

Column: Lichrosorb RP-18
Solvent: 60% Methanol

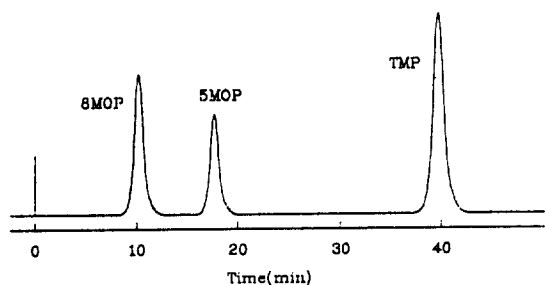


Figure 5. HPLC profile of 8MOP, 5MOP, and TMP.

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- Taking the CMC of SDS to be 1.4 mM¹⁴ and the degree of micellar ionization to be about 0.2¹⁵ at the ionic strength 0.1, the concentration of the free sodium ion due to the detergent is 3 mM which is considerably smaller than 0.1. Because the CMC of CTAB and CTAC at the ionic strength 0.1 is smaller than 0.95 and 1.4 mM reported in the absence of salts¹⁶, respectively, the contribution of these surfactants to the ionic strength can be neglected.
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New Crown Compounds Derived from 1,2-Bis(2-hydroxybenzyl)benzene (II): Bisaryl Crowns

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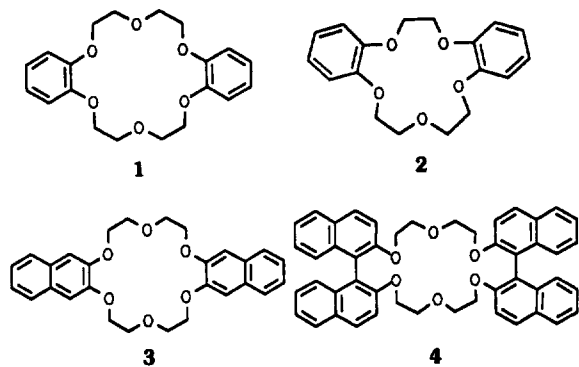
New bisaryl corands (crown ethers) bearing 1,2-dibenzyl- and 1,2-dibenzoylbenzene subunits have been synthesized: The reaction of 1,2-bis(2-hydroxybenzyl)benzene in base with mono-tetrahydropyranyl oligoethylene glycol tosylate, deprotection of the bis-condensation product to give a corresponding diol, tosylation of the free hydroxyls of the diol, and condensation of the ditosylate in base with 1,2-bis(2-hydroxybenzyl)benzene afforded a new type of bisaryl corand(I) of 1,2-dibenzylbenzene system. Oxidation of the benzylic positions of the corands(I) furnished novel aromatic corands(II) containing partly carbonyl functions.

Introduction

Various bisaryl crown ethers, such as 1, 2, 3 and 4, have been synthesized by many workers, in which two aromatic hydrocarbon subunits are linked symmetrically or unsymmetrically by two ethyleneoxy chains to form a macrocycle.

Although the crowns 1-4 are structurally analogous, their complexing properties vary markedly with the structures of the aromatic subunits and the polyether ring sizes. Dibenzo-18-crown-6(1), synthesized by C. J. Pederson in his early investigations for crown ether synthesis,^{1,2} and reasonably selective toward the complexation of potassium ions, is the first

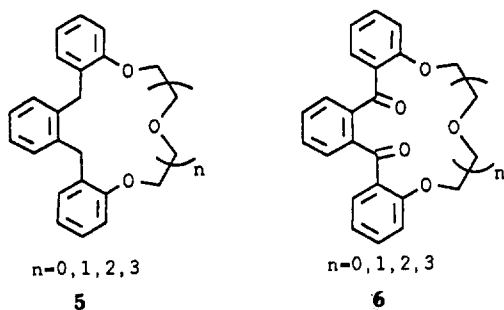
and most versatile of the aromatic crown ethers. Bis-binaphthyl crown 4, synthesized by Cram and his coworkers,³ is one of the chiral crowns which could be used in optical resolution of enantiomers. Now, it is of interest to prepare a new type of bisaryl corands bearing uncommon aromatic subunits, which are expected to have unique complexing character.



