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Synthesis and Characterization of a New (E, E)-Dioxime and Its Homo and Heteronuclear Complexes Containing Macrobicylic Moieties

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Abstract

A new *N*, *N*′-substituted diaminoglyoxime (**H_2L**) containing a diazatetraoxa macrobicycle [2.2.2_B] has been synthesized from an aromatic primary amine attached to the cryptand moiety and cyanogen-di-*N*-oxide. The BF_2^+-capped Co(III) and heterotri-nuclear complexes of the *vic*-dioxime were prepared. The new compounds were characterized by a combination of elemental analysis and ^{1}H NMR, ^{13}C NMR, IR and MS spectral data.

Introduction

The cryptands were developed by Lehn and are a class of macrobicyclic ligand systems bearing nitrogen bridgeheads, but otherwise these cryptands resemble macrocyclic polyethers [1]. They contain a three-dimensional intramolecular cavity whose size is governed by the length of the bridges and increases stepwise along the series [2]. Owing to their architectural and functional flexibility, macrobicyclic compounds are especially attractive for designing both biomimetic and abiotic receptor molecules for inorganic and organic substrates [3]. Some macrobicyclic ligands display very high selectivity for alkali or alkaline earth metal cation. For instance, the [$K^+ \subset$ 2.2.2] cryptate is more stable by a factor of 10^5 than the K^+ complex of its macrocyclic counterpart due to the macrobicylic cryptate effect [4]. The synthesis and characterization of 4′-nitro and amino derivatives of cryptands were reported by Gansow and Pettit [5] by a similar route used for the preparation of the cryptands.

In this study, 4′-nitro (**3**) and 4′-amino (**4**) substituted macrobicyclic compounds first reported here were synthesized by a different and simpler route than for the preparation of the cryptand described above. Additionally, the synthesis and structural properties of a (E, E)-dioxime containing a diazatetraoxamacrobicyclic moiety, its Co(III) complex as well as the properties of the BF_2^+-capped Co(III) complex are reported. Finally a heterotrinuclear complex has been prepared by the reaction of $Ca(ClO_4)_2{\cdot}4H_2O$ with the BF_2 bridged cobalt(III) complex.

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Experimental

All experiments except the preparation of the Co(III) complex were performed under argon by using a vacuum-line technique. Solvents were purified, dried and distilled according to the standard procedures [6] before use. 1,4,10,13-Tetraoxa-7,16-diaza-cyclooctadecane (**1**) [7] and 4-nitro-bis(2-iodoethoxy)benzene (**2**) [8] were prepared according to the literature. ^{1}H ^{13}C NMR and IR spectra were recorded on a Varian XL-200 spectrometer at 25 °C and on a Perkin-Elmer 1600 FTIR spectrometer, respectively. Mass spectra were recorded on Varian MAT 711 and VG Zapspec spectrometers. The elemental analysis and metal contents of the compounds were determined on a Hewlett-Packard 185 CHN analyser and a Unicam 929 AA spectrophotometer, respectively.

Preparation of 4,7,13,16,21,24-hexaoxa-5,6-(4′-nitrobenzo)-1,10-diazabicyclo[8.8.8]hexacosane (**3**)

1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane **1** (2.79 g, 10.66 mmol) was dissolved in dry acetonitrile (300 mL) containing finely ground anhydrous Cs_2CO_3 (9.75 g, 30 mmol) and purged under argon in a Schenk system connected to a vacuum-line. This solution was stirred at room temperature and a solution of 4-nitro-bis(2-iodoethoxy) benzene **2** (6.125 g, 13.22 mmol) in dry acetonitrile (50 mL) was added over a period of 30 min at 60 °C. The reaction was monitored by using TLC [chloroform/petroleum ether/methanol (7:3:2)] and was completed in 80 h at the above temperature. At the end of this period the reaction mixture was filtered through Celite and washed with dry acetonitrile. The solution was evaporated to dryness under reduced pressure to give an oily substance which was purified by silica gel column chromatography. The elution was carried out successively with chloroform:petroleum ether:methanol (7:3:2).

