

## Synthesis and characterization of isopropoxy borobridged macrocyclic complexes of Co(III)

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(Received: April 22, 2009; Accepted: May 26, 2009)

### ABSTRACT

Macrocyclic complexes of co(III) of the type,  $\text{CoCy}^{1-2}\text{B}'\text{X}$  where  $\text{Cy}^1$  represents the macrocyclic ligand 1,8-dichloro-2,7,9,14-tetraoxa-1,1,8,8-tetraisopropoxy-4,5,11,12-tetramethyl-1,3,6,10,13-tetraaza, cyclotetradeca-3,5,10,12-tetrene[boimacyclene(14)] and  $\text{cy}^2$ -represents the macrocyclic ligand 1,8-dibora-2,7,9,14-tetraoxa-1,1,8,8-tetraisopropoxy-4,5,11,12-tetraphenyl-1,3,6,10,13-Tetraazacyclotetradeca-3,5,10,12-tetrene [boiphacyclene(14)]; X represents Halide ions and B' represents nitrogen-donor bases such as pyridine or 3-or 4-methyl pyridines, have been prepared<sup>1-2</sup> and characterized on the basis of elemental analysis, spectral studies and electrochemical studies. All the complexes are found to possess octahedral symmetry around the Co(III) ion.

**Key words:** Macrocyclic ligand, boimacyclene, boiphacyclene, polarography.

### INTRODUCTION

In recent years electrochemical studies on structurally different metal complexes with macrocyclic ligands have acquired prominence. As the macrocyclic ligands have ability to stabilize coordination metal ions in wide range of oxidation states. Macrocyclic ligand elicit information on the fundamental relations that govern chemical reactions accompanied by charge transfer. This situation has prompted us to undertake the present study in which electrochemical studies on some alkoxy-borobridged macrocyclic complexes of Co(III) have been performed. For this purpose we have chosen polarography because it has resulted in an excellent and concise theoretical background which makes detailed analysis of experimental result possible thus yielding information on the mechanisms of redox process at the electrode.

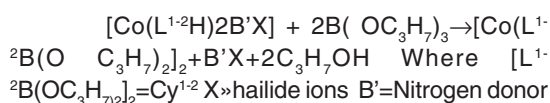
### EXPERIMENTAL

#### Materials and Method

All the metal salts solutions were prepared from A.R. Grade chemicals. The halopyridine cobalt (III) complexes  $\text{Co}(\text{L}^{1-2}\text{H})_2\text{B}'\text{X}$  have been prepared by methods as reported in the literature<sup>1-2</sup>.

#### Preparation of the metal complexes

In the first step  $\text{Co}(\text{L}^{1-2}\text{H})\text{B}'\text{X}$  have been prepared<sup>1</sup>. Now using these complexes as starting materials macrocyclic complexes of the type  $\text{CoCy}^{1-2}\text{B}'\text{X}$  have been prepared<sup>3</sup> by adding boron triisopropoxy etherate to an ethereal solution of  $\text{CoCy}^{1-2}\text{B}'\text{X}$ .



base such as pyridine, picoline (3or 4methyl pyridine).

### Representative preparation of Macrocyclic complexes

CoCy<sup>1</sup>PyCl-chloropyridine-bis(2,3-butanedione dioximato) cobalt (III)(1g) was suspended in either (30ml), to this, isoproxy ester (3.5ml) was slowly added while stirring. The colour of the compound changed from yellowish brown to light pink after stirring for additional 6 hours, left overnight, filtered, washed with ether and recrystallised from acetonitrile.

### RESULT AND DISCUSSION

The analytical data are given in tabular form (table1). The compounds were found insoluble in common organic solvents and soluble in the aqueous dimethyl formamide solution (DMF:H<sub>2</sub>O=80:20). DMF, perchloric acid (E.MerckAR)and tetramethyl (ammoniumhydroxide(25%solution, Eluka) were used for polarographic measurements. 2,3-butanedione dioxime and 1,2-diphenylethane-1,2-dione dioxime used were

Aldrich reagents. Pyridine, β-picoline and γ-picoline were BDH reagents and freshly distilled before use.