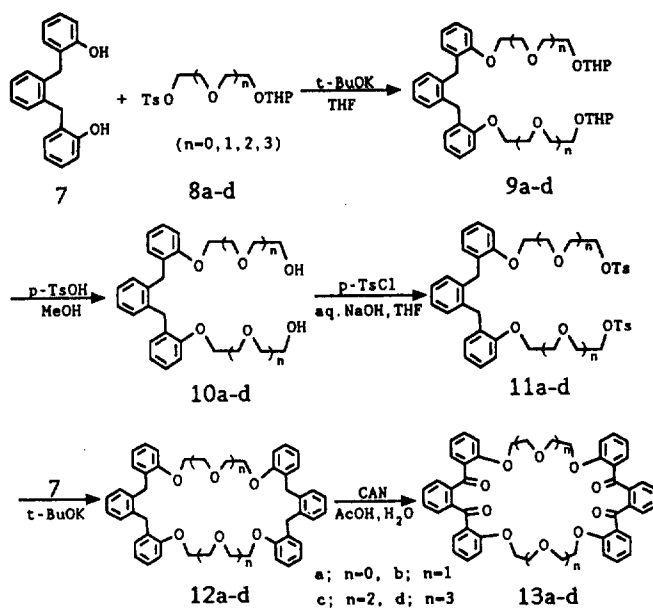
The goal of this work is the synthesis of a new type of corands shown in structure 12, in which two ethyleneoxy chains are bound to 1,2-dibenzylbenzene subunits to form a macrocycle. The bisaryl corands 12 may be much more flexible in conformational sense than the other corands reported so far, such as 1-4, in which the aromatic subunits are rigid. In this communication, we also report novel crown 13, which could be obtained by the oxidation of benzylic positions of the corands 12 and have ketonic carbonyls as part of the macroring.

Results and Discussion

Recently⁴ we reported the synthesis of monoaryl crowns 5 by the reaction of 1,2-bis(2-hydroxybenzyl)benzene(7) with oligoethylene glycol ditosylate in tetrahydrofuran in the presence of *t*-butoxide. Though the reaction proceeded to produce [1 + 1]-product 5 as a main product, we could also isolate a small amount of [2 + 2]-product 12 as a byproduct, the structure of which was determined by spectral data. The carbonyl-containing corand 6 was obtained by the oxidation of benzylic positions of 5.



In this work, we investigated the general and efficient synthesis of the new bisaryl crowns 12. A typical synthetic procedure is shown in the Scheme 1. An important reactant 1,2-bis(2-hydroxybenzyl)benzene(7) was prepared by the literature procedure,⁵ which involves the reaction of 2-bromoanisole Grignard reagent with 1,2-bis(bromomethyl)benzene in the presence of copper(I) iodide, followed by demethylation of the cross coupling product in acid to a corres-



Scheme 1

ponding bisphenol 7. The other reactant 8 was prepared by monoprotection of oligoethylene glycol with dihydropyran, followed by tosylation of remaining free hydroxy group.

The condensation of 7 with 8 in tetrahydrofuran in the presence of *t*-butoxide afforded a bis-tetrahydropyranyl ether 9, which was deprotected without purification to give a corresponding diol 10 almost quantitatively. For the direct synthesis of 10a, we examined the literature procedure reported by Rolla *et al.*⁶ in which the reaction of pyrocatechol with 2-chloroethanol in ethanolic sodium hydroxide solution gave a reasonable yield (75%) of bis-condensation product, 1,2-bis(2-hydroxyethoxy)benzene. However, the reaction of 7 in base with an excess amount of 2-chloroethanol or 2-bromoethanol did not furnish expected bis-condensation product leaving one of the two phenolic hydroxy groups unchanged. The free hydroxy groups of 10 were tosylated with *p*-toluenesulfonyl chloride in aqueous sodium hydroxide to give a ditosylate 11 of two-armed 1,2-dibenzylbenzene unit, which could serve as an electrophile. The reaction of 11 with 7 in tetrahydrofuran in the presence of *t*-butoxide furnished a cyclization product 12. The yield of the cyclization reaction was dependent upon the sizes of the ethyleneoxy units and the presence of template ions. In general, the larger the ethyleneoxy unit was, the lower the yield was. When $n = 3$, the yield of the cyclization was low (10–20%) in the presence of *t*-butoxide, but it could be raised (45–55%) by the addition of equivalent amount of cesium carbonate as a templating agent. In this reaction, a very small amount of higher analogs such as [4 + 4]-product ($n = 0$) was also formed, which was isolated and identified by spectral analysis. The physical and spectral data of 12 are summarized in Table 1.