A viscous amber oil (3.6 g, 76.8%) was obtained by the evaporation of solvents. IR (KBr pellets, cm^{-1}): 3045, 2919, 1587, 1513, 1341, 1275, 1096, 749; ^{1}H-NMR ($CDCl_3$): (δ) 8.03 (d, 1H, Ar—H), 7.94 (s, 1H, Ar—H), 7.29 (d, 1H, Ar—H), 4.45 (m, 4H, Ar—O—CH_2), 4.31 (m, 4H, —CH_2N), 3.66 (m, 16H, CH_2CH_2—OCH_2CH_2), 2.82 (m, 8H, CH_2N); ^{13}C-NMR ($CDCl_3$): (δ) 151.92, 146.21, 141.47, 118.60, 112.51, 107.46, 68.34-66.90, 52.62; MS (EI) *m/z* 469 $[M]^+$.

Anal. Calcd. for $C_{22}H_{35}N_3O_8$: C, 56.28; H, 7.46; N, 8.95. *Found*: C, 56.11; H, 7.62; N, 8.70.

4,7,13,16,21,24-Hexaoxa-5, 6-(4′-aminobenzo)-1, 10-diazabicyclo[8.8.8]hexacosane (**4**)

Compound **3** (3.16 g, 6.75 mmol) was dissolved in *n*-butanol (240 mL) by heating at reflux temperature. Palladium (10%)/activated carbon (1.0 g) was added to the solution under the same condition and 6 mL of hydrazine hydrate (100%) was then added drop-wise for 30 min. The reaction mixture was refluxed and stirred for 8 h and then filtered through Celite and washed with *n*-butanol (20 mL). The extent of the reaction was monitored by using TLC [petroleum ether/chloroform (3:7)]. The pale brown solution was concentrated to dryness under reduced pressure and then purified by using column chromatography [silica gel column (petroleum ether/chloroform)(3:7)]. A viscous, reddish amber oil (2.78 g, .93.91%) was obtained by the evaporated the solvent. IR (KBr pellets, cm^{-1}): 3332–3228, 3054, 2878, 1611, 1593, 1512, 1456, 1285, 1226, 1101, 944, 753 ; ^{1}H-NMR ($CDCl_3$): (δ) 6.78 (d, 1H, Ar—H), 6.65 (s, 1H, Ar—H), 6.22 (d, 1H, Ar—H), 4.44 (s, 2H, NH_2), 4.22 (m, 4H, Ar—O—CH_2), 3.58 (m, 16H, CH_2CH_2—O—CH_2CH_2), 2.74 (m, 8H, NCH_2); ^{13}C-NMR ($CDCl_3$): (δ) 145.12, 142.08, 138.43, 114.67, 107.45, 102.28, 69.38–67.56, 53.19; MS (EI) *m/z* 439 $[M]^+$.

Anal. Calcd. for $C_{22}H_{37}N_3O_6$: C, 60.13; H, 8.42; N, 9.56. *Found*: C, 60.28; H, 8.61; N, 9.38.

N, *N′*-*Bis[4,7,13,16,21,24-hexaoxa-5, 6-(4′-aminobenzo)-1, 10-diazabicyclo[8.8.8]hexacosane]diaminoglyoxime* (**H_2L**)

A solution of cyanogen-di-*N*-oxide in dichloromethane (150 mL), which was prepared from (E, E)-dichloroglyoxime (0.472 g, 3 mmol) and an aqueous solution of Na_2CO_3 (30 mL, 0.5 M), were added to a cold solution (−15 °C) of **4** (2.63 g, 6 mmol) in cold dichloromethane (50 mL). The reaction was continued for 10 h at this temperature and the pale brown product was obtained with separation by filtration, washed with cold dichloromethane and diethyl ether and then dried *in vacuo*. The pale yellow needles of the crystalline product (2.32 g, 80.55%) were obtained by recrystallization from ethanol, mp 164 °C (dec.). IR (KBr pellets, cm^{-1}): 3378, 3224, 3040, 2880, 1618, 1605, 1592, 1519, 1466, 1357, 1227, 1131, 1097, 935; ^{1}H-NMR (DMSO-d_6): (δ) 10.22 (s, 2H, OH), 7.94 (s, 2H, NH), 6.78 (d, 2H, Ar—H), 6.48 (s, 2H, Ar—H), 6.28 (d, 2H, Ar—H), 4.31 (m, 8H, Ar—O—CH_2), 3.68 (m, 32H, CH_2CH_2—O—CH_2CH_2), 2.86 (m, 16H, NCH_2); ^{13}C-NMR (DMSO-d_6): (δ) 146.24, 144.72, 142.86, 136.67, 113.63, 105.25, 100.43, 69.85–66.70, 53.66; MS (FAB positive) *m/z* 1008 $[M + C_2H_5OH]^+$, 962 $[M]^+$.

