Original Research Article

Synthesis and Characterization of a New (*E,E*)-Dioxime and its Homonuclear Complexes

EMİN KARAPINAR*

Department of Chemistry, Faculty of Arts and Sciences, Pamukkale University, 20017, Denizli, Turkey

Abstract

N'-(4′-Benzo[15-crown-5]naphthylaminoglyoxime (H_2L) and its sodium chloride complex ($H_2L \cdot NaCl$) have been prepared from 2-naphthylchloroglyoxime, 4′-aminobenzo[15-crown-5] and sodium bicarbonate or sodium bicarbonate and sodium chloride. Nickel(II), cobalt(II) and copper(II) complexes of H_2L and $H_2L \cdot NaCl$ have a metal–ligand ratio of 1:2 and the ligand coordinates through the two N atoms, as do most of the vic-dioximes. The BF_2^+-capped Ni(II), Co(III) and mononuclear complexes of the *vic*-dioxime were prepared. The macrocyclic ligands and their transition metal complexes have been characterized on the basis of IR, ^{1}H NMR spectroscopy and elemental analyses data.

Introduction

Synthesis macrocyles have been known for over 75 years, although a real spate of publications in this area occurred in the 1960 [1, 2]. In this period, more than five thousand macrocyclic compounds were reported, and since than their number has increased markedly from year to year [3].

Crown ethers have been found to be powerful extracting agents for alkali metal salts [4]. They are also accepted to be model compounds to mimic antibiotics in cation transport through lipid membranes [5]. Addition of crown ether substituents to various coordination compounds causes an increase in their solubility in common organic solvents and water [6].

The coordination chemistry of vicinal dioximes is interesting and numerous transition metal complexes of this group of ligands have been investigated [7, 8]. Both the presence of mildly acidic hydroxy groups and slightly basic nitrogen atoms make (*E,E*)-dioximes amphoteric ligands form which corrin-type square planar, square pyramidal and octahedral complexes with nickel(II), cobalt(II), copper(II), palladium(II) and cobalt(III) as central metal atoms [9–12].

In the present paper, the synthesis of two new *vic*-dioximes with macrocyclic ether groups in the some molecule and their complexes with various metal salts have been studied.

* Author for correspondence. E-mail: ekarapinar@pamukkale. edu.tr

Experimental

Benzo[15-crown-5] [4], 4′-nitrobenzo[15-crown-5] [13], 4′-aminobenzo[15-crown-5] [13, 14], isonitroso-2-acetylnaphthalene [15], 2-naphthylglyoxime [15, 16] and 2-naphthylchloroglyoxime [15] were prepared according to published methods. All reagents were purchased from Merck (Germany) and were used without further purification. Melting points were determined on a Gallenkamp melting point apparatus and were uncorrected. Elemental analyses (C, H, and N) were determined using a Leco, CHNS-932 model analyzer. ^{1}H NMR spectra were recorded on a Bruker DPX-400 400 MHz high performance digital FT-NMR, IR spectra on a Perkin Elmer 1605 FT-IR spectrometer in KBr pellets. The UV−visible spectra were recorded on a Shimadzu 160A spectrometer. The metal analyses were determined using a Unicam 929 AAS spectrometer.

N'-(4′-Benzo[15-crown-5]naphthylaminoglyoxime (**1**, $C_{26}H_{29}O_7N_3(H_2L)$)

4′-Aminobenzo[15-crown-5] (1411.6 mg, 5 mmol) dissolved in absolute ethanol (15 cm^3) was added under an atmosphere of N_2 at 60 °C to a solution of 2-naphthylchloroglyoxime (1243.3 mg, 5 mmol) in absolute ethanol (10 cm^3). The mixture was stirred efficiently and heated on a water bath at ca. 60 °C for 3 h. Then mixture was cooled to 0 °C and H_2L was precipitated by addition of cold diethyl ether with continuous stirring. The violet-coloured precipitate was filtered off, washed

with cold diethyl ether and dried. H_2L ($C_{26}H_{29}O_7N_3$), yield: 1.809 g (73%), Anal. Calcd. C: 63.02; H: 5.90; N: 8.48. Found: C: 62.89; H: 5.78; N: 8.44. ^1H NMR (CDCl$_3$) δ ppm: 11.33 (s, 1H, OH), 10.52 (s, 1H, OH), 7.69 (s, 1H, NH), 7.51−6.34 (m, 10H, Ar−H), 3.90−3.32 (m, 16H, O−CH$_2$−). IR (KBr, cm^{-1}): 3323 (N−H), 3198 (O−H), 2962 (C−H$_{Ar}$), 1640 (C=N), 1612 (N−H), 1508 (C=C$_{Ar}$), 1276−1232 (C$_{Ar}$−O−C), 1138−1040 (C−O−C), 940 (N−O).