The corands 12 have bulky hydrocarbon subunits and the two ethyleneoxy units are far from each other, separated by eight carbon atoms in the subunit. However, being rotatable about benzylic carbon atom, three benzene rings are not necessarily planar, but suitably bendable to make two phenolic oxygen atoms much closer so as to form a proper cavity for binding cations. The investigation for their complexation will

Table 1. Bisaryl Corands 12 of 1,2-Dibenzylbenzene System.
$$7 + 11a-d \xrightarrow[\text{THF, reflux}]{t\text{-BuOK}} 12a-d$$

Corands (n)	Yield (%) ^a	m.p. (°C)	MS <i>m/e</i> (M ⁺)	IR ν (cm ⁻¹)	¹ H-NMR(TMS) δ (ppm)
12a (n = 0)	50-60	225-226	632	3040, 2940, 1600 1480, 1450, 1290 1235, 1110, 1060	7.25-6.71(m, 24H, arom.) 4.16(s, 8H, benzylic) 3.89(s, 8H, OCH ₂)
12b (n = 1)	65-87	180-181	720	3065, 2920, 1600 1490, 1450, 1290 1250, 1120, 1050	7.23-6.71(m, 24H, arom.) 4.01-3.90(m, 8H, OCH ₂) 3.97(s, 8H, benzylic) 3.70-3.61(m, 8H, OCH ₂)
12c (n = 2)	20-30	125-126	808	3025, 2920, 1600 1490, 1450, 1240 1130, 1100, 1060	7.23-6.72(m, 24H, arom.) 4.09-3.98(m, 8H, OCH ₂) 3.98(s, 8H, benzylic) 3.78-3.65(m, 8H, OCH ₂) 3.53(s, 8H, OCH ₂)
12d (n = 3)	10-20 (45-55) ^b	120-121	896	3020, 2920, 2880 1600, 1490, 1450 1250, 1120, 1050	7.25-6.75(m, 24H, arom.) 4.11-3.97(m, 8H, OCH ₂) 3.97(s, 8H, benzylic) 3.80-3.67(m, 8H, OCH ₂) 3.55-3.50(m, 16H, OCH ₂)

^aIsolated yields. ^bYields in the presence of templating agent Cs₂CO₃.

Table 2. Carbonyl Corands 13 of 1,2-Dibenzoylbenzene System
$$12b-d \xrightarrow[\text{ACOH-H}_2\text{O}]{\text{CAN}} 13b-d$$

Corands (n)	Yield (%)	m.p. (°C)	MS <i>m/e</i> (M ⁺)	IR ν (cm ⁻¹)	¹ H-NMR(TMS) δ (ppm)
13b (n = 1)	50-55	228-229	776	3070, 2930, 1660 1600, 1480, 1440 1250, 1140, 1050	7.48-6.60(m, 24H, arom.) 3.97-3.65(t, 8H, OCH ₂) 3.44-3.32(t, 8H, OCH ₂)
13c (n = 2)	20-35	188-189	864	3070, 2890, 1660 1640, 1590, 1480 1445, 1250, 1110	7.46-6.76(m, 24H, arom.) 4.01-3.67(m, 8H, OCH ₂) 3.48-3.39(m, 16H, OCH ₂)
13d (n = 3)	10-20	148-149	952	3070, 2920, 1650 1600, 1485, 1450 1310, 1250, 1130	7.49-6.73(m, 24H, arom.) 4.00-3.67(m, 8H, OCH ₂) 3.51-3.32(m, 24H, OCH ₂)

be continued.

The carbonyl-containing bisaryl crowns **13** could be obtained by the oxidation of the benzylic positions of corands **12**. For the benzyl-to-carbonyl conversion, various oxidants were examined. But the oxidation in acidic media was not easy, since it was always accompanied by the cleavage of ether linkage. Among the oxidants, ammonium cerium nitrate (CAN)⁷ was reasonably effective, though it oxidized only **12b-d** to **13b-d**. The conversion of **12a** to **13a** could not be accomplished so far by any oxidants and methods such as benzylic bromination and then hydrolysis to alcohol followed by oxidation. The physical and spectral data of **13** are summarized in Table 2. The corands **13** are expected to have unique ligating character for cations, for they contain additional carbonyl functions compared with the parent crowns **12**. The investigation for their complexation will be continued.

