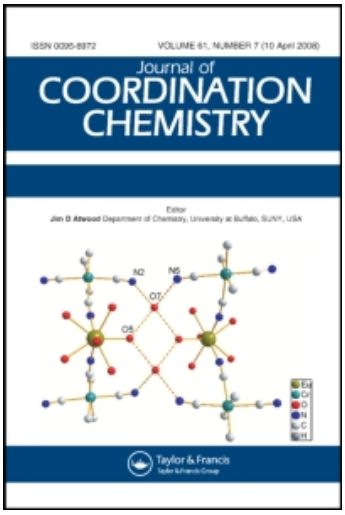

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Synthesis and characterization of novel vic-dioxime and its mononuclear complexes containing tetraazadioxamacrobicyclic moieties

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Synthesis and characterization of novel *vic*-dioxime and its mononuclear complexes containing tetraazadioxamacrobicyclic moieties

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A (*E*, *E*)-dioxime, *N*,*N*′-*bis*(7-aminobenzo-17,23-dimethyl-4,11-dioxa-1,14,17,23-tetraazapentacyclo[12.10.10$^{0.5,10}$]hexadiconta-1,5,7,12,14-pentane)diaminoglyoxime (**H_2L**) has been synthesized from (*E*, *E*)-dichloroglyoxime and 7-aminobenzo-17,23-dimethyl-4,11-dioxa-1,14,17,23-tetraazapentacyclo[12.10.10$^{0.5,10}$]hexadiconta-1,5,7,12,14-pentane which has been prepared from 7-nitro-17,23-dimethyl-4,11-dioxa-1,14,17,23-tetraazapentacyclo[12.10.10$^{0.5,10}$]hexadiconta-1,5,7,12,14-pentane. A mononuclear Ni(II) complex with a metal : ligand ratio of 1 : 2 was prepared and then a Ni(II) complex bridged with BF_2^+ was obtained by reaction with boron trifluoride etherate. The structure of the dioxime and its transition metal complexes are proposed according to elemental analysis, ^{1}H NMR, IR and mass spectral data.

Keywords: (*E*, *E*)-Dioxime; Macrobicycle; Template effect; Nickel(II) complex; BF2+-capped complex; Cyanogen di-*N*-oxide

1. Introduction

Interest in macropolycyclic chemistry has led to numerous synthetic routes for affecting macropolycyclization, giving access to a number of macropolycyclic molecules [1]. The reactivities of these compounds depend on features such as the nature, number and arrangement of donor groups, the nature of the backbone and macrocyclic hole size of the chelate rings. Macrocyclic or polymacrocyclic systems can be used as models for biological systems to study magnetic exchange phenomena as synthetic ionophores and host-guest interactions [2]. Synthetic macrocycles have been widely studied as complexation agents used for selective extraction of alkaline, earth alkaline and heavy metals, an area of great interest in environmental chemistry. The complexation properties of functionalized cyclams have been extensively studied in recent years [3]. Cyclam and its derivatives coordinate transition metal ions with very large

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stability constants [4]. The structure of cyclam show that the macrocycle adopts an endodentate, centrosymmetric conformation with two, three-center hydrogen bonds. Cryptands are bimetallic ligand system of three-dimensional structure able to encapsulate a metal ion. Owing to their architectural and functional plasticity, macrobicyclic compounds are especially attractive for designing biomimetic and abiotic receptors for inorganic and organic substrates [5]. The replacement of oxygen binding sites in cryptands by nitrogen or sulfur donors decreases both stability and selectivity of some metal cryptates. However, polyamines or mixed-donor macrobicycles provide a means of trapping transition metal ions inside the molecular cavity [6].