### Polarographic Study

Polarographic curves were recorded. A dropping mercury electrode (d.m.e) was used as an indicator electrode and an external saturated calomel electrode (S.C.E.) was used as the reference electrode. Half-wave potentials were measured at a scanning rate of 100mv/min. Sodium perchlorate (0.1) was used as the supporting electrolyte<sup>1</sup>. Electrochemical data for Boimacyclene<sup>14</sup> and Boiphacyclene<sup>14</sup> Co(III) complexes and their parent complexes are given in the table 2 and 3 respectively.

### Spectral Characteristics

#### I.R. Spectra

The I.R. spectra of the macrocyclic complexes exhibit quite complicated patterns. However, certain important features can be identified which helps in structure determination.

In the case of Co(III) and six coordinate Cu(II) and Ni(II) complexes the spectra shows bands

**Table 1: Analytical data for boimacyclene (14) and boiphacyclene (14) Cobalt(III) complexes**

S.No.	Complexes	Colour	Cobalt (%)	Nitrogen(%)	Halogen(%)
1.	CoCy <sup>1</sup> PyCl	Pink	9.02(8.94)	8.47(8.49)	5.32(5.38)
2.	CoCy <sup>1</sup> PyBr	Light yellow	8.17(8.38)	7.90(7.95)	11.24(11.36)
3.	CoCy <sup>1</sup> PyI	Reddish violet	7.77(7.85)	7.37(7.45)	11.85(16.91)
4.	CoCy <sup>1</sup> β-picCl	light pink	8.68(8.76)	8.18(8.31)	5.19(5.27)
5.	CoCy <sup>1</sup> β-pic Br	light greenish Yellow	8.14(8.21)	7.74(7.79)	10.08(11.14)
6.	CoCy <sup>1</sup> β-pic I	Dark red	7.63(7.71)	7.27(7.32)	16.36(16.66)
7.	CoCy <sup>1</sup> γ-picCl	Light pink	8.65(8.76)	8.16(8.31)	5.20(5.27)
8.	CoCy <sup>1</sup> γ-picBr	Light greenish Yellow	8.10(8.21)	7.72(7.79)	11.05(11.14)
9.	CoCy <sup>1</sup> γ-picI	Reddish violet	7.66(7.71)	7.21(7.32)	16.35(16.60)
10.	CoCy <sup>2</sup> pyCl	Reddish	6.41(6.50)	6.05(6.17)	3.90(3.91)
11.	CoCy <sup>2</sup> PyBr	Yellowish brown	6.11(6.19)	5.62(5.68)	8.36(8.40)
12.	CoCy <sup>2</sup> PyI	Chocolate brown	5.72(5.90)	5.54(5.60)	12.65(12.71)
13.	CoCy <sup>2</sup> β-picCl	orange yellow	6.33(6.40)	5.90(6.07)	3.78(3.85)
14.	CoCy <sup>2</sup> β-picBr	yellowish Brown	6.08(6.10)	5.72(5.79)	8.20(8.28)
15.	CoCy <sup>2</sup> β-picI	Reddish Brown	5.69(5.82)	5.30(5.52)	12.42(12.53)
16.	CoCy <sup>2</sup> γ-pic Cl	Light orange Yellow	6.31(6.40)	5.95(6.07)	3.73(3.85)
17.	CoCy <sup>2</sup> γ-picBr	Greenish yellow	6.08(6.10)	5.72(5.79)	8.25(8.28)
18.	CoCy <sup>2</sup> γ-picI	Reddish brown	5.77(5.82)	5.34(5.52)	12.63(12.53)

