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## Synthesis, Characterization and X-Ray Crystal Structure of a Cobalt(III) Complex with 2-Bis(pyridine-2-carboxamido)-4,5-dimethylbenzene Ligand

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An octahedral cobalt(III) complex, *trans*-[(Me<sub>2</sub>bpb)Co(bzlan)<sub>2</sub>ClO<sub>4</sub>] (1), with H<sub>2</sub>Me<sub>2</sub>bpb = *N,N'*-(4,5-dimethyl-1,2-phenylene)dipicolinamide and bzlan = benzylamine, has been synthesized and characterized by elemental analyses, IR, UV-Vis, and <sup>1</sup>H NMR spectroscopy. The structure of this complex has been determined by X-ray crystallography. The Me<sub>2</sub>bpb<sup>2-</sup> is a di-anionic tetradentate ligand furnishing a N<sub>4</sub> set, such that two N atoms of the two pyridine rings and two amido N atoms occupy four equatorial positions. The two benzylamine ligands occupy the two axial positions leading to a distorted octahedral geometry around the central cobalt ion. The electrochemical behavior of this complex in acetonitrile solution indicates that the irreversible oxidation of 4,5-dimethylorthophenylene moiety and reduction of pyridine rings of the free ligand appear as reversible waves in the cyclic voltammogram of its cobalt(III) complex. Concomitant Co(III)/Co(II) redox process and solvolysis in acetonitrile solution is observed. This irreversible redox process becomes reversible in the presence of excess benzylamine.

**Keywords:** Substituted bispyridylamide, Cobalt(III) complex, Crystal structure, Cyclic voltammetry

### INTRODUCTION

In the recent years, the coordination chemistry of various metal complexes of the ligands containing pyridine-2-carboxamide moieties has received much attention due to their biological applications, [1-10] use in catalysis [11-13], and for selective binding of the toxic metal ion or as building blocks of new functional metal complexes [14-16]. Pyridinecarboxamides, as multidentate ligands are available from condensation reactions between pyridyl-bearing amine or carboxylic acid precursors, promoted by coupling agents such triphenylphosphite [17,18].

In continuation of our interest in the metal complexes of pyridine carboxamide ligands [18-22], herein we report the synthesis and characterization of the cobalt(III) complex of H<sub>2</sub>Me<sub>2</sub>bpb with two ancillary amines in the axial positions.

The IR, UV-Vis, <sup>1</sup>H NMR spectra, the X-ray crystal structure, and electrochemical properties of this complex are also presented and discussed.

### EXPERIMENTAL

#### Materials and General Methods

All solvents and chemicals were of commercial reagent grade and used as received from Aldrich and Merck. The ligand H<sub>2</sub>Me<sub>2</sub>bpb was synthesized according to an environmentally benign method developed in our laboratory, using TBAB as the reaction medium [18]. Elemental analyses were performed by using a Perkin-Elmer 2400II CHNS-O elemental analyzer. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer. Infrared spectra (KBr pellets) were obtained on a FT-IR JASCO 680 plus spectrophotometer. <sup>1</sup>H NMR spectra were measured with a Bruker AVANCE DR X500 spectrometer

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(500 MHz). Proton chemical shifts are reported in ppm relative to Me<sub>4</sub>Si as internal standard. Cyclic voltammograms were recorded by using a SAMA Research Analyzer M-500. A conventional three-electrode cell assembly consisting of a platinum wire as an auxiliary electrode, Ag wire as reference electrode, and a glassy carbon as a working electrode was used. The glassy carbon working electrode (Metrohm 6.1204.110) with 2.0 ± 0.1 mm diameter was manually cleaned with 1 μm alumina polish prior to each scan. Tetrabutylammonium hexafluorophosphate (TBAH) was used as supporting electrolyte. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated vs. internal Fe<sup>+6</sup> (E° = 0.45 V vs. SCE) couple under the same conditions [23].

**Caution.** perchlorate salts with organic compounds are potentially explosive and should be handled with care.

### Synthesis of *Trans*-[Co<sup>III</sup>(Me<sub>2</sub>bpb)(bzlan)<sub>2</sub>]ClO<sub>4</sub> (1)

To a solution of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (24.9 mg, 0.1 mmol) in methanol (25 ml) was added 2 drops of H<sub>2</sub>O<sub>2</sub> followed by a solution of H<sub>2</sub>Me<sub>2</sub>bpb (34.6 mg, 0.1 mmol) in dichloromethane (25 ml). To this solution was added dropwise 6.86 mmol (0.75 ml) of benzylamine within 3 h. The final reaction mixture was filtered off and a solution of (24.2 mg, 0.2 mmol) of NaClO<sub>4</sub>·H<sub>2</sub>O in methanol was added slowly to the filtrate. Dark brown crystals of the complex were obtained by slow evaporation of solvents at room temperature. The crystals were filtered off and washed with a mixture of methanol and diethyl ether (9:1 v/v), and dried under vacuum. Yield: 72%. Anal. Calcd. for C<sub>34</sub>H<sub>34</sub>ClCoN<sub>6</sub>O<sub>6</sub>: C, 56.96; H, 4.78; N, 11.72. Found: C, 55.80; H, 4.76; N, 11.41%. FT-IR (KBr, cm<sup>-1</sup>) ν<sub>max</sub>: 3199, 3121 (m, N-H), 1627, 1599 (s, C=O), 1566 (s, C-N). UV-Vis: λ<sub>max</sub> (nm) (ε, M<sup>-1</sup> cm<sup>-1</sup>) (CH<sub>3</sub>CN): 273 (26910), 314 (16920), 419 (8796), 611 (208). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ = 2.30 (s, 6H, CH<sub>3</sub>), 2.72 (m, 4H, CH<sub>2</sub>), 2.93 (m, 4H<sub>NH</sub>), 6.72-7.14 (m, 10H<sub>g,g',h,h',i</sub>), 7.92-8.31 (m, 6H<sub>b,c,d</sub>), 8.64 (s, 2H<sub>e</sub>), 9.39 (d, 2H<sub>a</sub>).