Anal. Calcd. for $C_{44}H_{74}N_8O_{14}$: C, 57.38; H, 7.69; N, 11.64. *Found*: C, 57.53; H, 7.50; N, 11.45.

Preparation of the cobalt(III) complex **[Co(HL)$_2$pyCl]** (**5**)

A solution of $CoCl_2 \cdot 6H_2O$ (0.117 g, 0.5 mmol) in ethanol (20 mL) was added to a hot solution (60 °C) of **H_2L** (0.962 g, 1 mmol) in ethanol (75 mL) with stirring. A distinct change in colour and a decrease in the pH of the reaction mixture (pH = 2.24) was observed. While cooling, a solution of Lewis base, pyridine (0.04 g, 0.5 mmol), in ethanol (2 mL) was added to the above-mentioned reaction mixture. Then the mixture was allowed to cool to room temperature, and a stream of oxygen was bubbled through the solution for 4 h. After this period, the solution was concentrated to 20 mL, and placed in a refrigerator at −10 °C overnight, whereupon the product was crystallized from the reaction mixture. The pale brown microcrystalline product (0.72 g, 68.25%) was filtered off, washed with cold ethanol and diethyl ether and then dried *in vacuo*, mp 284 °C (dec.). IR (KBr pellets, cm^{-1}): 3392, 3048, 2874, 1700, 1612, 1601, 1592, 1510, 1461, 1354, 1223, 1132, 1098, 927; ^{1}H-NMR (DMSO-d_6): (δ) 16.82 (s, 2H, O—H···O), 8.01 (br, 4H, NH), 7.72 (d, 2H, py-H), 7.51 (t, 1H, py-H), 6.86 (m, 6H, Ar—H, py-H), 6.45 (s, 4H, Ar—H), 6.36 (m, 4H, Ar—H), 4.37 (m, 16H, Ar—O—CH_2), 3.72 (m, 64 H, CH_2CH_2—O—CH_2CH_2), 2.90 (m, 16H, NCH_2); MS (FAB) *m/z* 2095 $[M + 1]^+$, 2016 $[M\text{-py} + 1]^+$.

Anal. Calcd. for $C_{97}H_{151}N_{17}O_{28}CoCl$: C, 55.54; H, 7.20; N, 11.35; Co, 2.81. *Found*: C, 55.73; H, 7.02; N, 11.16; Co, 3.05.

Preparation of the BF_2^+-capped cobalt(III) complex **[Co(LBF$_2$)$_2$** (**6**)

A suspension of the cobalt(III) complex (**5**) (0.63 g, 0.3 mmol) in 60 mL of freshly distilled dry acetonitrile was brought to reflux temperature in an argon atmosphere. An equivalent amount of the boron trifluoride diethyl ether complex (0.25 mL) was added with continuous stirring to the above mentioned suspension, which changed its colour immediately to red. After being allowed to stand at reflux temperature for 20 min, the solvent was removed under reduced pressure, and the residue was dissolved in 25 mL of dry acetonitrile and evaporated to dryness. The dark red crude product was dissolved in 10 mL of dry acetonitrile and allowed to stand at −18 °C overnight, whereupon the compound crystallized from the solution. The crystallized product (0.41 g, 62.4%) was collected by filtration, washed with cold dry acetonitrile and diethyl ether and then dried *in vacuo*, mp 172 °C. IR (KBr pellets, cm^{-1}): 3404, 3061, 2882, 1636, 1603, 1590, 1511, 1474, 1355, 1287, 1101, 940; ^{1}H-NMR ($CDCl_3$): (δ) 8.12 (br, 4H, NH), 7.85 (d, 2H, py-H), 7.61 (t, 1H, py-H), 6.93 (m, 6H, Ar—H, py-H), 6.49 (s, 4H, Ar—H), 6.44 (m, 4H, Ar—H), 4.43 (m, 16H, Ar—O—CH_2), 3.70 (m, 64H, CH_2CH_2—O—CH_2CH_2), 2.86

(m, 16H, NCH_2); ^{13}C-NMR ($CDCl_3$): (δ) 149.78, 145.89; 145.08, 142.77, 137.10, 136.68, 124.80, 114.02, 105.34, 100.61, 69.93–66.82, 53.54; MS (FAB) *m/z* 2188.2 $[M]^+$.

