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# Synthesis and Characterization of Novel Octahedral Cobalt(Iii) Complexes

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# SYNTHESIS AND CHARACTERIZATION OF NOVEL OCTAHEDRAL COBALT(III) COMPLEXES

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#### ABSTRACT

The novel octahedral cobalt(III) complexes  $[Co(HL)BrL']ClO_4$  have been prepared by the reaction of (E,E)-3,9-dimethyl-5,7-di-oxa-4,8-diaza-3,8-undecadiene-2,10-dione dioxime (H<sub>2</sub>L) and CoBr<sub>2</sub>.6H<sub>2</sub>O. The complexes of H<sub>2</sub>L have a metal : ligand ratio of 1:1 and the ligand coordinates through the N atoms, as in most oximes, with axial ligation by substitued pyridines (L') and bromide ion. The cobalt complexes have been characterized by <sup>1</sup>H NMR, IR, MS spectral and elemental analysis data.

#### **INTRODUCTION**

Vitamin  $B_{12}$  coenzyme and alkylcobalamin are recognized to play very important and distinctive biochemical roles<sup>1</sup>. Model studies in search of the mechanism for the enzymatic reactions catalyzed by coenzym  $B_{12}$  and methylcobalamin (methyl  $B_{12}$ ) exceeded this objective and have made a general contribution to coordination chemistry<sup>2</sup>. Coordination compounds of small organocobalt complexes, such as the cobal-oximes and Costa complexes (Fig. 1), have been widely investigated as mimics of coenzyme  $B_{12}^3$ . Most of these model compounds have been designed to assess the factors that affect the strength of the Co-C bond in the coenzyme<sup>4</sup>, the only known example in nature being methyl  $B_{12}$ . The biochemical reactivity of alkyl-cobalamin coenzymes is influenced extensively by axial ligation through electronic effects. The influence of the electronic effects on the Co-N bond lengths, in the axial base, in non-organometallic Costa-type

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Fig. 1. Costa-type Complex,  $R = CH_3$ , L' = N-Donor Heterocyclic Ligands



Fig. 2. The Structure of  $H_2L$ 

complexes studied recently by Gerli and Marzilli<sup>5</sup> reveals a lengthening of the Co-N distance with the donor ability of the <u>trans</u> axial base<sup>6</sup>.

A new coenzym  $B_{12}$  model based on a Costa-type model built upon the quadridentate ligand (E,E)-3,9-dimethyl-5,7-dioxa-4,8-diaza-3,8-undecadiene-2-10dione dioxime (H<sub>2</sub>L) (Fig. 2) has been reported recently<sup>7</sup>. In that study, examination of molecular models led to a novel complex shown in Fig. 1, in which the propylene bridge of the classic Costa-type ligand has been replaced by a methylenedioxy bridge. As a result of this replacement, the N-O and C-O bonds in this new model are shorter than the corresponding N-C and C-C bonds in a Costa-type complex.

This difference between the above mentioned model compound and the Costa-type complex will cause an increase of the rigidity in the equatorial ligand and stronger steric repulsion between the methylene group and axial ligands<sup>7</sup>. This quadridentate ligand coordinates with cobalt in the equatorial position as a mono-anion.

In this study, the synthesis and characterization of non-alkyl cobalt(III) complexes of  $H_2L$  with a series of Lewis bases such as 2- and 4-methylpyridine, 2,6-dimethyl-pyridine, 2-aminopyridine and 2,6-diaminopyridine and a bromide ion in the axial sites (Fig. 3) are described.

## **RESULTS AND DISCUSSION**

(E,E)-3,9-Dimethyl-5,7-dioxa-4,8-diaza-3,8-unde-cadiene-2,10-dione dioxime was synthesized by the condensation reaction of (E,E)-3,9-dimethyl-5,7-dioxa-4,8-diaza-3,8-undecadiene-2,10-dione with hydroxylamine hydrochloride according to a reported procedure<sup>7</sup>. The elemental analyses of the cobalt(III) complexes of H<sub>2</sub>L/L' given in Table I are in reasonably good agreement with the proposed composition. The complexes were characterized by the combination of <sup>1</sup>H NMR, IR and MS spectral and elemental analysis data. The coordination compounds have the general formula [Co(HL)L'Br]ClO<sub>4</sub> [L' = 2-methylpyridine, 4-methylpyridine, 2,6-dimethyl-pyridine, 2-aminopyridine and 2,6-diaminopyridine] (Fig. 3). The dibromo Costa complex has been prepared according to the standard literatute procedure<sup>7-8</sup> which may be represented by the equation (1) below.