Experimental Section

General. All anhydrous reactions were conducted with the unusual precautions for rigorous exclusion of air and moisture. Diethyl ether and tetrahydrofuran were purified by refluxing for hours with sodium benzophenone ketyl under nitrogen, followed by distilling prior to use. Dichloromethane was dried by distilling over calcium hydride. Flash chromatography was carried out using silica gel 60 (E. M. Merck, particle size 0.040-0.063 mm, 230-400 mesh ASTM). Thin layer chromatography was conducted on precoated silica gel plates (E. M. Merck, F₂₅₄, 0.2 mm thickness). Proton NMR spectra were recorded on a Bruker AC-80 FT NMR spectrometer to an internal standard of tetramethylsilane. All proton chemical shifts (δ) are reported in parts per million (ppm). Infrared spectra were obtained on a Perkin-Elmer Model 782

and JASCO IR-810 spectrometer. Mass spectra were recorded on a Shimadzu-LKB 9000 GC/MS system. All melting points were measured on an Electrochemical Digital Melting Point Apparatus, and were uncorrected. When necessary, chemicals were purified according to the reported procedure⁸.

1,2-Bis(2-hydroxybenzyl)benzene (7). A Grignard reagent prepared from 2-bromoanisole (24g, 128 mmol) and magnesium turnings (4.0 g, 167 mmol) in THF (60 ml) was added by cannulation, with stirring under nitrogen, to a solution, previously cooled to -30°C , of 1,2-bis(bromomethyl)benzene (10.5 g, 40 mmol) in THF(30 ml). The mixture was stirred for 30 min at -30°C , allowed to warm to room temperature, and stirred for 5 h. After aqueous work-up, the crude product was chromatographed (silica gel/dichloromethane) to give 85–95% yield of colorless crystals of the coupling product, a dimethoxy compound, mp $112\text{--}113^{\circ}\text{C}$.

A mixture of the dimethoxy compound (10 g), 47% HBr (40 ml), and AcOH (40 ml) was refluxed for 10h. After normal work-up, the crude product was chromatographed (silica gel/dichloromethane) to give colorless crystals of bisphenol 7, mp $93\text{--}94^{\circ}\text{C}$, in 80–85% yield: IR(KBr) 3430 and 3300 (strong, OH), 3060, 3010, 2920, 1585, 1490, 1360, 1330 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3), δ 6.8–7.3 (m, 12H, arom.), 5.3 (s, 2H, OH), 4.0 (s, 4H, benzylic); MS (m/e) 290 (M^+).

Mono-tetrahydropyranyl Oligoethylene Glycol Tosylate(8).

General Procedure. To a solution of an oligoethylene glycol (1.0 mol) and a catalytic amount of *p*-TsOH(1 g) in CH_2Cl_2 (150 ml) was added dropwise with stirring a solution of dihydropyran (0.3 mol) in CH_2Cl_2 (25 ml) over a period of 20 min, and stirred the mixture for 5–6 h at room temperature. The reaction mixture was washed with aqueous NaHCO_3 and water successively, and dried over anhyd. MgSO_4 . After evaporated the solvent, the crude product was chromatographed on silica gel using dichloromethane (or ether) as an eluent. The yield of the mono-THP ether was dependent upon the sizes of the glycols (30–55%).

To a solution of the mono-THP ether (35 mmol) and *p*-TsCl (40 mmol) in THF (40 ml) was added dropwise 40% aqueous NaOH solution (10 ml), and the mixture was stirred for 5 h at room temperature. To this reaction mixture was added saturated NH_4Cl solution (15 ml), and the solvent was removed at a reduced pressure. The resulting aqueous layer was extracted with ether, washed with water, and dried over anhyd. MgSO_4 . The solvent was evaporated *in vacuo* to give a sticky oil of the corresponding tosylate(8) in good yield (>95%), which was almost pure and used in next experiment without further purification.

Bis-tetrahydropyranyl Ether 9.

General Procedure. To a solution of 7(5.8 g, 20 mmol) and *t*-BuOK(4.7 g, 42 mmol) in THF(120 ml), previously stirred for 30 min at room temperature, was added 8(41 mmol), refluxed the mixture for 24 h, and allowed to cool to room temperature. The reaction mixture was neutralized with dilute HCl, removed the solvent at a reduced pressure, extracted the aqueous layer with dichloromethane, washed the organic layer with water, and dried over anhyd. MgSO_4 . The solvent was evaporated to give a viscous liquid of crude di-THP ether 9 in good yield(90–95%), which was deprotected without further purification.