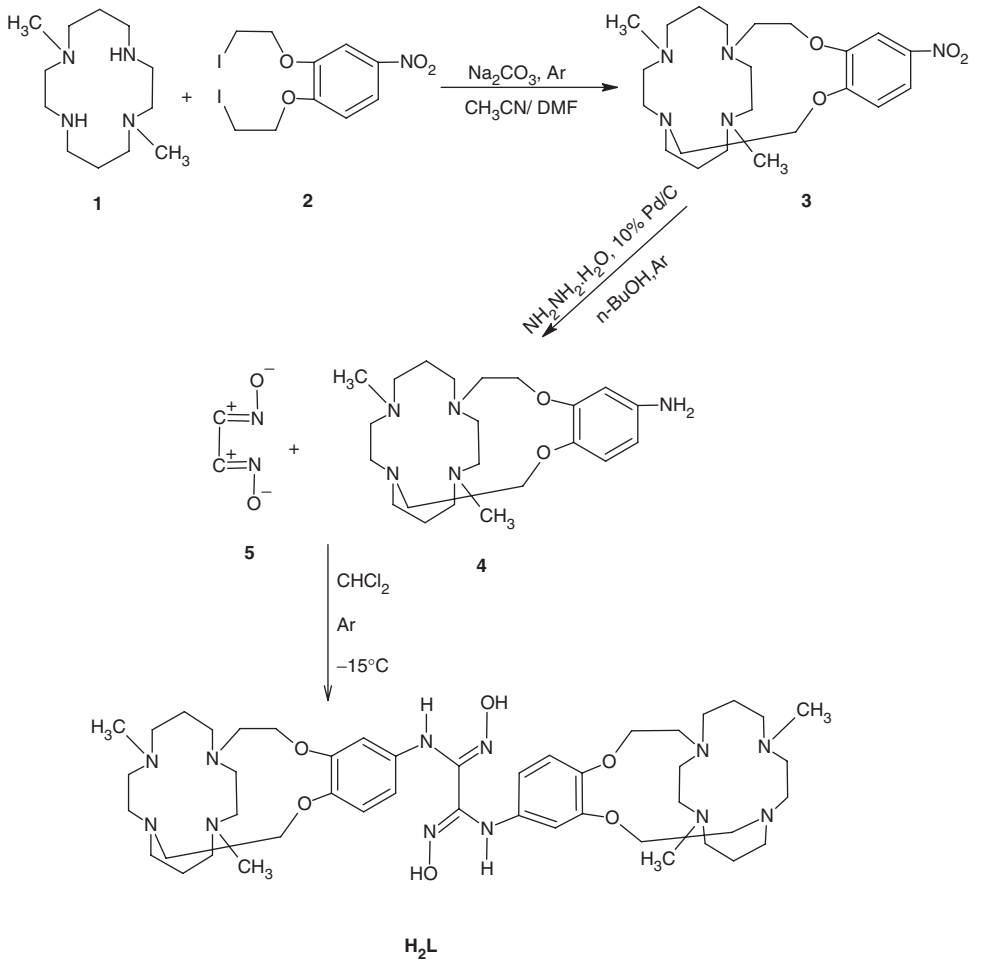
(*E*, *E*)-Dioximes and their transition metal complexes have been widely investigated as analytical reagents, as models for biological systems such as vitamin B_{12}, as compounds having stacking important for semiconducting properties [7]. The exceptional stability and unique electronic properties of the (*E*, *E*)-dioxime complexes can be attributed to their planar structure, stabilized by hydrogen bridges. Bridging protons of dioxime ligands have been replaced by BF_2^+ groups, firming the macrocyclic structure while removing acidic protons [8]. (*E*, *E*)-Dioximes and their mono or polynuclear complexes with features of transition metal, alkaline metal, alkaline earth metal and macrobicyclic chemistry all in the same molecule have been recently reported [9].

We report here synthesis and characterization of an (*E*, *E*)-dioxime containing a macrobicyclic moiety and its nickel(II) complex as well as the properties of the BF_2^+-capped complex. The structure of the ligand and complexes has been examined by a combination of elemental analysis, ^{1}H NMR, IR and MS spectral data.

2. Results and discussion

The synthesis of macrobicyclic compound **3** was performed by condensation of 1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane [10] with 4-nitro-1,2-*bis*(2-iodoethoxy)benzene [11] in the presence of Na^+ as promotor [12], refluxing the mixture of dry acetonitrile and DMF to give 77% yield (scheme 1). The ^{1}H NMR spectrum of **3** shows doublets at $\delta = 7.95$ and 6.90 ppm and a singlet at $\delta = 7.79$ ppm indicating the presence of ArH protons. Triplets at $\delta = 4.67$ and 4.14 ppm correspond to neighboring $ArOCH_2$ groups; multiplets at $\delta = 3.81$, 3.39 and 2.80 ppm are due to NCH_2 protons which also indicates a different chemical environment. Disappearance of the N–H stretching vibrations (seen in the IR spectrum of the precursor tetraaza compound) also suggests formation of macrobicycle (**3**). This compound displays the expected molecular ion peak in its mass spectrum at $m/z = 436$ corresponding to $[M+1]^+$.