$$2Co(II)Br_2.6H_2O + 2H_2L \xrightarrow{[O_2]} 2[Co(III)(HL)Br_2] + 12H_2O + H_2O_2$$
 (1)

In order to prepare the octahedral cobalt(III) complexes  $[Co(HL)L'Br]ClO_4$  formed by equation (2) we used the dibromo Costa complex and the axial substituted pyridine ligand (L'). We preferred the neutral Costa complex because the complex would be more soluble in common organic solvents and easier to manipulate than ionic complexes. The commonly used N-bases, such as substituted pyridines used as axial ligation, show slight sterical hindrance<sup>9</sup> but the formation of octahedral complexes of these ligands was not blocked<sup>10</sup>. The reaction of equivalent amounts of substituted pyridines with  $[Co(HL)Br_2]$  and excess of

Compound	Color	M.p.	Yield	FW	Found (Calcd.)			
		(°C)	(%)		%C	%H	%N	%M
[Co(HL)L' <sup>1</sup> Br]ClO <sub>4</sub> <sup>a</sup> (C <sub>15</sub> H <sub>22</sub> N <sub>5</sub> O <sub>8</sub> BrClCo)	Brown	>350	67.9	574.4	31.48 (31.33)	3.97 (3.82)	12.02 (12.18)	10.05 (10.26)
[Co(HL)L' <sup>2</sup> Br]ClO <sub>4</sub> <sup>a</sup> (C <sub>15</sub> H <sub>22</sub> N <sub>5</sub> O <sub>8</sub> BrClCo)	Light brown	>350	70.0	574.4	31.52 (31.33)	3.60 (3.82)	12.37 (12.1 <b>8</b> )	10.11 (10.26)
[Co(HL)L <sup>13</sup> Br]ClO <sub>4</sub> <sup>a</sup> (C <sub>16</sub> H <sub>24</sub> N <sub>5</sub> O <sub>8</sub> BrClCo)	Brown	>350	64.6	588.4	32.41 (32.62)	3.90 (4.07)	11.65 (11.89)	10.24 (10.01)
$\begin{array}{l} [\mathrm{Co(HL)L'^4Br}]\mathrm{ClO_4^a} \\ (\mathrm{C_{14}H_{21}N_6O_8BrClCo}) \end{array}$	Dark brown	>350	60.9	575.4	29.00 (29.19)	3.81 (3.64)	14.87 (14.59)	10.05 (10.24)
[Co(HL)L <sup>15</sup> Br]ClO4 <sup>a</sup> (C <sub>14</sub> H <sub>22</sub> N <sub>7</sub> O <sub>8</sub> BrClCo)	Reddish brown	>350	69.5	590.4	(28.67 (28.45)	3.90 (3.72)	16.38 (16.59)	9.77 (9.98)

Table I. Analytical and Physical Data of the H<sub>2</sub>L Complexes

<sup>a</sup>Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. L'<sup>1</sup> = 2-methylpyridine; L'<sup>2</sup> = 4-methylpyridine; L'<sup>3</sup> = 2,6-dimethylpyridine; L'<sup>4</sup> = 2-aminopyridine; L'<sup>5</sup> = 2,6-diaminopyridine



Fig. 3. Suggested Structure of the Co(III) Complexes of H<sub>2</sub>L and L'. L'<sup>1</sup> = 2-Methylpyridine, L'<sup>2</sup> = 4-Methylpyridine, L'<sup>3</sup> = 2,6-Dimethylpyridine, L'<sup>4</sup> = 2-Aminopyridine, L'<sup>5</sup> = 2,6-Diaminopyridine

 $NaClO_4$ , as con-firmed by analytical and spectral data (experimental section), may be represented by the equation (2) below.