Anal. Calcd. for $C_{97}H_{149}N_{17}O_{28}B_2F_4CoCl$: C, 53.12; H, 6.80; N, 10.86; Co, 2.69. *Found*: C, 52.94; H, 6.98; N, 10.61; Co, 2.87.

Preparation of the BF_2^+-caped cobalt(III) complex **$[Ca_4Co(LBF_2)_2pyCl](ClO_4)_8$ (7)**

A solution of calcium perchlorate tetrahydrate (0.124 g, 0.88 mmol) in dry methanol (5 mL) was added to a refluxing solution of **6** (0.22 g, 0.1 mmol) in dry methanol (15 mL) and the reaction was monitored by TLC [chloroform:methanol (7:3)]. After the addition was complete, the mixture was refluxed for 1 h then concentrated to 5 mL and allowed to cool at −18 °C in a refrigerator overnight. The crystalline dark red product (0.26 g, 82.8%) was filtered off, washed with cold chloroform and diethyl ether then dried *in vacuo*, mp 212 °C. IR (KBr pellets, cm^{-1}): 3397, 3058, 2923, 1639, 1606, 1593, 1514, 1464, 1350, 1271, 1113, 1092, 938; ^{1}H-NMR (DMSO-d_6): (δ) 8.09 (br, 4H, NH), 7.82 (d, 2H, py-H), 7.63 (t, 1H, py-H), 6.98 (m, 6H, Ar—H), 6.53 (s, 4H, Ar—H), 6.46 (m, 4H, Ar—H), 4.38 (m, 16H, Ar—O—CH_2), 3.82 (m, 64H, CH_2CH_2—O—CH_2CH_2), 3.04 (m, 16H, NCH_2); ^{13}C-NMR (DMSO-d_6): (δ) 149.87, 145.80, 145.13, 142.81, 137.21, 136.63, 124.85, 114.49, 105.39, 100.67, 70.13–66.99, 53.71.

Anal. Calcd. for $C_{97}H_{149}N_{17}O_{60}B_2Cl_9F_4Ca_4Co$: C, 36.98; H, 4.73; N, 7.56; Co, 1.87;. Ca, 5.08. *Found*: C, 36.79; H, 4.56; N, 7.78; Co, 1.70; Ca, 5.31.