**Table 2: Electrochemical data for Boiphacycline (14) cobalt(111) complexes and their parent complexes**

S. No.	Complexes	Co <sup>3+</sup> E <sup>1/2</sup> (v)	Co <sup>2+</sup> slope <sup>-1</sup> (mv)	Co <sup>2+</sup> E <sup>1/2</sup> (v)	Co <sup>+</sup> slope <sup>-1</sup> (mv)
1.	CoCy <sup>1</sup> pyCl	-0.790	69	-0.980	65
2.	CoCy <sup>1</sup> pyBr	-0.788	61	-0.988	68
3.	CoCy <sup>1</sup> pyI	-0.784	68	-0.982	87
4.	CoCy <sup>1</sup> (β-pic)Cl	-0.825	68	-01.015	58
5.	CoCy <sup>1</sup> (β-pic)Br	-0.794	55	-0.966	76
6.	CoCy <sup>1</sup> (β-pic)I	-0.809	67	-0.994	86
7.	CoCy <sup>1</sup> (γ-pic)Cl	-0.822	74	-1.025	87
8.	CoCy <sup>1</sup> (γ-pic)Br	-0.796	54	-0.994	76
9.	CoCy <sup>1</sup> (γ-pic)I	-0.808	69	-0.998	89
10.	Co(L'H) <sub>2</sub> pyCl	-1.030	93	-1.772	82
11.	Co(L'H) <sub>2</sub> pyBr	-1.015	88	-1.762	88
12.	Co(L'H) <sub>2</sub> pyI	-1.012	91	-1.766	83
13.	Co(L'H) <sub>2</sub> (β-pic)Cl	-1.057	86	-1.765	85
14.	Co(L'H) <sub>2</sub> (β-pic)Br	-1.028	96	-1.496	102
15.	Co(L'H) <sub>2</sub> (β-pic)I	-1.005	118	-1.774	89
16.	Co(L'H) <sub>2</sub> (γ-pic)Cl	-1.029	75	-1.778	95
17.	Co(L'H) <sub>2</sub> (γ-pic)Br	-0.992	72	-1.757	68
18.	Co(L'H) <sub>2</sub> (γ-pic)I	-0.982	82	-1.752	72

**Table 3 : Electrochemical Data for Boimacyclene(14) -Cobalt(111) Complexes and their parent Complexes**

S. No	Complexes	Co <sup>3+</sup> E <sup>1/2</sup> (v)	Co <sup>2+</sup> E <sup>1/2</sup> (v)	Co <sup>2+</sup> Slope <sup>-1</sup>	Co <sup>+</sup>
1.	Cocyc <sup>2</sup> pyCl	-0.526	75	-0.848	73
2.	Cocyc <sup>2</sup> pyBr	-0.516	80	-0.844	75
3.	Cocyc <sup>2</sup> pyI	-0.538	65	-0.857	78
4.	Cocyc <sup>2</sup> (β-pic)Cl	-0.532	78	-0.787	79
5.	Cocyc <sup>2</sup> (β-pic)Br	-0.595	76	-0.882	77
6.	Cocyc <sup>2</sup> (β-pic)I	-0.561	70	-0.903	88
7.	Cocyc <sup>2</sup> (γ-pic) Cl	-0.565	74	-0.780	80
8.	Cocyc <sup>2</sup> (γ-pic)Br	-0.525	75	-0.790	70
9.	Cocyc <sup>2</sup> (γ-pic)I	-0.559	82	-0.940	70
10.	Co(L <sup>2</sup> H) <sub>2</sub> pyCl	-0.755	71	-1.495	75
11.	Co(L <sup>2</sup> H) <sub>2</sub> pyBr	-0.760	69	-1.562	72
12.	Co(L <sup>2</sup> H) <sub>2</sub> PyI	-0.776	77	-1.570	80
13.	Co(L <sup>2</sup> H) <sub>2</sub> (β-pic)Cl	-0.762	66	-1.550	82
14.	Co(L <sup>2</sup> H) <sub>2</sub> (β-pic)Br	-0.750	65	-1.601	69
15.	Co(L <sup>2</sup> H) <sub>2</sub> (β-pic)I	-0.768	67	-1.524	83
16.	Co(L <sup>2</sup> H) <sub>2</sub> (γ-pic)Cl	-0.752	63	-1.528	81
17.	Co(L <sup>2</sup> H) <sub>2</sub> (γ-pic)Br	-0.762	61	-1.526	79
18.	Co(L <sup>2</sup> H) <sub>2</sub> (γ-pic)I	-0.760	83	-1.612	71

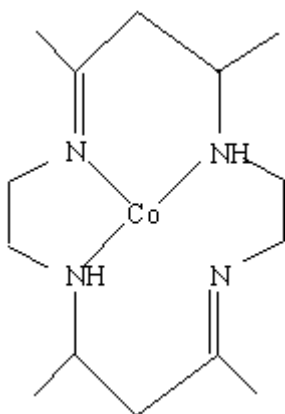


Fig. 1:

corresponding to the axial ligands in addition to the above bands.

### Electronic Spectra

The electronic spectra of macrocyclic complexes have been assigned on the basis of molecular orbital diagrams and the ligand field parameters evaluated in a number of cases. The appearance of characteristic bands in the spectra of these complexes tells about the geometry associated with these complexes.