Reduction of the nitro-substituted macrobicycle (**3**) using 10% palladium-activated charcoal and hydrazine hydrate (100%) in hot *n*-butanol gave the amine-substituted macrobicycle (**4**) in 81.6% yield [13]. In the ^{1}H NMR spectrum of **4**, there is a broad signal at $\delta = 4.86$ ppm due to the primary aromatic amine protons, confirming reduction. The proton chemical shifts of **4** are upfield for the aromatic protons as doublets at $\delta = 6.73$ and 6.13 ppm and a singlet at $\delta = 6.27$ ppm from formation of aromatic primary amine instead of nitro. The other chemical shifts of this compound are very similar to those of **3**. The disappearance of the $ArNO_2$ resonance at 1340 cm^{-1} and appearance of $Ar–NH_2$ stretching and bending vibrations at 3290–3164



Scheme 1. Synthesis of H_2L.

and 1600 cm^{-1}, respectively, also confirm formation of **4**. The mass spectrum of **4** shows an expected molecular ion peak at $m/z = 406$ $[M+1]^+$, supporting the proposed formulation.

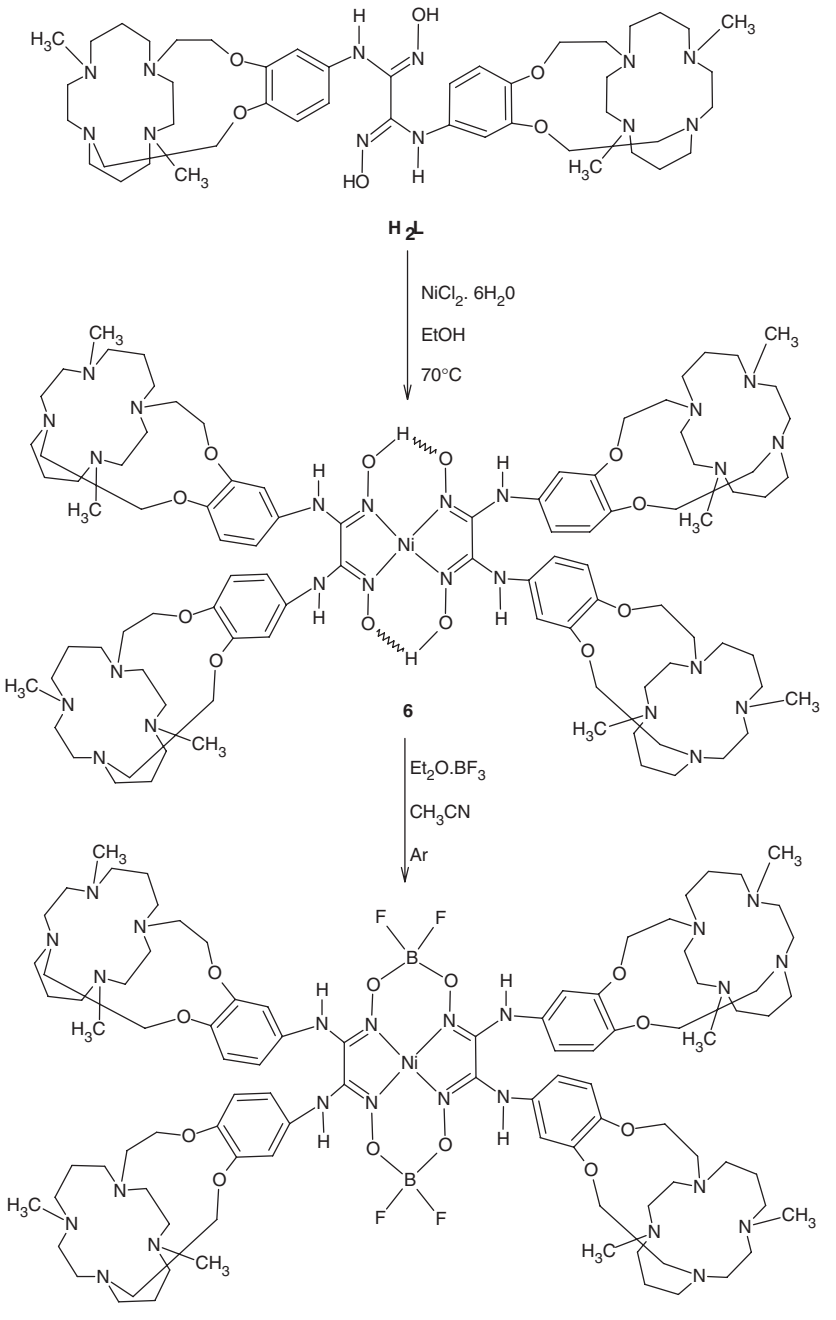
The amine substituted macrobicycle (**4**) was converted into the diaminoglyoxime by reaction with cyanogen di-*N*-oxide (**5**) at $-15^{\circ}C$ under argon in dichloromethane in 65.8% yield. In the ^1H NMR spectrum of $\mathbf{H_2L}$, the broad signal at $\delta = 4.86$ ppm of the NH_2 group disappeared and deuterium exchangeable new signals at $\delta = 8.11$ and 10.87 ppm were observed, assigned to NH connected to hydroxyimino group and N–OH protons, respectively. A single chemical shift for N–OH protons clearly indicates that the oxime stereoisomers are (*E*, *E*) [14]. In the IR spectrum of $\mathbf{H_2L}$, the stretching vibrations at 3390, 3198 and 1636 cm^{-1} are assigned to the oxime N–H, O–H and C=N groups, respectively. These values are consistent with previously reported diaminoglyoxime derivatives [15]. This was also supported by the presence of the characteristic molecular ion peak $m/z = 895$ $[M+1]^+$.