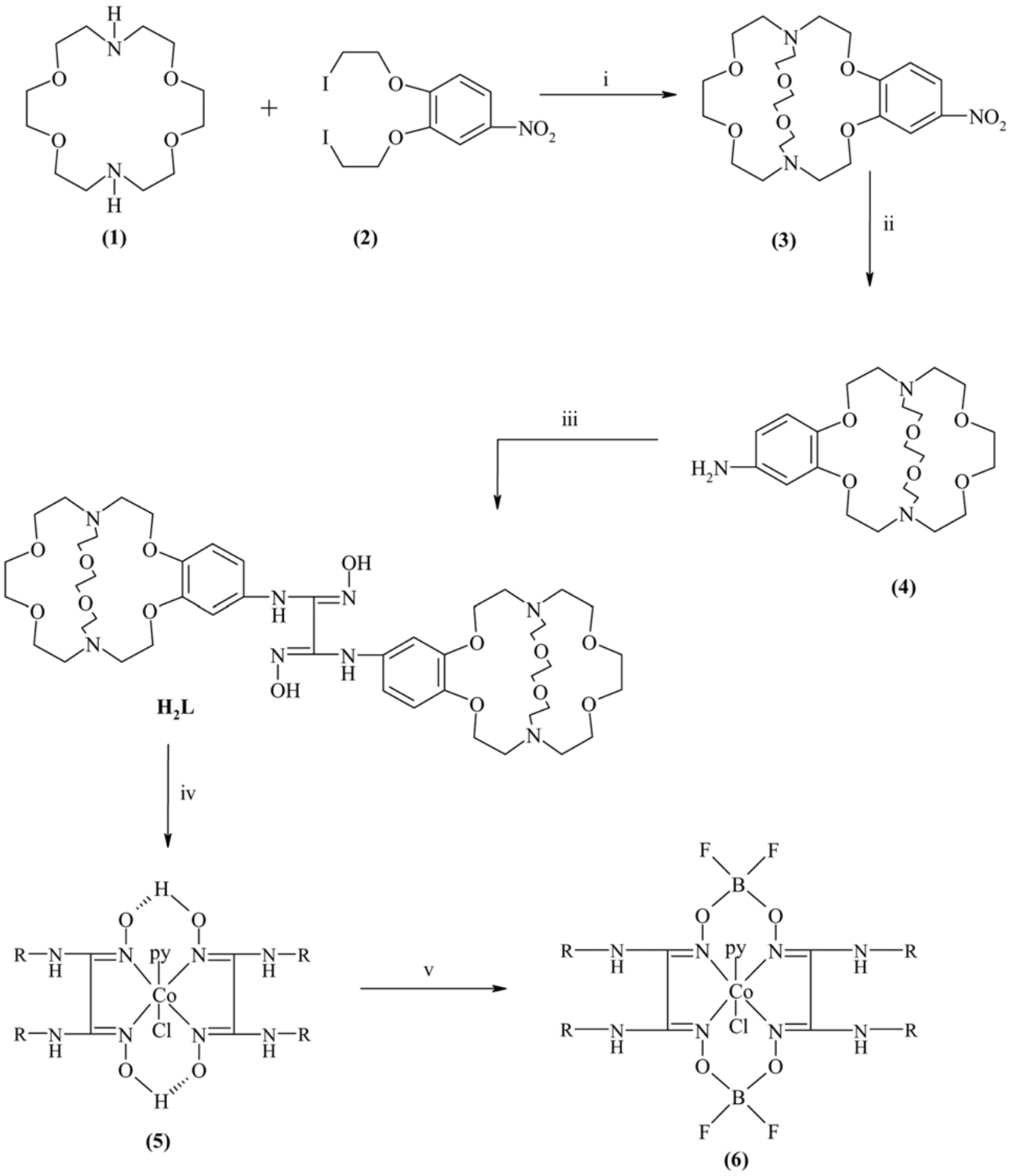
Results and discussion

The reaction of **3**, which was required for a comparison between our macrobicyclization reaction and those reported by Gansow and Pettit [5] is illustrated in Scheme 1. The macrobicyclization reaction was carried out in an acetonitrile solution of 4,13-diaza-18 crown-6 (**1**) [7] using a 25% excess of 4-nitro-bis(2-iodoethoxy)benzene [8], a three-fold excess of Cs_2CO_3 and 0.5 equivalent amount of NaI. The use of excess compound **2** generally gave a higher yield than when an equivalent amount was used. The lower yield obtained when an equivalent amount of **2** is used is probably due to an increase in ammonium salt formation. We observed that added NaI generally gave fewer byproducts making the reaction mixture easier to purify. This can be attributed to the presence of a small amount of NaI, which acts as a template and aids in the macrobicyclization reaction [8]. The other methods mentioned above involve the reaction of 4,13-diaza-18-crown-6 with 1,2-bis-(oxyacetylchloride)-4-nitrobenzene to give cryptand (**3**). In addition to this, the reduction of the bis(amides) with the diborane-tetrahydrofuran complex leads to the formation of the desired product. Our one-step macrobicyclization method involves the formation of the target cryptand, so the yield (76.8%) is significantly higher than the known procedure. Comparative reaction steps and yield obtained by using the 4,13-diaza-18-crown-6 with the diiodide macrobicyclization approach indicate that the new method is more efficient than the known method despite the greater number of steps and the high dilution conditions involved in the former. Initially catalytic hydrogenation or reduction with stannous chloride had been used in the reduction of nitro compounds but they were sufficiently unstable to make the characterization difficult or the production was obtained as an amine complex. In generally, we have observed that reduction using hot 10% palladium/activated charcoal and hydrazine hydrate (100%) gives better yields and purer products than reduction with other methods [10]. The structures of these cryptands (**3**, **4**) indicated agreement with the spectral and analytical data and they are identical to the same macrobicycles obtained by stepwise synthesis [5].