This ligand is soluble in EtOH, CHCl$_3$, DMF, DMSO, CH$_2$Cl$_2$ and MeOH but insoluble in CCl$_4$.

Sodium chloride complex of N′-(4′-benzo[15-crown-5] naphthylaminoglyoxime
(2, $C_{26}H_{29}O_7N_3 \cdot NaCl$ ($H_2L \cdot NaCl$))

A solution of 2-naphthylchloroglyoxime (1243.3 mg, 5 mmol) dissolved in absolute ethanol (10 cm^3) was added under an atmosphere of N$_2$ at 60 °C to a solution of 4′-aminobenzo[15-crown-5] (1411.6 mg, 5 mmol) in absolute ethanol (15 cm^3) containing solid NaHCO$_3$ (820 mg, 10 mmol) and NaCl (292.5 mg, 5 mmol). The mixture was stirred efficiently and heated on a water bath at ca. 60 °C for 3 h. After cooling to room temperature, the mixture was filtered and the solid washed with ethanol (10 cm^3). The filtrate was cooled to 0 °C and $H_2L \cdot NaCl$ was precipitated by addition of cold diethyl ether with continuous stirring. The pink-coloured precipitate was filtered off, washed with cold diethyl ether and dried. $H_2L \cdot NaCl$ ($C_{26}H_{29}O_7N_3 \cdot NaCl$), yield: 2.354 g (85%) Anal. Calcd. C: 56.37; H: 5.28; N: 7.59. Found: C: 56.31; H: 5.12; N: 7.41. ^1H NMR (CDCl$_3$) δ ppm: 11.45 (s, 1H, OH), 10.39 (s, 1H, OH), 7.80 (s, 1H, NH), 7.58−6.30 (m, 10H, Ar-H), 3.82−3.45 (m, 16H, O−CH$_2$−). IR (KBr, cm^{-1}): 3364 (N−H), 3216 (O−H), 2969 (C−H$_{Ar}$), 1642 (C=N), 1610 (N−H), 1508 (C=C$_{Ar}$), 1272−1230 (C$_{Ar}$−O−C), 1132−1059 (C−O−C), 938 (N−O).

This ligand is soluble in EtOH, CHCl$_3$, DMF, DMSO, CH$_2$Cl$_2$ and MeOH but insoluble in CCl$_4$.

Ni(II), Co(II) and Cu(II) complexes of the ligands
(3−8)

A solution of 0.25 mmol metal salt [NiCl$_2$·6H$_2$O (59.4 mg), CoCl$_2$·6H$_2$O (59.5 mg), CuCl$_2$·2H$_2$O (42.6 mg)] dissolved in EtOH (5 cm^3), was added to a stirred solution of the H_2L (247.7 mg, 0.5 mmol) or $H_2L \cdot NaCl$ (276.9 mg, 0.5 mmol) dissolved in EtOH (5 cm^3). The mixture was heated up to 60 °C and NaOH (20 mg, 0.5 mmol) added dropwise. The reaction was allowed to continue for 3 h at 60 °C. The mixture was allowed to stand a day at room temperature. The precipitated complexes were filtered off, washed with EtOH and dried.

For $C_{52}H_{56}N_6NiO_{14}$ (**3**): yield:191 mg (73%), m.p.: 186 °C, Anal. Calcd.: C: 59.61; H: 5.39; N: 8.02; Ni: 5.60, Found: C: 59.24; H: 5.19; N: 7.98; Ni: 5.48. IR (KBr, cm^{-1}): 3310 (N−H), 2988 (C−H$_{Ar}$), 1715 (O···H−O), 1622 (C=N), 1608 (N−H), 1508 (C=C$_{Ar}$), 1259−1227 (C$_{Ar}$−O−C), 936 (N−O).