This ligand has four nitrogen donors in the macrocyclic cavity in addition to two oxime groups; all or some of these donor groups can participate in complex formation depending on reaction conditions [16]. Under mild conditions, only mononuclear Ni(II) complex was obtained even when the metal ion was used in excess. Since a distinct lowering in the pH of the solution was observed during complex formation, deprotonation of the ligand with subsequent *N*,*N*′-chelation with the *vic*-dioxime groups probably occurs. Complexation of the (*E*, *E*)-dioxime with Ni(II) was carried out by addition of a solution of $NiCl_2 \cdot 6H_2O$, an equivalent amount of KOH in ethanol and a hot solution of **H_2L** in ethanol to afford the 1 : 2 (metal : ligand) complex **[Ni(HL)$_2$]** in 91.3% yield (scheme 2). The ^{1}H NMR spectrum of this complex provides evidence for square-planar Ni(II). Disappearance of the signal at $\delta = 10.87$ ppm for N–OH in the precursor *vic*-dioxime and existence of deuterium exchangeable intramolecular hydrogen-bridge protons at lower field ($\delta = 16.92$ ppm) indicate formation of the Ni(II) complex. The other chemical shifts of **H_2L** and **[Ni(HL)$_2$]** are similar to those of the free ligand. Upon complexation with Ni(II), the free ligand resonances shifted slightly as expected. The disappearance of the O–H stretching vibrations and the presence of weak bending absorptions observed at 1702 cm^{-1} indicates the existence of intramolecular hydrogen bonds, supporting formation of complex. Shift of the C=N resonance to lower frequency in the IR spectrum of **[Ni(HL)$_2$]** can also be attributed to *N*,*N*′-chelation [17]. The mass spectrum of this complex showed the expected molecular ion peak at $m/z = 1845$ $[M+1]^+$, confirming formation of the mononuclear complex. All these data support formation of the square-planar Ni(II) complex.

