230 (N–H), 3065 (Ar–H), 2924–2854 (C–H), 1711 (O–H···O), 1622 (C=N), 1597, 1463, 1325–1158 (SO2), 1287, 1122, 1071, 965 (N–O). ^{1}H-n.m.r. (DMSO-d_6), (δ:ppm): 16.21 (s, 2H, O–H···O), 8.23 (d, 2H, py–H), 8.06 (br, 4H, N–H), 7.97 (t, 2H, py–H), 7.84 (t, 1H, py–H), 7.55 (d, 8H, Ar–H), 7.30 (d, 8H, Ar–H), 6.71 (s, 4H, Ar–H), 3.90 (t, 8H, CH_2–O), 3.41 (t, 8H, CH_2–N), 3.14 (t, 8H, CH_2–N), 2.70 (t, 8H, CH_2–N), 2.41 (s, 12H, CH_3), 2.38 (t, 16H, CH_2–CH_2), 1.66 (m, 8H, CH_2). ^{13}C-n.m.r. (DMSO-d_6), (δ:ppm): 151.42, 148.04, 143.72, 143.02, 140.76, 133.83, 130.64, 128.06, 126.66, 125.38, 100.42, 76.48, 53.62, 52.52, 48.82, 23.31, 22.63. (Found: C, 53.3 ; H, 5.8 ; N, 13.5 ; Co, 3.5 ; $C_{77}H_{99}N_{17}O_{16}S_4CoCl$ calcd.: C, 53.1; H, 5.7; N, 13.7; Co, 3.4%). MS (FAB), (m/z): 1742 $[M + 1]^+$.

Preparation of $[Ni(LBF_2)_2]$ (**9**)

A suspension of complex **7** (0.18 g, 0.11 mmol) in (40 ml) MeCN was refluxed under an Ar atmosphere. $Et_2O.BF_3$ (0.15 ml, 0.55 mmol) was added with stirring, immediately giving a red solution. The mixture was boiled under reflux for 5 h. The solvent was removed under vacuum and the residue was dissolved in 15 ml of MeCN and then evaporated to dryness. The product was recrystallized from EtOH, then filtered off, washed with Et_2O and dried in vacuo. Yield: 0.13 g (70%), m.p: >300 °C. I.r. (KBr tablet), (cm^{-1}): 3211 (N–H), 3056 (Ar–H), 2925–2854 (C–H), 1624 (C=N), 1596, 1455, 1328–1157 (SO_2), 1110 (B–O), 1083 (B–F), 972 (N–O). ^{1}H-n.m.r. (DMSO-d_6), (δ:ppm): 8.25 (br, 4H, N–H), 7.70 (d, 8H, Ar–H), 7.38 (d, 8H, Ar–H), 6.83 (s, 4H, Ar–H), 3.97 (t, 8H, CH_2–O), 3.52 (t, 8H, CH_2–N), 3.22 (t, 8H, CH_2–N), 2.73 (t, 8H, CH_2–N), 2.45 (s, 12H, CH_3), 2.38 (t, 16H, CH_2–CH_2), 1.64 (m, 8H, CH_2). ^{13}C-n.m.r. (DMSO-d_6), (δ:ppm): 148.23, 143.86, 143.30, 133.80, 130.87, 128.23, 126.50, 100.70, 76.48, 53.59, 52.43, 48.76, 23.22, 22.66. (Found: C, 50.4 ; H, 5.5 ; N, 13.1 ; Ni, 3.5; $C_{72}H_{92}N_{16}O_{16}S_4B_2F_4Ni$ calcd.: C, 50.2; H, 5.4; N, 13.0; Ni, 3.4%). MS (FAB), (m/z): 1719 $[M-3]^+$.

Preparation of $[Co(LBF_2)_2pyCl]$ (**10**)

A suspension of complex **5** (0.2 g, 0.11 mmol) in MeCN (40 ml) was refluxed under an Ar atmosphere. $Et_2O.BF_3$ (0.15 ml, 0.55 mmol) was added with stirring, immediately giving a red solution. The reaction was allowed to stand at the reflux temperature for 5 h. The solvent was removed under vacuum and the residue was dissolved in 10 ml of MeCN and then evaporated to dryness. The product was recrystallized from EtOH, then filtered off, washed with Et_2O and dried in vacuo. Yield: 0.14 g (68%), m.p: >300 °C. I.r. (KBr tablet), (cm^{-1}): 3296 (N–H), 3063 (Ar–H), 2925–2851 (C–H), 1638 (C=N), 1597, 1489, 1331–1155 (SO_2), 1148 (B–O), 1067 (B–F), 956 (N–O). ^{1}H-n.m.r. (DMSO-d_6), (δ:ppm): 8.27 (d, 2H, py–H), 8.13