The trans  $(\text{CoN}_4\text{X}_2)^{n+}$  Complexes have a basic  $D_{4h}$  symmetry with  ${}^1A_{2g} \rightarrow {}^1T_{1g}(oh)$  splitting into

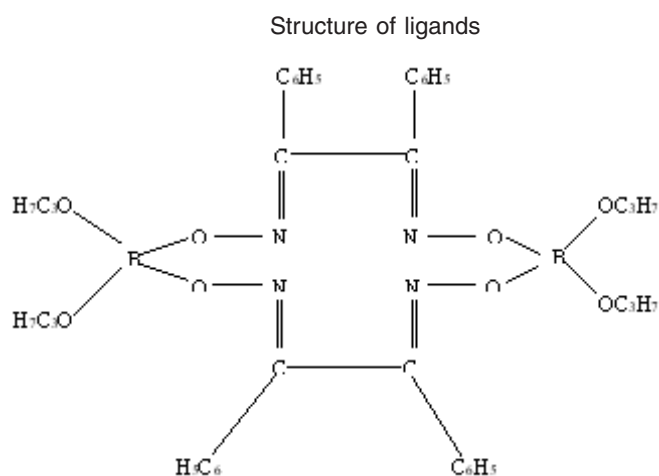


Fig. 2: Boiphacyclene(14)

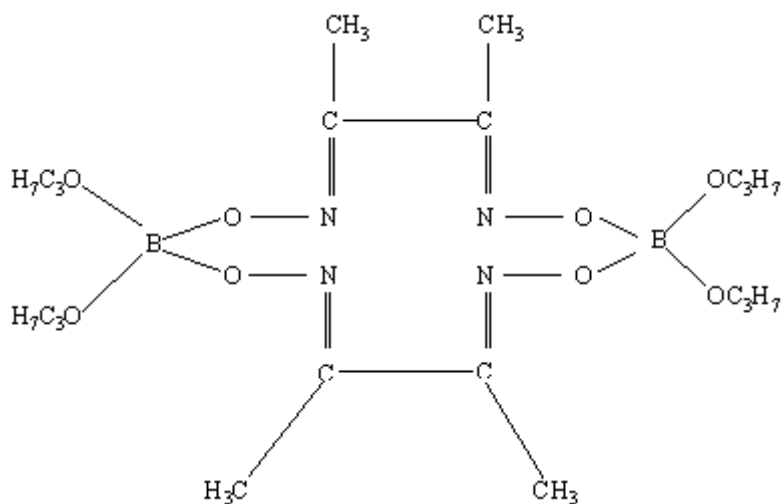


Fig. 3 : Boiamacyclene(14)

two components ( ${}^1A_g \rightarrow {}^1E_g(D_4h)$  and  ${}^1A_g \rightarrow {}^1A_2g(D_4h)$ ).

When the tetragonal splitting is not very large, only a single absorption band is observed under the  ${}^1A_g \rightarrow {}^1T_1g(oh)$  envelope.

The  $CoN_6$ ,  $CoN_5O$  or *Cis-*  $CoN_4O_2$

chromophores exhibit two bands associated with  ${}^1A_g \rightarrow {}^1T_1g(oh)$  and  ${}^1A_g \rightarrow {}^1T_2g(oh)$  transition<sup>4</sup>.

### NMR Spectra

The  ${}^1H$  NMR spectra of the macrocyclic complexes helps in identifying the macrocyclic structure. In the case of  $[Co(Me_4[14]diene)]^{2+}$  (fig.1), the single methyl occurs as a doublet at