[Ni(LBF$_2$)$_2$] was prepared in 65.7% yield by adding an equivalent of boron trifluoride etherate as linking reagent to an acetonitrile suspension of the hydrogen-bridged precursor Ni(II) complex (scheme 2). This linking reagent readily reacts with O–H···O bridge in the precursor molecule, yielding an extremely stable complex containing two O–BF_2–O bridges according to spectral and elemental analysis data of **[Ni(BF$_2$)$_2$]**. The hydrogen-bridge protons were replaced by BF_2 moieties, but all other characteristics were retained. In the ^{1}H NMR spectrum of BF_2^+ -capped Ni(II) complex, the O–H···O signal disappeared after the formation by BF_2-bridging macrocyclic compound **[Ni(LBF$_2$)$_2$]**. Upon macrocyclization, the precursor hydrogen-bridged Ni(II) complex resonances shift slighty, however, their number is unchanged. The IR spectrum of this complex exhibits upward shifts in the stretching vibrations of the C=N groups due to strong electron-withdrawing effects of BF_2^+ incorporated in the macrocycle [18]. The O–H···O bending vibration at 1702 cm^{-1} disappeared with the appearance of stretching vibrations due to the BF_2^+ moieties at around 1160 and 827 cm^{-1} for B–O and B–F, respectively [19]. This BF_2^+ -capped nickel(II) complex is also confirmed by its mass spectrum, which gives a molecular ion peak at $m/z = 1940$ $[M+1]^+$.

3. Experimental

(*E*, *E*)-Dichloroglyoxime [20], cyanogen di-*N*-oxide [21], 4-nitro-1,2-*bis*(2-iodoethoxy) benzene [11] and 1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane [10] were prepared by reported procedures. All solvents were reagent grade and purified according to standard procedures [22]. ^{1}H spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on a Varian Mercury 200 MHz spectrometer using TMS as the internal reference. The IR spectra



Scheme 2. Synthesis of nickel complexes.

were taken on a Perkin-Elmer Spectrum One FTIR spectrometer using KBr pellets. The elemental analyses and metal determination of the compounds were determined by a Carlo Erba 1106 instrument and Unicam 929 AA spectrophotometer, respectively. Mass spectra were measured on a Micromass Quatro LC/ULTIMA LC-MS

MS spectrometer. Melting points were determined in open capillaries on an Electrothermal apparatus and are uncorrected.

3.1. *7-Nitrobenzo-17,23-dimethyl-4,11-dioxa-1,14,17,23-tetraazapentacyclo[12.10.10$^{0.5,10}$]hexadiconta-1,5,7,12,14-pentane (3)*

A solution of 1,8-dimethyl-1,4,8,11-tetraazacyclotetradecane (**1**) (1.14 g, 5 mmol) in a mixture of dry acetonitrile and dry dimethyl formamide [260 mL (200 : 60)] and an excess of finely ground anhydrous Na_2CO_3 (0.424 g, 4 mmol) were charged into a three-necked flask and purged under argon in a Schlenk system connected to a vacuum line at 45°C for 30 min. A solution of 4-nitro-1,2-*bis*(2-iodoethoxy)benzene (**2**) (2.31 g, 5 mmol) in dry acetonitrile (60 mL) was added dropwise to this solution under argon at the same temperature and refluxed for 6 days. The reaction was monitored by TLC [silica gel (chloroform : methanol) (4 : 1)]. The reaction mixture was cooled to room temperature and filtered using Celite and washed with dichloromethane; then the solvent mixture was evaporated to dryness under reduced pressure. The brown oily product was dissolved in a minimum of chloroform and ethanol was added (5 mL) to the solution, whereupon a pale yellow solid precipitated. The reaction mixture was filtered off, washed with ethanol and stirred in diethyl ether for 24 h and then filtered and dried *in vacuo*. The pale yellow solid was dissolved in chloroform (5 mL) and then purified using column chromatography [silica gel (chloroform : methanol) (4 : 1)]. Yield: 1.675 g (77%), m.p. 242°C. Calculated for $C_{22}H_{37}N_5O_4$: C, 60.68; H, 8.50; N, 16.09. Found: C, 60.81; H, 8.65; N, 15.84%. IR (KBr, cm^{-1}): $\nu = 3076$ (Ar–H), 2927–2851 (C–H), 1588 (Ar–H), 1340 (NO_2), 1276 (Ar–O–CH_2). ^{1}H NMR ($CDCl_3$): δ 7.95 (d, 1H, ArH), 7.69 (s, 1H, ArH), 6.90 (d, 1H, ArH), 4.67 (t, 2H, OCH_2), 4.14 (t, 2H, OCH_2), 3.81 (m, 4H, NCH_2), 3.39 (m, 8H, NCH_2), 2.80 (m, 8H, NCH_2), 1.82 (s, 6H, CH_3), 1.48 (m, 4H, CH_2). MS (m/z) = 436 $[M+1]^+$.