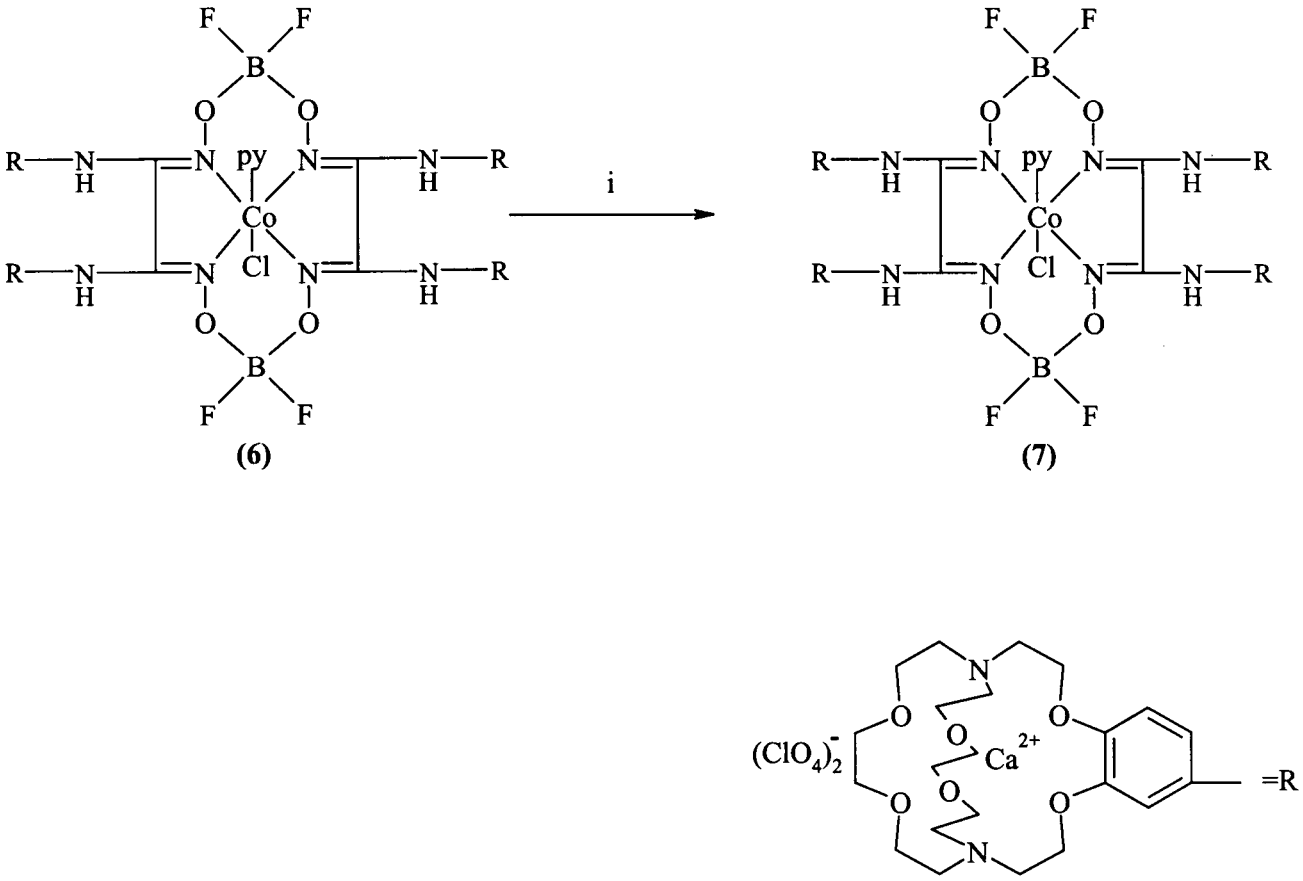
vic-Dioxime containing a macrobicyclic moiety [$\mathbf{H_2L}$] was synthesized in good yield (80.55%) according to the previously reported procedure [11] involving the reaction of 2 equivalents of **4** with 1 equivalent of cyanogen-di-*N*-oxide [12] in dichoromethane at −15 °C for 10 h (Scheme 1). In the ^{1}H-NMR spectrum of $\mathbf{H_2L}$, the deuterium exchangeable NH and OH protons appear as two singlets at δ = 7.94 and 10.22 ppm, respectively. The resonance observed at δ = 144.72 ppm in the ^{13}C-NMR spectrum of this compound should be related to azomethine carbon atoms [13]. The equivalent carbon and proton resonances belonging to the hydroxyimino groups confirm the *S-trans* form of the *vic*-dioxime [14]. The disappearance of NH_2 stretches, along with the appearance of new bands at 3224, 1618 and 935 cm^{-1} arising form O—H, C=N and N—O groups, respectively, are in agreement with the proposed structure. The result of the mass spectral data at *m/z* = 962 also confirm the formation of the *vic*-dioxime.