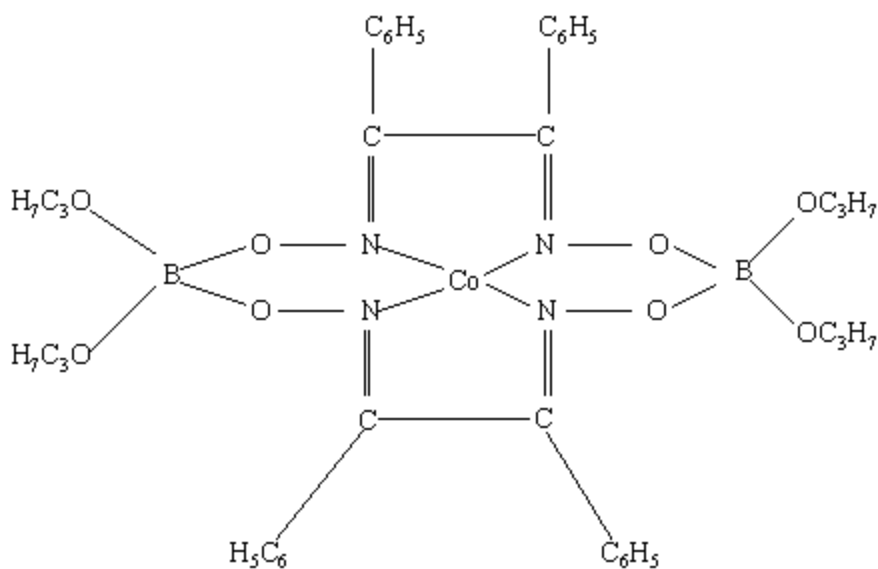


Fig. 4 : Cobalt (III) Boiphacyclene(14)

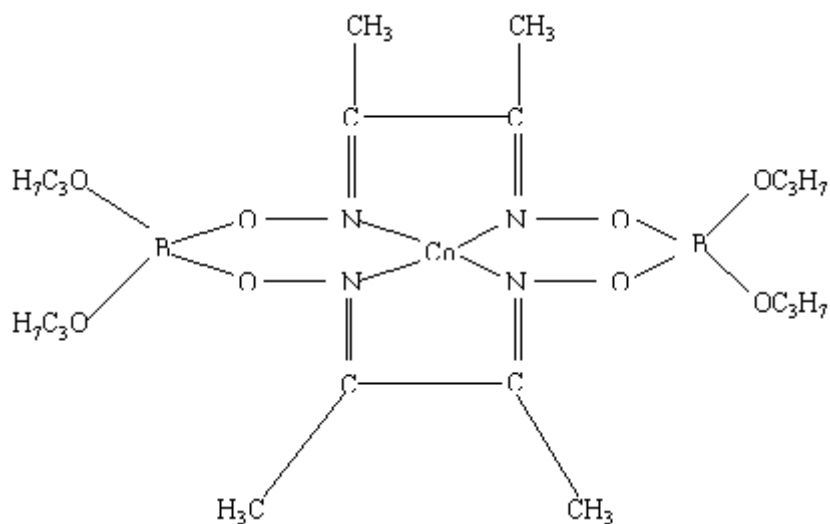


Fig. 5 : Cobalt (III) Boiamacyclene(14)

1.45p.p.m. due to coupling with the single proton on C-7 and C-14. The imine methyl occurs further downfield as a singlet at 2.51 p.p.m. for trans N-meso-[Co(Me)<sub>6</sub>[14]diene)Cl<sub>2</sub>]<sup>+</sup> and the Corresponding N-rac. isomer. The equatorial methyl occurs at 1.68p.p.m. and the axial methyl at 1.37p.p.m.

The NMR spectra can also be used to monitor the course of a reaction to form a macrocyclic complex. The structure of some macrocyclic complexes has been established on the basis of <sup>13</sup>CNMR spectra<sup>5</sup>.

#### Elemental Analysis

Characterisation data for Boiamacyclene (14)-and Boiphacyclene (14) cobalt (III) Complexes<sup>6-7</sup> containing pyridine and picoline have been given in table 1.

On the basis of above studies following structures have been proposed.

#### Polarographic Study

Polarographic curves were recorded. A dropping mercury electrode (d.m.e.) was used as an indicator electrode and an external saturated calomel electrode (S.C.E.) was used as the reference electrode. Half-wave potentials were measured at a scanning rate of 100mv/min. sodium perchlorate (0.1M) was used as the supporting electrolyte. Electrochemical data for Biomacycline (14) and Boiphacycline (14) Cobalt (III) Complexes and their parent complexes are given in the table 2 and 3 respectively.

#### Spectral characteristics

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The I.R. Spectra of the macrocyclic complexes exhibit quite complicated patterns. However, certain important features can be identified which helps in structure determination.

In the Case of Co(III) and six Coordinate Cu(II) and Ni(II) Complexes the spectra shows bands corresponding to the axial ligands in addition to the above bands.

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