 $[Co(HL)Br_2] + L' NaClO_4 [Co(HL)L'Br]ClO_4 + NaBr (2)$ 

#### <sup>1</sup><u>H NMR Spectra</u>

The two singlets appeared at  $\delta = 2.57$  and 2.64 ppm in the spectra of the dicomplex of H<sub>2</sub>L were assigned to the methyl groups, each singlet bromo represents two equal chemical shifts belonging to equal methyl groups<sup>7</sup>. However, comparison of the proton NMR spectra of the dibromo cobalt(III) complexes and substituted pyridino(bromo) II<sub>2</sub>L complexes shows that there is a considerable difference in the chemical shifts of the equatorial ligands. The signals occurring at  $\delta = 1.75 \cdot 2.71$  ppm were assigned to the methyl groups of the axial ligands (L<sup>1</sup>, L<sup>2</sup> and L'3) and equatorial ligand (H<sub>2</sub>L). The chemical shift difference between the two doublets that constitute the AB system of the H<sub>2</sub>L complexes (3)-(7), is considerable indicating a great difference in the chemical environmet of the two protons of the methyl-enedioxy group. On the other hand, the inductive effect of the axial ligands has a greater influence on the shift of the methylene protons than that of the other protons. The equatorial methyl group protons shifted upfield relative to those of the free ligand<sup>4</sup> due to the increase of electron density in the equatorial ligand on replacement of one bromide by a substituted pyridine group. Apparently, 2,3-di-methyl- or diaminosubstituted pyridine groups have a stronger electron donation effect towards cobalt(III) ion than the bromide ions. The increasing electron density in cobalt(III) complex in the order 4-methylpyridine < 2methylpyridine < 2,6-di-methylpyridine < 2-aminopyridine < 2,6-diaminopyridine, was reported on the basis of their proton NMR spectra<sup>7</sup>. The chemical shifts of the dioxime methyl protons decrease in the same order<sup>7</sup>. Very little variation is observed in the chemical shifts of equatorial methyl and other methyl groups belonging to the axial ligands of all three complexes (3)-(5). Furthermore, the chemical shifts of the methylenedioxy protons and amino protons of the amino substituted pyridine have almost the same shifts in the related complexes. Although the deuterium-exchangeable protons of the =N-OH group occurring at  $\delta$  = 11.80 ppm in the free ligand disappeared; the hydrogen-bonded protons signal, generally seen in the region of  $\delta = 17.08-17.28$  ppm in the (E,E)-dioxime cobalt(III) complexes<sup>1,11</sup>, is not detected for these complexes either because of the rapid exchange of this proton with solvent at room temperature or the presence of trace amounts of moisture in the solvent combined with the poor solubility of these complexes<sup>5</sup> in DMSO-d<sub>6</sub>.

The cobalt(III) complex (4) containing 4-methylpyridine as axial ligand is the only  $H_2L$  complex whose methylenedioxy group shows a singlet instead of an AB system. This result could be explained by assuming that this complex is much more flexible than the other  $H_2L/L'$  complexes.

### IR Spectra

The O-H stretching vibrations appearing at 3240 cm<sup>-1</sup> in the free ligand are shifted to around 2280-2218 cm<sup>-1</sup> in the substituted pyridinocobalt(III) complexes, indicating the formation of hydrogen bonding during the complexation of H<sub>2</sub>L<sup>12</sup>. The appearance of only one signal at 1262 cm<sup>-1</sup> in the free ligand shows that the two -NOH groups are identical while the two different bands at 1232 and 1089 cm<sup>-1</sup>, are both assignable to NO stretching vibrations in the [Co(HL)(2-Mepy)]<sup>+</sup> complex. This result confirms the presence of two unequal N-O linkages, C=N-O+H and C=N-O-H<sup>1,6</sup>. The characteristic infrared absorption bands of the free ligand are shifted and lowered in intensity on complex formation, and new vibrational bands characteristics of the complex, especially those of the axial base, appear. The v(N-O) bands of the other complexes, [Co(HL)(4-Mepy) Br]<sup>+</sup>, [Co(HL)(2,6-Dimepy)Br]<sup>+</sup>, [Co(HL)(2-Aminopy)Br]<sup>+</sup> and [Co(HL)(2,6-Diaminopy)Br]+, appear at 1232-1086, 1242-1140, 1223-1086 and 1233-1002 cm-1, respectively. The v(C=N) bands appearing in the region of 1648-1628 cm<sup>-1</sup> in H<sub>2</sub>L are shifted to 1638-1617 cm<sup>-1</sup> as sharp bands. These suggest that the ligands are coordinated to cobalt(III) ions through the nitrogen donors of the azomethine groups. The complexes of 2-aminopyridine and 2,6-diaminopyridine exhibit symmetric and asymetric N-H vibrations in the 3414-3337 cm<sup>-1</sup> region. All of the perchlorate salts show band at around 1089-1140 cm<sup>-1</sup> and sharp bands in the region of 640-654 cm<sup>-1</sup>, indicative of uncoordinated perchlorate anions<sup>13</sup>. The complexes of 2-aminopyridine and 2,6-diaminopyridine exhibit symmetric and asymmetric N-H vibrations in the 3414-3337 cm<sup>-1</sup> region. The presence of the above mentioned bands, characteristic of a free amino group, indicates that 2aminopyridine or 2,6-diaminopyridine coordinate through their cyclic nitrogen. All of the complexes exhibit stretching vibrations belonging to a Co-N bond in the 629-621 cm<sup>-1</sup> region. The strenght of the Co-N bond in these complexes is due to the  $\pi$  accepting tendencies of these ligands.