For $C_{52}H_{56}CoN_6O_{14}$ (**4**): yield: 204 mg (78%), m.p.: 231 °C, Anal. Calcd.: C: 59.60; H: 5.38; N: 8.02; Co: 5.34, Found: C: 59.42; H: 5.29; N: 7.77; Co: 5.22. IR (KBr, cm^{-1}): 3318 (N−H), 2980 (C−H$_{Ar}$), 1717 (O···H−O), 1621 (C=N), 1608(N−H), 1508 (C=C$_{Ar}$), 1260−1224 (C$_{Ar}$−O−C), 937 (N−O).

For $C_{52}H_{56}CuN_6O_{14}$ (**5**): yield: 210 mg (80%), m.p.: 220 °C, Anal. Calcd.: C: 59.34; H: 5.36; N: 7.98; Cu: 6.04, Found: C: 59.26; H: 5.30; N: 7.88; Cu: 5.75. IR (KBr, cm^{-1}): 3330 (N−H), 2952 (C−H$_{Ar}$), 1720 (O···H−O), 1625 (C=N), 1604(N−H), 1510 (C=C$_{Ar}$), 1263−1230 (C$_{Ar}$−O−C), 934 (N−O).

For $C_{52}H_{56}Cl_2N_6Na_2NiO_{14}$ (**6**): yield: 200 mg (69%), m.p.: 211 °C, Anal. Calcd.: C: 53.63; H: 4.85; N: 7.22; Ni: 5.04, Found: C: 53.34; H: 4.72; N: 7.28; Ni: 4.79. IR (KBr, cm^{-1}): 3360 (N−H), 2966 (C−H$_{Ar}$), 1718 (O···H−O), 1624 (C=N), 1600(N−H), 1508 (C=C$_{Ar}$), 1270−1230 (C$_{Ar}$−O−C), 936 (N−O).

For $C_{52}H_{56}Cl_2CoN_6Na_2O_{14}$ (**7**): yield: 216 mg (74%), m.p.: 268 °C, Anal. Calcd.: C: 53.62; H: 4.85; N: 7.21; Co: 5.06, Found: C: 53.51; H: 4.70; N: 7.02; Co: 5.00. IR (KBr, cm^{-1}): 3364 (N−H), 2960 (C−H$_{Ar}$), 1718 (O···H−O), 1625 (C=N), 1612(N−H), 1510 (C=C$_{Ar}$), 1269−1224 (C$_{Ar}$−O−C), 937 (N−O).

For $C_{52}H_{56}Cl_2CuN_6Na_2O_{14}$ (**8**): yield: 251 mg (86%), m.p.: 244 °C, Anal. Calcd.: C: 53.41; H: 4.83; N: 7.19; Cu: 5.43, Found: C: 53.40; H: 4.76; N: 7.01; Cu: 5.28. IR (KBr, cm^{-1}): 3352 (N−H), 2968 (C-H$_{Ar}$), 1717 (O···H-O), 1624 (C=N), 1600(N−H), 1510 (C=C$_{Ar}$), 1270−1226 (C$_{Ar}$−O−C), 934 (N−O).

Preparation of [Ni(LBF$_2$)$_2$] the nickel(II) complex,
(9, $C_{52}H_{54}B_2F_4N_6NiO_{14}$)

A suspension of the precursor nickel complex (0.2619 g, 0.25 mmol) in 50 cm^3 of freshly distilled acetonitrile was brought to reflux temperature under an oxygen-free nitrogen atmosphere. Boron trifluoride diethyl etherate (0.06 cm^3, 0.5 mmol) was slowly added by stirring to the suspension of nickel complex. The resulting reaction mixture immediately turned red. After the colour change, the solution was refluxed for 1.5 h. The solvent was evaporated under reduced pressure up to dryness and the residue was dissolved in dry acetonitrile (15 cm^3), filtered and evaporated to dryness. The last step was repeated twice and the residue dissolved in 10 cm^3 of dry acetonitrile and allowed to stand at −18 °C overnight. The crystalline red product was filtered off, washed with cold acetonitrile and diethyl ether and dried in vacuum. Yield: 166 mg (58%), m.p.: 126 °C, Anal. Calcd.: C: 54.63; H: 4.76; N: 7.35; Ni: 5.13, Found: C: 54.41; H: 4.74; N: 7.12; Ni: 4.98. ^1H NMR (DMSO-d$_6$) δ ppm: 7.82 (s, 2H, NH), 7.44−6.50 (m, 20H, Ar-H), 3.86−3.16