3.2. *7-Aminobenzo-17,23-dimethyl-4,11-dioxa-1,14,17,23-tetraazapentacyclo[12.10.10$^{0.5,10}$]hexadiconta-1,5,7,12,14-pentane (4)*

Compound **3** (1.50 g, 3.45 mmol) was dissolved in *n*-butanol (200 mL) by heating at 70°C and palladium (10%) activated carbon (1.1 g) was added to the solution at the same temperature, heated and then allowed to stand at 120°C for 10 min; 8 mL of hydrazine hydrate (100%) was then added dropwise. The reaction mixture was heated and stirred for 8 h at the same temperature and then filtered using Celite and washed with *n*-butanol. The colorless solution was concentrated on an evaporator to 10 mL. The crude product was allowed to stand at −18°C overnight, whereupon the compound crystallized from the solution. Colorless crystallized product was collected by filtration, washed with diethyl ether and then dried *in vacuo*. Yield: 1.14 g (81.6%), m.p. 172–173°C. Calculated for $C_{22}H_{39}N_5O_2$: C, 65.18; H, 9.62; N, 17.28. Found: C, 65.00; H, 9.87; N, 17.03%. IR (KBr, cm^{-1}): $\nu = 3290$–3164 (NH_2), 3038 (Ar–H), 2925–2851 (C–H), 1600 (NH_2), 1256 (OCH_2). ^{1}H NMR ($CDCl_3$): δ 6.73 (d, 1H, ArH), 6.27 (s, 1H, ArH), 6.13 (d, 1H, ArH), 4.86 (br, 2H, NH_2), 4.25 (t, 2H, OCH_2), 4.01 (t, 2H, OCH_2), 3.86 (m, 4H, NCH_2), 3.38 (m, 8H, NCH_2), 2.77 (m, 8H, NCH_2), 1.81 (s, 6H, CH_3), 1.44 (m, 4H, CH_2). MS(m/z): 406 $[M+1]^+$.

3.3. *N,N′*-Bis*(7-aminobenzo-17,23-dimethyl-4,11-dioxa-1,14,17,23-tetraazapentacyclo[12.10.10$^{0.5,10}$]hexadiconta-1,5,7,12,14-pentane)diaminoglyoxime (H_2L)*

A solution of cyanogens di-*N*-oxide (**5**) in dichloromethane (15 mL), which was prepared from (*E*, *E*)-dichloroglyoxime (0.235 g, 1.5 mmol) and an aqueous solution of Na_2CO_3 (10 mL, 0.5 M), was added to a cold solution (−15°C) of **4** (1.04 g, 2.56 mmol) in dichloromethane (75 mL) under argon. The reaction was continued for 12 h at the same temperature and then allowed to warm to room temperature. Solvent was evaporated to 10 mL under reduced pressure and the mixture was allowed to stand in a refrigerator overnight at −18°C. The pale brown solid was filtered off and washed with cold methanol and then dried *in vacuo*. The crude product was recrystallized from methanol/diethyl ether. Yield: 0.75 g (65.8%), m.p. 189°C (dec.). Calculated for $C_{46}H_{78}N_{12}O_6$: C, 61.74; H, 8.72; N, 18.79. Found: C, 61.97; H, 8.59; N, 18.51%. IR (KBr, cm^{-1}): $\nu = 3390$ (N–H), 3198 (O–H), 3036 (Ar–H), 2912–2846 (C–H), 1636 (C=N), 1605 (N–H), 1262 (O–CH_2), 954 (N–O). ^{1}H NMR (DMSO-d_6): δ 10.87 (s, 2H, OH), 8.11 (s, 2H, NH), 7.50 (d, 2H, ArH), 7.24 (s, 2H, ArH), 6.94 (d, 2H, ArH), 4.37 (m, 4H, OCH_2), 4.18 (m, 4H, OCH_2), 3.82 (m, 16H, NCH_2), 2.96 (m, 16H, NCH_2), 2.00 (s, 12H, CH_3), 1.56 (m, 8H, CH_2). MS (*m*/*z*): 927 $[M+CH_3OH+1]^+$, 895 $[M+1]^+$.