Diol 10.

General Procedure. A mixture of 9(10 mmol), *p*-TsOH (1 g) and MeOH(100 ml) was stirred at room temperature for 2 h. To this reaction mixture was added saturated NaHCO_3 solution(50 ml), removed the solvent *in vacuo*, extracted with ether, dried over anhyd. MgSO_4 , and evaporated the solvent. The crude product was chromatographed(silica gel/dichloromethane) to give a viscous oil of the diol 10 in 85–90% yield.

Preparation of Ditosylate 11.

General Procedure. To a solution of 10(8 mmol) and *p*-TsCl(6 g, 32 mmol) in THF(50 ml), was added dropwise with stirring 40% aqueous NaOH solution(20 ml) over a period of 30 min, and stirred the mixture for 5 h at room temperature. To this reaction mixture was added water(60 ml), and removed the solvent *in vacuo*. The resulting aqueous layer was extracted with ether, washed the organic layer with water, dried over anhyd. MgSO_4 , and evaporated the solvent. The crude product was chromatographed(silica gel/dichloromethane) to give a sticky oil of ditosylate 11 in 90–95% yield.

Bisaryl Corands 12 a–d

General Procedure. In THF(130 ml) in a 250 ml three-necked round-bottomed flask, fitted with a reflux condenser and a dropping funnel, were dissolved 7(1.45g, 5 mmol) and *t*-BuOK(1.2 g, 11 mmol), and the mixture was refluxed for 30 min. To this mixture was added a solution of 11(4.4 g, 5.7 mmol) in THF(50 ml), refluxed the mixture for 20 h, and allowed to cool to room temperature. The reaction mixture was neutralized with dilute HCl, and removed the solvent at a reduced pressure. The resulting aqueous layer was extracted with ether, washed the organic layer with water, dried over anhyd. MgSO_4 , and evaporated the solvent. Recrystallization of the crude cyclization product from *n*-hexane/dichloromethane furnished a colorless crystalline compound 12(Table 1).

Oxidation of Crowns 12 to Carbonyl Crowns 13. The corands 12, except 12a, can be oxidized easily with ammonium cerium nitrate(CAN) to 13. The oxidation of 12a to 13a could by no means be carried out.

General Procedure. To a solution of 12b-d(2.0 mmol) in AcOH(40 ml) was added a solution of CAN(11 g, 20 mmol) in AcOH- H_2O (50 ml, 40:10 v/v), and the mixture was stirred for 24 h at room temperature. After the normal work-up, the crude product was purified by chromatography(silica gel/dichloromethane), and recrystallized from *n*-hexane/dichloromethane to give a white crystalline solid of crowns 13b-d(Table 2).

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Dichloro, Alanine and S-Methylcysteine Cobalt (III) Complexes of Ethylenediamine-N,N'-di- α -isobutyric Acid

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Synthesis of dichloro cobalt (III) complexes of a flexible N_2O_2 -type tetradentate ligand, ethylenediamine-N,N'-di- α -isobutyric acid (eddib), has yielded two geometrical isomers, *s-cis*-(Co(eddib)Cl₂)⁻ and *uns-cis*-(Co(eddib)Cl₂)⁻. A series of substitution reactions, (Co(eddib)Cl₂)⁻ → (Co(eddib)Cl(H₂O)) → (Co(eddib)CO₃)⁻ → (Co(eddib)(H₂O)₂)⁺ have been run for each of the two geometrical isomers. The reaction between the *s-cis*-(Co(eddib)Cl₂)⁻ complex and L-alanine (L-als) or S-methyl-L-cysteine (L-mcy) gave the meridional *s-cis*-[Co(eddib)(aa)] (aa = L-ala or L-mcy) complex. The S-methyl-L-cysteine was found to coordinate to cobalt (III) ion *via* the nitrogen and oxygen donor atoms.

Introduction

A linear flexible edda-type ligand (edda = ethylenediaminediacetic acid, HOOCCH₂NHCH₂CH₂NHCH₂COOH) can occupy four coordination sites with three geometric isomers possible: *s-cis*-(symmetric *cis*), *uns-cis* (unsymmetric *cis*), and *trans* (Figure 1).