(m, 32H, O—CH$_2$—). IR (KBr, cm^{-1}): 3340 (N—H), 2932 (C—H$_{Ar}$), 1642 (C=N), 1604(N—H), 1508 (C=C$_{Ar}$), 1260–1226 (C—O—C), 1176 (B—O), 1020 (B—F), 936 (N—O).

Preparation of the cobalt(III) complex,
*[Co(HL)$_2$ pyCl] (**10**, C$_{57}$H$_{61}$ClCoN$_7$O$_{14}$)*

A solution of CoCl$_2$·6H$_2$O (0.2376 g, 1 mmol) in absolute ethanol (20 cm^3) was added to a hot solution of H$_2$L (0.99 g, 2 mmol) in absolute ethanol (100 cm^3). Pyridine (0.079 g, 1 mmol) in absolute ethanol (2 cm^3) was added to the above solution during heating process. The reaction mixture was heated and stirred for 1 h at 60 °C then cooled to room temperature and a stream of air was bubbled through the solution for 6 h. After this period, the solution was concentrated to 20 cm^3 and placed in a refrigerator at −18 °C overnight, whereupon a brown solid precipitated from the reaction mixture. The pale brown crystalline product was filtered off, washed with cold ethanol and diethylether and dried in vacuum. Yield: 756 mg (65%), m.p.: 154 °C, Anal. Calcd.: C: 58.89; H: 5.29; N: 8.43; Co: 5.07, Found: C: 58.64; H: 5.06; N: 8.35; Co: 4.87. ^{1}H NMR (DMSO-d$_6$) δ ppm: 16.84 (s, 2H, O···H—O), 7.88 (s, 2H, NH), 7.56 (d, 2H, py—H), 7.42 (t, 1H, py—H), 7.10 (t, 2H, py—H), 7.44–6.50 (m, 20H, Ar—H), 3.86–3.16 (m, 32H, O—CH$_2$—). IR (KBr, cm^{-1}): 3334 (N—H), 2980 (C—H$_{Ar}$), 1720 (O···H—O), 1624 (C=N), 1608(N—H), 1510 (C=C$_{Ar}$), 1259–1226 (C$_{Ar}$—O—C), 936 (N—O).

Preparation of BF$_2^+$-capped cobalt(III) complex,
*[Co(LBF$_2$)$_2$pyCl] (**11**, C$_{57}$H$_{59}$B$_2$ClCoF$_4$N$_7$)*

A suspension of 0.5 mmol [of Co(HL)$_2$pyCl] (0.5813 g) in 40 cm^3 of freshly distilled acetonitrile was refluxed in an oxygen-free nitrogen atmosphere. The boron triflu-

oride diethyl etherate (0.25 cm^3, 2 mmol) was added to the above mentioned stirred suspension, which immediately converted the colour of the reaction mixture to a red solution. The reaction was allowed to stand at reflux temperature for 30 min. then the solvent was removed under reduced pressure and the residue was dissolved in 30 cm^3 of acetonitrile, then evaporated to dryness. The last step was repeated and the residue was dissolved in 15 cm^3 of acetonitrile and then allowed to cool in a refrigerator at −18°C overnight whereupon the product crystallized from the solution. The product was filtered off, washed with cold acetonitrile and diethylether and then dried in vacuum. Yield: 308 mg (49%), m.p.: 139 °C, Anal. Calcd.: C: 54.42; H: 4.73; N: 7.79; Co: 4.68, Found: C: 54.25; H: 4.61; N: 7.52; Co: 4.65. ^{1}H NMR (DMSO-d$_6$) δ ppm: 7.90 (d, 2H, py—H) 7.81 (s, 2H, NH), 7.50 (t, 1H, py—H), 7.08 (t, 2H, py—H), 7.40–6.60 (m, 20H, Ar—H), 3.90–3.32 (m, 32H, O—CH$_2$—). IR (KBr, cm^{-1}): 3364 (N—H), 2998 (C—H$_{Ar}$),1658 (C=N), 1610(N—H), 1510 (C=C$_{Ar}$), 1260–1220 (C$_{Ar}$—O—C), 1180 (B—O), 995 (B-F), 934 (N—O).