(br, 4H, N–H), 8.05 (t, 2H, py–H), 7.85 (t, 1H, py–H), 7.57 (d, 8H, Ar–H), 7.33 (d, 8H, Ar–H), 6.73 (s, 4H, Ar–H), 3.92 (t, 8H, CH_2–O), 3.44 (t, 8H, CH_2–N), 3.15 (t, 8H, CH_2–N), 2.73 (t, 8H, CH_2–N), 2.44 (s, 12H, CH_3), 2.39 (t, 16H, CH_2–CH_2), 1.68 (m, 8H, CH_2). ^{13}C-n.m.r. (DMSO-d_6), (δ:ppm): 151.48, 148.09 143.77, 143.09, 140.82, 133.87, 130.67, 128.08, 126.68, 125.41, 100.46, 76.50, 53.61, 52.50, 48.80, 23.35, 22.66. (Found: C, 50.5 ; H, 5.5 ; N, 13.0 ; Co, 3.3; $C_{77}H_{97}N_{17}O_{16}S_4B_2F_4CoCl$ calcd.: C, 50.3; H, 5.3; N, 12.9; Co, 3.2%). MS (FAB), (m/z): 1836 $[M]^+$. (Fig. 1–4).

Result and discussion

The synthesis of the [E, E]-dioxime [H_2L] and its mononuclear complexes are summarized in Scheme 1. The macrocyclic compound (**3**) was synthesized by the condensation of compound (**1**) with compound (**2**) in the presence of Cs_2CO_3 under an argon atmosphere at 110 °C. This compound was synthesized in a moderate yield (61%). In the ^{1}H-NMR. spectrum of (**3**), the chemical shifts due to Ar–H, CH_2–O, CH_2–N protons were observed at δ = 7.78, 3.83, 3.49 ppm., respectively. In the ^{1}H-NMR spectrum of this compound the chemical shift of NH proton in starting compound (**1**) disappear after the macrocyclization reaction. ^{13}C-NMR spectral data were also in good agreement with the formation of (**3**). The chemical shifts for aromatic carbon atoms, CH_2–O and CH_2–N were observed at δ = 146.06, 137.25, 101.51, 73.77 and 52.34 p.p.m. respectively. In the IR spectrum of compound (**3**), the characteristic stretching vibrations, belonging to NO_2 and SO_2 groups, were observed at 1540–1335 cm^{-1} and 1327–1158 cm^{-1}, respectively. The mass spectrum (EI) of (**3**) showed a molecular ion peak (EI) at m/z = 761 $[M + 1]^+$, confirming formation of the desired compound.

Reduction of the dinitro-substitued macrocycle (**3**) using 10% palladium-activated charcoal and hydrazine hydrate (100%) in hot dioxane as previously utilized [13], gave the diamine-substitued macrocycle (**4**) in 68%. In the ^{1}H-NMR spectrum of (**4**), the chemical shifts due to Ar–H, NH_2, CH_2–O and CH_2–N protons were observed at δ = 6.28, 4.21, 3.73 and 3.34 ppm., respectively. ^{13}C-NMR spectral data were also in good agreement with the formation of

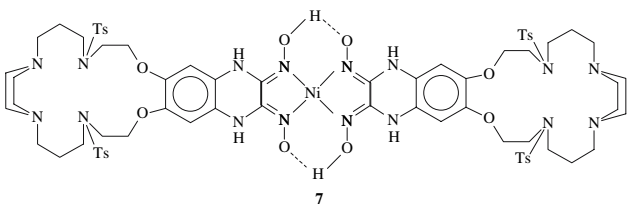

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Fig. 1 [Ni(HL_2)]

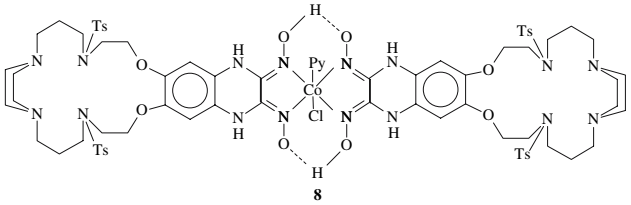

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Fig. 2 [Co(HL_2)pyCl]