Mori *et al.*¹ reported the synthesis of the *s-cis* cobalt(III) complexes of edda. Legg and Cooke² prepared both the *s-cis* and *uns-cis* isomers for the [Co(edda)(am)]⁺ (am = en, 2NH₃) as well as the cobalt(III) complexes of N-alkyl substituted analogue of edda. Kuroda³⁻⁵ observed that the coordination mode of edda depended upon the temperature. Later, Legg^{6,7} and others⁸⁻¹¹ prepared and characterized *uns-cis* isomers of [Co(edda)(L)]⁺ (L = en, S-alanine, R-propylenediamine).

The C-alkyl-substituted analogue of edda, ethylene-diamine-N,N'-di-S- α -propionate, ⁻OOCCH(CH₃)NHCH₂CH₂NHCH(CH₃)COO⁻ (SS-eddp), has been prepared by Liu and Co-workers¹², in which both *s-cis* and *uns-cis* isomers of (Co(SS-eddp)(L))⁺ (L=en, R=Pn) were isolated. The cobalt(III) complexes of S-stibenediamine-N,N'-diacetate (S-sdda)¹³ gave only the *s-cis* isomer. The cobalt(III) complexes of ethylenediamine-N,N'-di-S- α -isovalerate(ven)^{14,15} yielded only the *s-cis* isomer for (Co(ven)(H₂O)NO₃), while in the case of (Co(ven)(H₂O)₃)⁺ and (Co(ven)(en))⁺ both *s-cis* and *uns-cis* isomers were found to exist. The cobalt(III) complexes of 2S, 2'S-1,1'-(ethane-1,2-diyl) bis(pyrrolidine-2-carboxylate) (pren), Co(pren)L₂⁺⁺, have yielded only the *s-cis* isomer when L = Cl or H₂O, while both the *s-cis* and *uns-cis* isomers have been isolated when L₂ = en.^{16,17} Recently, we prepared a C-ethyl-substituted analogue of edda, ethylenediamine-N,N'-di- α -butyric acid, HOOCCH(C₂H₅)NHCH₂CH₂NHCH(C₂H₅)COOH(eddb), which yielded *s-cis*-(Co(eddb)Cl₂)⁻ complex.¹⁸

This paper will describe the preparation of the dichloro, alanine, and S-methylcysteine cobalt(III) complexes of a

C-alkyl-substituted analogue of edda, ethylenediamine-N,N'-di- α -isobutyric acid, HOOC(CH₃)₂NHCH₂CH₂NH(CH₃)₂COOH(eddib). We reported previously the synthesis of the eddib ligand and the dichloro cobalt (III) complex of eddib, in which only the *s-cis* isomer was obtained.¹⁹ We have recently been able to isolate the *uns-cis* isomer. It will be shown that both *s-cis* and *uns-cis* isomers are formed from the preparation of the dichloro cobalt(III) complexes of eddib. Complexes of the type [Co(eddib)L]⁺ (L = ClH₂O, CO₃²⁻ or 2H₂O) or Co(eddib)(aa) (aa = L-alanine or S-methylcysteine) were also prepared in this work. It will be shown that the amino acid is coordinated to the cobalt(III) ion via the nitrogen and oxygen donor atoms to give a meridional isomer.

Experimental

Physical Measurements. Electronic absorption spectra, and infrared spectra were recorded on a Shimadzu UV-240 double beam Spectrophotometer and a Shimadzu IR 435 spectrophotometer, respectively. ¹H-NMR spectra were measured with a varian EM 360-L spectrometer using D₂O solvent with internal standard, Sodium 2,2-dimethyl-2-silapentane-S-sulfonate(DSS). Elemental analyses were performed by Micro-Tech Lab., Skokie, Illinois, U.S.A. 2-Amino-isobutyric acid and 1,2-dibromoethane were purchased from Aldrich and used without further purification.

Preparation of Ethylenediamine-N,N'-di- α -isobutyric Acid. This was prepared from the reaction between 2-aminoisobutyric acid and 1,2-dibromoethane.¹⁹

Preparation of Hydrogen Dichloro(ethylenediamine-N,N'-di- α -isobutyrate)cobaltate(III), H[Co(eddib)Cl₂]. In 60 ml of water 2.3g of ethylenediamine-N,N'-di- α -isobutyric acid, 0.8g of sodium hydroxide, and 2.3 g of cobalt dichloride hexahydrate were added in order. Carbon diox-