Results and discussion

By a method similar to that for *N,N'*-bis(4′-benzo[15-crown-5]diaminoglyoxime [6,19], *N'*-(4′-benzo[15-crown-5]naphthylamino-glyoxime (H$_2$L) and its sodium chloride complex (H$_2$L·NaCl) have been prepared by the reaction of 4′-aminobenzo[15-crown-5] [13, 14] with 2-naphthylchloroglyoxime [15]. To obtain H$_2$L·NaCl, NaHCO$_3$ was added to the reaction mixture in order to neutralize HCl formed during the reaction; NaCl was produced as a by-product and the sodium was found to complex with the crown ether groups to yield a product of type; therefore, the ligand was obtained as a sodium chloride
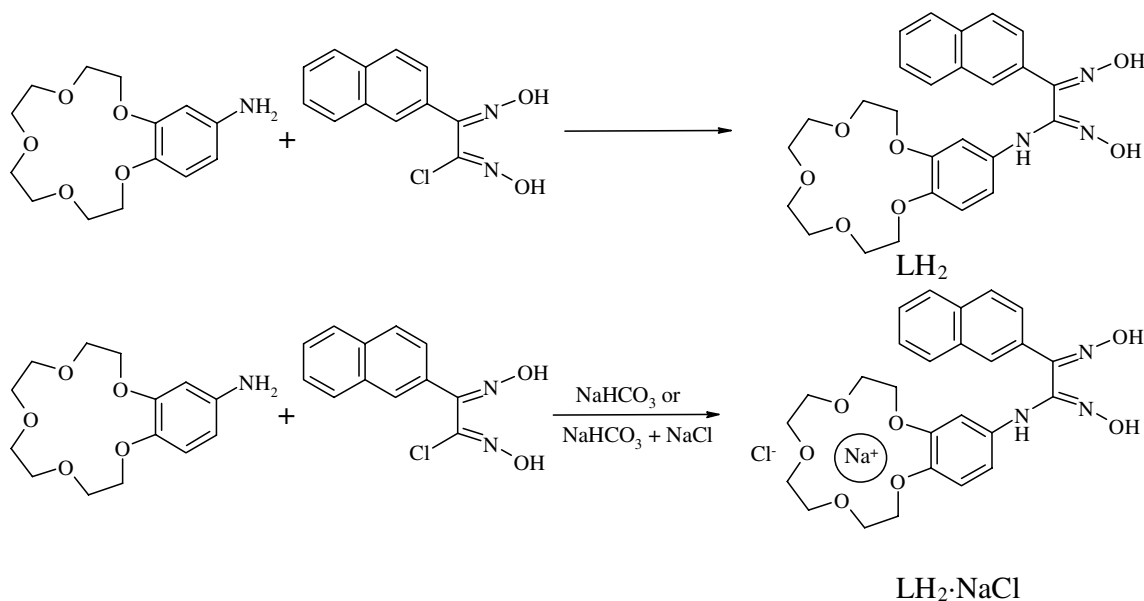

Scheme 1. General formulas of the ligands.

salt, $H_2L \cdot NaCl$. No further attempt was made to isolate the free ligand, since $H_2L \cdot NaCl$ could be used directly to prepare the transition metal complexes.

In the ^1H NMR spectra of the ligands, two peaks are appeared for the $-OH$ protons of the oxime groups. These two deuterium-exchangeable singlets correspond to two non-equivalent $-OH$ protons which indicates an *anti*-configuration of the $-OH$ groups [3, 6, 17–19] (Scheme 1). When the chemical shifts of the two $-OH$ groups in the two different ligands are compared, the ones at lower field quite closely resemble each other (11.33–11.45 ppm) whereas a considerable difference is observed for the chemical shifts at higher field (11.52–10.39 ppm). The D_2O exchangeable $-NH-$ protons of the aminoglyoximes and $O-CH_2-$ protons are appeared 7.69–7.80 ppm and 3.90–3.32 ppm, respectively. Addition of D_2O causes the disappearance of the $-NH-$ and $-OH$ peak.