#### Mass Spectra

Mass spectrometric analysis (FAB, matrix = <u>m</u>-nitrobenzylalcohol) convincingly demonstrated these complexes to be monomers. The most abundant fragment in the mass spectra of complexes (3), (4) and (5) are m/z = 474, 474 and 489, respectively, which are most probably due to  $[M-ClO_4]^+$  or  $[M-ClO_4+1]^+$  ions. In the mass spectra of the complexes (6) and (7) the m/z value of 575  $[M+1]^+$  and 590  $[M+1]^+$ , respectively, were seen.

### **EXPERIMENTAL**

<sup>1</sup>H NMR spectra were recorded on a Bruker WM 250 spectrometer. Tetramethylsilane was used as standard; *J* values are given in Hz. IR spectra were recorded in the solid state using KBr pellets on a Perkin-Elmer 1600 FT-IR specrometer. Mass spectra were recorded on a Concept H Series mass spectrometer. The metal contents and elemetal analyses of the complexes were determined using a Unicam 929 AA spectrophotometer and a Hewlett-Packard 185 CHN analyzer, respectively. (E,E)-3,9-dimethyl-5,7-dioxa-4,8-diaza-3,8-undecadi-ene-2,10dione dioxime and its dibromo cobalt(III) complex were prepared by a reported procedure<sup>7</sup>.

Bromo-substituted Pyridino[(3,9-dimethyl-5,7-dioxa-4,8-diaza-3,8-undecadiene-2,10dione dioximato)(1-)-N,N',N'',N''']cobalt Perchlorate (3)-(7).

To a suspension of the dibromo cobalt(III) complex<sup>7</sup> of  $H_2L$  (0.46 g, 1 mmol) in hot methanol (40 mL) was added 2 mL of a saturated aqueous solution of sodium perchlorate followed by the addition of 1 mmol of substituted pyridine [2methylpyridine (0.092 g), 4-methylpyridine (0.092 g), 2,6-dimethylpyridine (0.106 g), 2-aminopyridine (0.094 g), or 2,6-diaminopyridine (0.108 g)] in methanol (2 mL) with stirring and the mixture was refluxed on a water bath for four hours. Evaporation of the solvent to 10 mL on a water bath led to precipitation of the complexes. On standing for 2 h at 35° C, a large amount of product was formed, which was filtered off, washed with cold water followed by dry methanol and diethyl ether and then drying <u>in vacuo</u>.

[Co(HL)L'<sup>1</sup>Br]ClO<sub>4</sub> (L'<sup>1</sup> = 2-Methylpyridine) (3). Yield, 0.39 g (67.9%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ: 17.28 (s, 1H, O-H•O), 8.45 (d, 1H, py-H, J = 5.0), 7.45 (t, 1H, py-H, J = 8.5), 6.98 (m, 2H, py-H), 6.42 (d, 1H<sub>b</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 1H<sub>a</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d, 2H, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 6.11 (d,

 $J_{a,b} = 8.5$  ), 2.67 (s, 3H, CH<sub>3</sub>), 2.30 (s, 6H, CH<sub>3</sub>), 2.17 (m, 6H, CH<sub>3</sub>). IR (KBr pellets, cm<sup>-1</sup>): 3035 (Ar-H), 2924 (C-H), 2244 (O-H-O), 1635 (C=N), 1621 (C=N), 1232 (N-O), 1089 (ClO<sub>4</sub>)<sup>-</sup>, 625 (Co-N). MS (FAB) (m/z): 474 [M-ClO<sub>4</sub>]<sup>+</sup>.

 $\frac{[\text{Co}(\text{HL})\text{L}^{2}\text{Br}]\text{CIO}_{4} (\text{L}^{2} = 4-\text{Methylpyridine}) (4)}{(\text{DMSO-d}_{6}) \delta: 17.17 (s, 1\text{H}, \text{O-H-O}), 8.53 (d, 1\text{H}, \text{py-H}, J = 5.2), 7.15 (d, 2\text{H}, \text{py-H}, J = 5.0), 6.03 (s, 2\text{H}, \text{CH}_{2}, J = 8.4), 2.71 (s, 3\text{H}, \text{CH}_{3}), 2.36 (s, 6\text{H}, \text{CH}_{3}), 2.21 (m, 6\text{H}, \text{CH}_{3}).$  IR (KBr pellets, cm<sup>-1</sup>): 3029 (Ar-H), 2918 (C-H), 2282 (O-H O), 1638 (C=N), 1618 (C=N), 1232 (N-O), 1086 (ClO<sub>4</sub>)<sup>-</sup>, 625 (Co-N). MS (FAB) (m/z): 474 [M-ClO<sub>4</sub>]<sup>+</sup>.