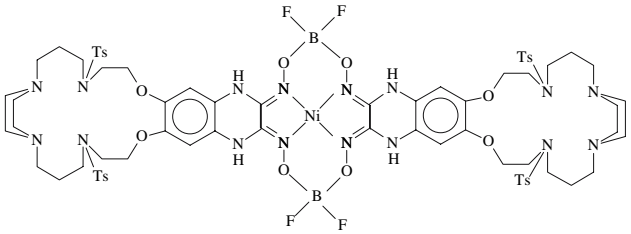

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Fig. 3 [Ni(LBF_2)$_2$]

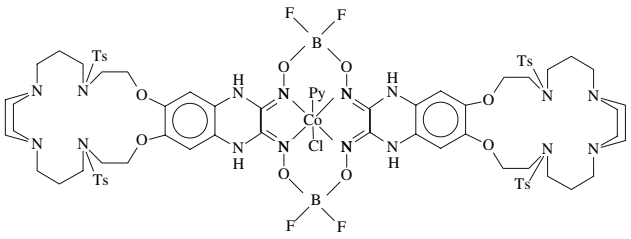

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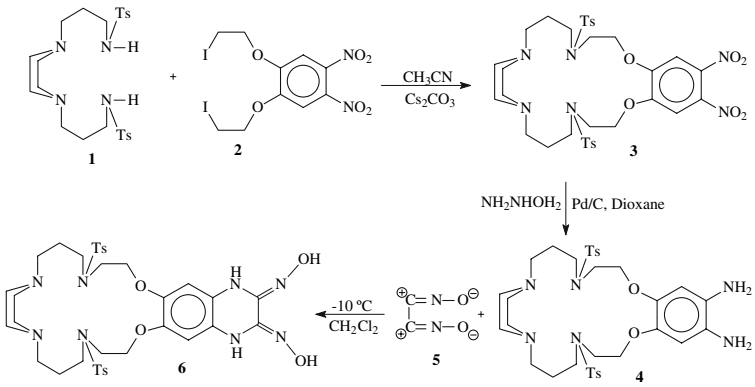
Fig. 4 [Co(LBF_2)pyCl]

compound (**4**). The chemical shifts for aromatic carbon atoms, CH_2–O and CH_2–N were observed at δ = 148.67, 134.62, 104.46, 73.63 and 52.46 p.p.m. respectively. In the IR spectrum of compound (**4**), the characteristic strecthing vibrations, belonging to NH_2, SO_2 groups, were observed at 3339–3197 and 1328–1157 cm^{-1}, respectively. The mass spectrum (EI) of (**6**) showed a molecular ion peak (EI) at m/z = 701 $[M + 1]^+$ confirming formation of the desired compound.

H_2L which containing a tetraazadioxamacrocyclic unit, was prepared in yield 72% by condensation of (**4**) with cyanogen-di-N-oxide (**5**) in CH_2Cl_2 under a nitrogen atmosphere at –10 °C . In the ^{1}H-n.m.r. spectrum of [H_2L], the chemical shifts assigned to the OH, NH, CH_2–O, CH_2–N and CH_2–CH_2 protons were observed at 10.15, 9.38, 3.92, 3.42 and 2.33 ppm., respectively. These OH and NH protons were also identified easily by D_2O exchange. The equivalent signals from the hydroxyimino groups confirms the (E, E)-form of the *vic*-dioxime [14]. More detailed information about the structure of [H_2L] was obtained by ^{13}C-NMR spectral data. A signal assigned to the azomethine carbon atom is found at 142.47 ppm. In the proton-decoupled ^{13}C-NMR spectrum of [H_2L], the resonance of

Scheme 1



the azomethine group is found at 142.47 ppm and this unique signal for the oxime groups again confirms the E,E form of the *vic*-dioxime [15]. In the IR spectrum of this compound, the characteristic stretching vibrations, of the OH, NH and C=N groups, were observed at 3326, 3208 and 1637 cm^{-1}, respectively. The mass spectrum (EI) of (H_2L) showed a molecular ion peak at m/z = 785 $[M]^+$.