The present ligands exhibit the following stretching frequencies $-NH$ (3323–3364 cm^{-1}), $-OH$ (3198–3216 cm^{-1}), $C=N-$ (1640–1642 cm^{-1}) and NO (940–938 cm^{-1}) which are similar to substituted aminoglyoximes [3, 6, 12, 17, 20].

The metal complexes (**3–8**) of the ligands were prepared under similar conditions by adding metal salts and strong base to the ligands. The literature furnishes examples of oximato ions coordinated to a metal center (Ni(II), Co(II), Cu(II), etc.) as a bidentate ligand[8]. The mononuclear complexes **3–8** have a metal:ligand ratio of 1:2, as it is the case for most (*E,E*)-dioxime metal complexes [3, 6, 8, 12, 18, 19–22].

The complexes (**3–8**) of H_2L and $H_2L \cdot NaCl$ support the structures shown in Scheme 2 by the weak bending vibration of the $O-H \cdots O$ bridges *ca.* et. 1715–1720 cm^{-1} and the shift of the $C=N$ vibration to lower frequencies at 1621–1625 cm^{-1} is due to N,N-metal coordination [6, 12, 16, 17, 20]. In the IR
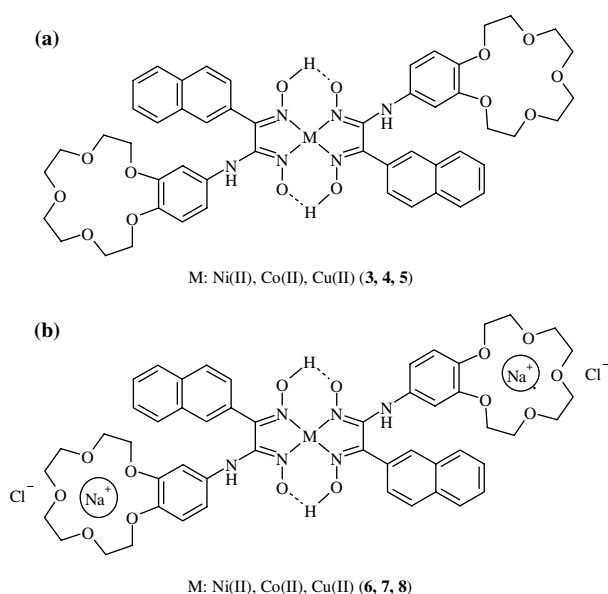
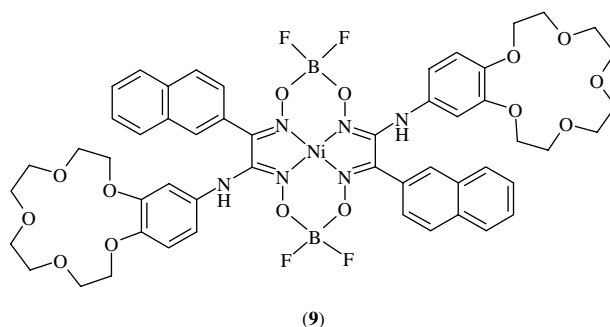spectrum, a downward shift, relative to the free ligand, of about 17–21 cm^{-1} for $C=N$ absorption, indicates coordination through the N atoms. As a result of the disappearance of the $O-H$ resonances, hydrogen bonds were formed and the removal of electron density from the $N-O$ bond caused a decrease in the $N-O$ stretching frequency [23]. As with most *vic*-dioximes [6, 8, 19, 20], the nickel(II) complex of LH_2 is planar N,N'-coordination is verified by the diamagnetism of this compound, since it is known that a d^8 metal complex does not have unpaired electrons in a square planar field.
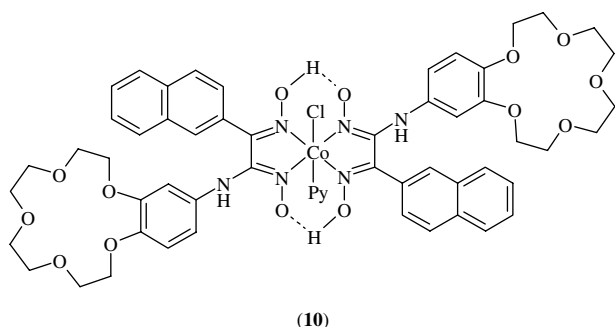
The IR spectrum of **3** contains a weak band at 1715 cm^{-1} which can be attributed to the absorbance of the O-H$\cdots$O intramolecular hydrogen bridges [24]. IR spectroscopy can be used to distinguish between the hydrogen-bridged (**3**) and the BF_2^+-bridged (**9**) complexes. The frequency of the $C=N$ stretching vibration increases by 20 cm^{-1} on going from the hydrogen-bridged complex to the BF_2^+-capped compound. The weak and broad band at 1715 cm^{-1} is a characteristic O-H$\cdots$O in-plane deformation of the hydrogen bond and disappears when substituting the H-bonded Ni(II) complex with BF_2^+, with the concomitant appearance of peaks around 1176 and 1020 cm^{-1} due to the B-O and B-F bonds [3, 12]. (Scheme 3).