3.4. *[Ni(HL)$_2$] (6)*

A solution of nickel(II) chloride hexahydrate (0.119 g, 0.5 mmol) in ethanol (15 mL) was added to a solution of **H_2L** (0.894 g, 1 mmol) in ethanol (40 mL) at 60°C; a distinct change in color from pale brown to red and a decrease in the pH (1.02) of the solution was observed. While heating the reaction mixture to 70°C in a water-bath, an ethanolic solution of KOH (0.1 M) was added and red precipitate of **6** formed. After heating and stirring the reaction mixture for 2 h in a water-bath, the precipitate was filtered off, washed with water, ethanol and diethyl ether and then dried *in vacuo* to give red solid. Yield: 0.84 g (91.3%), m.p. > 300°C. Calculated for $C_{92}H_{154}N_{24}O_{12}Ni$: C, 59.84; H, 8.34; N, 18.21; Ni, 3.18. Found: C, 59.97; H, 8.09; N, 18.55; Ni, 2.93%. IR (KBr, cm^{-1}): $\nu = 3374$ (N–H), 3031 (Ar–H), 2921-2850 (C–H), 1702 (O–H···O), 1624 (C=N), 1601 (N–H), 1253 (O–CH_2), 948 (N–O). ^{1}H NMR (DMSO-d_6): δ 16.92 (s, 2H, O–H···O), 8.21 (s, 4H, NH), 7.54 (m, 4H, ArH), 7.31 (m, 4H, ArH), 7.04 (m, 4H, ArH), 4.43 (m, 8H, OCH_2), 4.15 (m, 8H, OCH_2), 3.89 (m, 32H, NCH_2), 3.01 (m, 32H, NCH_2), 1.94 (m, 24H, CH_3), 1.61 (m, 16H, CH_2). MS (*m*/*z*): 1845 $[M+1]^+$.

3.5. *[Ni(LBF$_2$)$_2$] (7)*

A suspension of **6** (0.737 g, 0.4 mmol) in freshly distilled acetonitrile (50 mL) was brought to reflux under argon. Boron trifluoride diethyl ether complex (0.2 mL, 0.80 mmol) in dry acetonitrile was slowly added to the suspension. The reactant was completely dissolved and turned dark red within 10 min. After the color changed, the reaction mixture was refluxed and stirred 1 h further and solvent was removed to dryness under reduced pressure. The residue was dissolved in dry acetonitrile (10 mL) and evaporated to dryness under reduced pressure. The last step was repeated twice and the mixture was allowed to stand at −18°C in a refrigerator overnight. The dark red crystalline product was filtered off, washed with cold acetonitrile and diethyl ether and

then dried *in vacuo*. Yield: 0.51 g (65.7%), m.p. > 300°C. Calculated for $C_{92}H_{152}N_{24}O_{12}B_2F_4Ni$: C, 56.89; H, 7.83; N, 17.31; Ni, 3.02. Found: C, 57.18; H, 7.66; N, 17.69; Ni, 2.71%. IR (KBr, cm^{-1}): $\nu = 3388$ (N–H), 3037 (Ar–H), 2925–2857 (C–H), 1638 (C=N), 1609 (N–H), 1247 (O–CH_2), 1160 (B–O), 827 (B–F). ^1H NMR ($CDCl_3$): δ 8.17 (s, 4H, NH), 7.58 (m, 4H, ArH), 7.37 (m, 4H, ArH), 6.98 (m, 4H, ArH), 4.48 (m, 8H, OCH_2), 4.20 (m, 8H, OCH_2), 3.80 (m, 32H, NCH_2), 2.97 (m, 32H, NCH_2), 1.89 (m, 24H, CH_3), 1.57 (m, 16H, CH_2). MS (*m*/*z*): 1940 $[M+1]^+$.

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