The mononuclear nickel(II) complex (**7**), was synthesized by a standard procedure in good yield (69%) [16]. This mononuclear complex has a metal:ligand ratio of 1:2 according to the elemental analysis and mass spectral data. The ^{1}H-NMR spectrum of (**7**), does not show signals equivalent to the OH protons observed for free [H_2L], but a new resonance at lower field at (16.32 ppm) could be assigned to the formation of hydrogen bridges which could easily be identified by deuterium Exchange [17]. The ^{13}C-NMR spectrum of this complex (**7**), was similar to that of the free dioxime but with slight shift, as expected. In the IR spectrum of (**7**), the absence of O–H stretching vibrations and presence of bending vibrations assigned to O–H···O groups observed at 1716 cm^{-1}, also supports the formation of desired complex. The fast atom bombardment mass spectrum of (**7**) showed a molecular ion peak at m/z = 1624 $[M]^+$ confirming formation of the desired compound.

The mononuclear cobalt(III) complex (**8**) was obtained when O_2 was bubbled through a suspension of the cobalt(II) complex in ethanol in the presence of pyridine as the axial ligand. This complex again has a metal:ligand ratio of 1:2 according to elemental analysis data and mass spectra. In the ^{1}H-NMR spectrum of the mononuclear cobalt(III) complex the resonance of the intramolecular binding O–H···O protons appears as a singlet at 16.21 ppm and this shift could easily be identified by deuterium exchange. The proton decoupled ^{13}C-NMR spectrum of [$Co(HL)_2$(py)C1] is displayed as a singlet at 143.02 ppm corresponding to the hydroxyimino group. In the i.r. spectrum of [$Co(HL)_2$(py)C1], the weak deformation assigned to the intramolecularly hydrogen bonded O–H···O bending vibration was observed at 1711 cm^{-1}. The C=N stretch decreases from 1637 cm^{-1} in the free ligand to 1622 cm^{-1} in (**8**). A lowering of the vibration frequency (relative to free ligands) for the C=N absorbtion in the H-bonded cobalt(III) complex indicates coordination through the N atoms [18]. The fast atom bombardment mass spectrum of this complex exhibits a molecular ion peak at m/z = 1742 $[M + 1]^+$ confirming formation of the desired compound.

The template synthesis of the macrocyclic nickel(II) complex (**9**) was prepared by adding boron trifluoride to a refluxing solution of precursor nickel(II) complex (**7**) in acetonitrile. The hydrogen-bridging protons were replaced by BF_2^+ groups. In the ^{1}H-NMR spectrum of the BF_2^+-capped macrocyclic complex, the O–H···O bridged protons belonging to the precursor complex (**9**) are absent. The bridging BF_2 groups cause the resonances of complex (**9**) to shift downfield relative to these of (**7**). The IR spectrum of (**9**) shows bands assigned to NH, C=N and N–O stretching vibrations at 3211, 1624 and 972 cm^{-1}, respectively. The bending vibration of the O–H···O is absent, but new peaks assigned to the BF_2 moiety appear at 1110 and 1083 cm^{-1} for the B–O and B–F bonds, respectively [19]. The fast atom bombardment mass spectrum of this complex exhibits a molecular ion peak at m/z = 1719 $[M\text{-}3]^+$ confirming formation of the desired compound.

The BF_2-bridged macrocyclic cobalt(III) complex [$Co(LBF_2)_2$(py)C1] (**10**) was prepared from cobalt(III) complex (**8**) by a similar procedure as for the nickel complex (**9**). In the ^{1}H-NMR spectrum of (**10**), the O–H···O bridged protons of the precursor were absent, and the BF_2 groups caused the other resonances shift downfield relative to these of (**8**). The IR spectrum of (**10**) shows strong bands assigned to NH, C=N and N–O at 3296, 1638 and 956 cm^{-1}, respectively. The O–H···O bond was absent and new peaks due to the BF_2 group were observed at 1148 and 1067 cm^{-1} for the B–O and B–F bonds, respectively. The fast atom bombardment mass spectrum of this complex exhibits a molecular ion peak at m/z = 1836 $[M]^+$, confirming formation of the desired compound.

We tried to isolate crystalline product (preferably 9 and 10) but, we couldn't achieve it. We couldn't obtain these

product as a single crystal. We obtained its solid product. So, we couldn't observe its X-ray crystallography.

Acknowledgements This study was supported by the Research Fund of Karadeniz Technical University, (Trabzon-Turkey).

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