The six-coordinated cobalt(III) complex (**10**) was obtained when air was bubbled through the suspension of the cobalt(II) complex in ethanol in the presence of pyridine. It was necessary to use exact stoichiometric amount of pyridine because the presence of excess base in the reaction mixture was reported to yield a complex in which one of the linking protons had been removed and contained two axially bound nitrogen bases [25]. In the ^1H NMR spectrum of diamagnetic Co(III) complex, signals at δ = 7.56, 7.42 and 7.10 ppm were caused by the coordinated pyridine molecule. The IR spectrum of this complex exhibited $C=N$ absorptions at 1624 cm^{-1}. In addition, **10** does not show the $O-H$ vibrations at 3198 cm^{-1}. These facts suggest that the ligand is N,N'-coordinated with cobalt(III) ion and look like the proposed structure shown in Scheme 4.
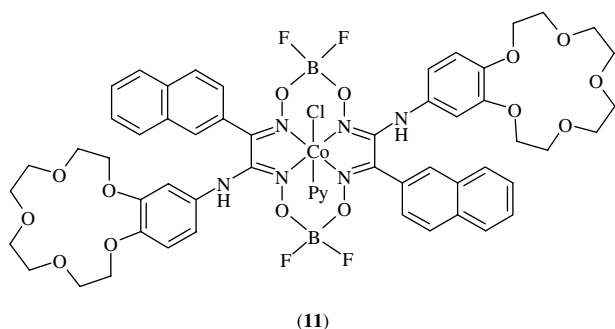
The mononuclear BF_2^+-bridged cobalt(III) complex [Co(LBF$_2$)$_2$pyCl] (in Scheme 5) was obtained by refluxing the appropriate hydrogen-bridged complex (**10**) with an equivalent amount of boron trifluoride etherate in acetonitrile for 30 min. Satisfactory analyti-

(a)

M: Ni(II), Co(II), Cu(II) (**3, 4, 5**)

(b)

M: Ni(II), Co(II), Cu(II) (**6, 7, 8**)

Scheme 2. Square-planar metal complexes of the ligands [(a) H_2L, (b) $H_2L \cdot NaCl$ M = Ni(II), Co(II) and Cu(II)].

(**9**)

Scheme 3. Structure of [Ni(LBF$_2$)$_2$] (**9**).

Scheme 4. Structure of [Co(HL)₂pyCl] (**10**).

Scheme 5. Structure of [Co(LBF₂)₂pyCl] (**11**).

cal data were obtained for BF_2^+-bridged mononuclear Co(III) complex. The chemical shifts in this complex, belonging to aromatic, aliphatic and NH protons, were very similar to those of the hydrogen-bonded Co(III) complex. In IR spectrum of this complex (**11**), a downward shift for the C=N frequencies indicates coordination through the N atoms [26]. In contrast to this downward shift, this BF_2^+-bridged complex exhibited an upward shift to about a 1658 cm^{-1}. The broad band at 1717 cm^{-1} assigned to the O-H···O bending vibrations was disappeared upon insertion of the BF$_2$ group with the simultaneous appearance of peaks at 1180 and 995 cm^{-1} for the B—O and B—F resonances, respectively [27].

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