[Co(HL)L<sup>3</sup>Br]ClO<sub>4</sub> (L<sup>3</sup> = 2,6-Dimethylpyridine) (5). Yield, 0.38 g (64.6%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>) δ: 17.11 (s, 1H, O-H·O), 8.33 (t, 1H, py-H, J = 6.2), 7.28 (m, 2H, py-H), 6.54 (d, 1H<sub>b</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 5.92 (d, 1H<sub>a</sub>, CH<sub>2</sub>,  $J_{a,b} = 8.5$ ), 2.48 (s, 6H, CH<sub>3</sub>), 2.06 (s, 6H, CH<sub>3</sub>), 1.95 (m, 6H, CH<sub>3</sub>). IR (KBr pellets, cm<sup>-1</sup>): 3040 (C-H), 2890 (C-H), 2297 (O-H·O), 1635 (C=N), 1615 (C=N), 1242 (N-O), 1089 (ClO<sub>4</sub>)<sup>-</sup>, 629 (Co-N). MS (FAB) (m/z): 489 [M-ClO<sub>4</sub>+1]<sup>+</sup>.

 $\frac{[\text{Co(HL)}\text{I}.'^4\text{Br}]\text{ClO}_4 (\text{L}'^4 = 2-\text{Aminopyridine}) (6)}{(6)}. \text{ Yield, } 0.35 \text{ g} (60.8\%). ^{1}\text{H} \text{ NMR} (\text{DMSO-d}_6) \delta: 17.20 (s, 1\text{H}, \text{O-H-O}), 8.28 (d, 1\text{H}, \text{py-H}, J = 3.8), 7.26 (t, 1\text{H}, \text{py-H}, J = 3.1), 6.61 (t, 1\text{H}, \text{py-H}, J = 6.2), 6.45 (t, 1\text{H}, \text{py-H}, J = 8.6), 6.63 (d, 1\text{H}_b, \text{CH}_2, J_{a,b} = 8.3), 5.80 (d, 1\text{H}_a, \text{CH}_2, J_{a,b} = 8.3), 5.21 (br s, 2\text{H}, \text{NH}_2), 2.35 (s, 6\text{H}, \text{CH}_3), 1.92 (m, 6\text{H}, \text{CH}_3). \text{ IR (KBr pellets, cm}^{-1}): 3414 (\text{NH}_2), 3038 (\text{Ar-H}), 2895 (\text{C-H}), 2018 (\text{O-H-O}), 1636 (\text{C=N}), 1617 (\text{C=N}), 1223 (\text{N-O}), 1086 (\text{ClO}_4)^-, 626 (\text{Co-N}). \text{MS (FAB)(m/z): 575 [M+1]^+, 482 [M-L'+2]^+.}$ 

 $\frac{[\text{Co}(\text{HL})\text{L}^{5}\text{Br}]\text{ClO}_{4} (\text{L}^{5} = 2,6-\text{Diaminopyridine})}{(7)}$  Yield, 0.41 g (69.5%). <sup>1</sup>H NMR (DMSO-d<sub>6</sub>)  $\delta$ : 17.08 (s, 1H, O-H•O), 6.75 (t, 1H, py-H, J = 8.0), 6.01 (m, 2H), 6.69 (d, 1H<sub>b</sub>, CH<sub>2</sub>,  $J_{a,b}$  = 8.5), 5.71 (d, 1H<sub>a</sub>, CH<sub>2</sub>,  $J_{a,b}$  = 8.5), 5.00 (br s, 4H, NH<sub>2</sub>), 2.27 (s, 6H, CH<sub>3</sub>), 1.75 (m, 6H, CH<sub>3</sub>). IR (KBr pellets, cm<sup>-1</sup>): 3337 (NH<sub>2</sub>), 3048 (C-H), 2911 (C-H), 2280 (O-H•O), 1628 (C=N), 1616 (C=N), 1233 (N-O), 1095 (ClO<sub>4</sub>)<sup>-</sup>, 629 (Co-N). MS (FAB)(m/z) 590 [M+1]<sup>+</sup>, 482 [M-L'+2]<sup>+</sup>.

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