The Co(III) complex of $\mathbf{H_2L}$ has a metal:ligand ratio of 1:2 according to the elemental analysis and mass spectral data, and the metal is coordinated by the N,N' atoms of the dioxime (Scheme 2). The disappearance of the O—H stretching vibrations and the shift of C=N resonances to lower frequency in the IR spectrum of **$[Co(HL)_2pyCl]$** (**5**) can be attributed to N, N'-chelation [15]. The weak and broad bending vibrations observed at 1701 cm^{-1} also indicate the formation of a complexation reaction. ^{1}H-NMR spectral data confirm the intermolecular hydrogen bonding structure with a chemical shift of δ = 16.82 ppm for the deuterium exchangeable O—H···O protons. Upon coordination to Co(III), the ligand resonances shift sslightly but their number is unchanged. The additional signals due to the presence of the coordinated pyridine molecule are also present.

The template BF_2^+-capped macrocycle can be prepared by adding an equivalent amount of $BF_3{\cdot}Et_2O$ to an acetonitrile suspension of the hydrogen-bridged Co(III) complex (Scheme 2). The bridging protons of **5** are exchanged by BF_2^+ groups and the axial base, pyridine, is retained according to the ^{1}H, ^{13}C-NMR and MS spectral data and elemental analysis. The other spectral data of **6** are similar to those of $\mathbf{H_2L}$ except some stretching vibrations in the infrared



Scheme 1. Reagents and conditions: (i) Cs_2CO_3 in dry acetonitrile under argon at 60 °C; (ii) NH_2—NH_2, 10% Pd/C in *n*-butanol at reflux temperature; (iii) cyanogen-di-*N*-oxide in CH_2Cl_2 at −15 °C; (iv) $CoCl_2 \cdot 6H_2O$, py in EtOH at 60 °C; (v) $BF_3 \cdot Et_2O$ in dry acetonitrile under argon at reflux temperature.



Scheme 2. Reagents and conditions; (i) $Ca(ClO_4)_2 \cdot 4H_2O$ in dry methanol at reflux temperature.

spectrum. The C=N stretching vibrations of **6**, in contrast with **5**, are shifted to the higher frequency region, which exhibits upward shifts of about 22 cm^{-1} due to the strong electron-withdrawing effect of the BF_2^+ groups [16].

The crystalline calcium complex (**7**) was obtained by adding a solution of $Ca(ClO_4)_2 \cdot 4H_2O$ in methanol to a methanol solution of the equivalent amount of **6**. Elemental analysis of **7** indicates an alkaline earth metal:BF_2^+-capped complex ratio of 4:1. In the ^{1}H-NMR spectrum of cryptate **7** in $CDCl_3$, as a consequence of complex formation, the signal at $\delta = 3.06$ ppm, assigned to the CH_2N protons, is accompanied by a 0.20 ppm down-field shift of the signal centre. A similar down-field shift is also observed for the CH_2O resonances of the cryptate at $\delta = 3.72$ ppm. The cryptate formation may also be observed directly by following the changes in the ^{13}C-NMR spectrum of **7** in the presence of Ca^{2+} cations. These observations are consistent with the NMR shift changes found upon cryptate formation between the cryptands and various alkali earth cations, as reported earlier [17], and indicate that a similar conformational transition occurs during the coordination of the calcium cation and it is located inside the molecular cavity [2].

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