### X-Ray Crystallography

X-ray data of complex 1H<sub>2</sub>O were obtained at T = 100 K on a Bruker Kappa APEX-2 CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

Cell refinement and data reduction were performed with the help of program SAINT [24]. Corrections for absorption were carried out with the multi-scan method and program SADABS [24]. The structure was solved with direct methods using program SHELXS97 and structure refinement on F<sup>2</sup> was carried out with program SHELXL97 [25]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were inserted in idealized positions and refined riding with the atoms to which they were bonded. In the course of the structure determination a solvent water molecule (O7w) was found that resides in a suitable cavity of the structure and appears to be anchored by hydrogen bonds although its hydrogen atoms could not be located. Crystal data, together with other relevant information on structure determination, are listed in Table 1. The R-values for this structure are comparatively large because all available crystals showed subparallel intergrowth and broad reflection profiles causing troubles with frame data integration. It is possible that the crystals had suffered from desolvation.

## RESULTS AND DISCUSSION

### Description of Structure of *Trans*-[Co<sup>III</sup>(Me<sub>2</sub>bpb)(bzlan)<sub>2</sub>]ClO<sub>4</sub>·H<sub>2</sub>O (1H<sub>2</sub>O)

The crystal structure determination revealed that the Co complex crystallizes as a hydrate of triclinic symmetry, space group *P* $\bar{1}$ , with one H<sub>2</sub>O per Co in an elongated centrosymmetric cavity of ca. 61 Å<sup>3</sup> solvent accessible volume containing two H<sub>2</sub>O. Figure 1 shows the molecular structure of the cobalt complex together with the atomic numbering scheme. The structure exhibits a distorted octahedral geometry around cobalt. Selected bond angles and distances are listed in Table 2. As expected, the ligand (Me<sub>2</sub>bpb<sup>2-</sup>), binds to the trivalent metal ion (Co<sup>III</sup>), *via* two pyridine moieties and two amido nitrogen donor atoms in the equatorial plane of the octahedral polyhedron around the metal ions. There are two benzylamine molecules attached to the metal to fill its axial sites. All Co-N bond distances are within 1.870(5)-1.979(5) Å range, and are indicative of a low-spin t<sub>2g</sub><sup>6</sup> configuration on the central cobalt(III) ion [26].

Of the four Co-N bonds in the equatorial plane, the Co-N<sub>amide</sub> bond distances, (Co-N2 = 1.892(5) Å and Co-N3 =

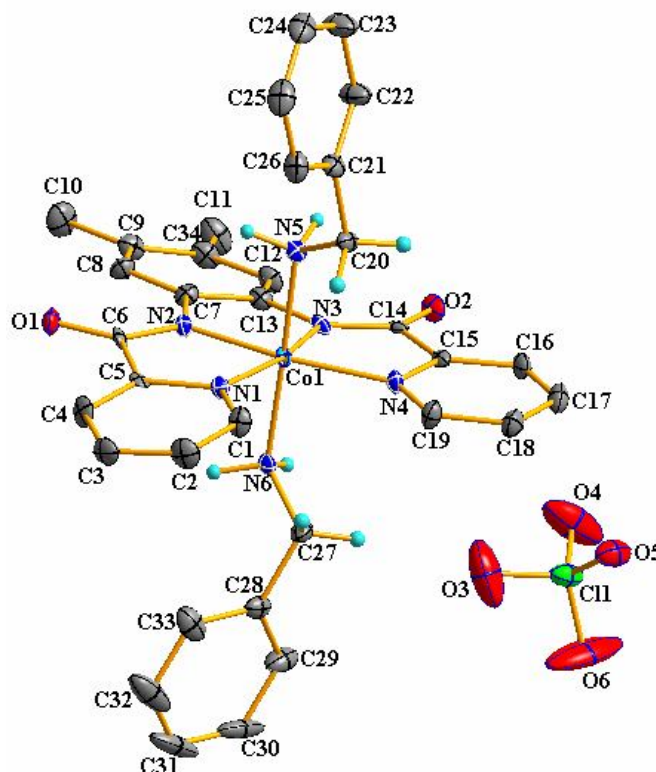
**Table 1.** Crystal Data and Structure Refinement for Compound 1H<sub>2</sub>O

|   |   |
|---|---|
| Chemical formula  | [C <sub>34</sub> H <sub>34</sub> CoN <sub>6</sub> O <sub>2</sub> ] <sup>+</sup> ClO <sub>4</sub> <sup>-</sup> ·H <sub>2</sub> O |
| Formula weight  | 735.07  |
| Temperature (K)   | 100(2)  |
| Crystal system  | Triclinic   |
| Space group   | <i>P</i> $\bar{1}$  |
| <i>a</i> (Å)  | 10.653(7)   |
| <i>b</i> (Å)  | 11.717(7)   |
| <i>c</i> (Å)  | 13.436(9)   |
| $\alpha$ (°)  | 83.623(9)   |
| $\beta$ (°)   | 76.051(8)   |
| $\gamma$ (°)  | 86.839(9)   |
| <i>V</i> (Å <sup>3</sup> )  | 1620.1(18)  |
| <i>Z</i> , <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )                 | 2, 1.507  |
| Crystal size (mm)   | 0.36 × 0.20 × 0.04  |
| $\mu$ (mm <sup>-1</sup> )   | 0.67  |
| <i>F</i> (000)  | 764   |
| $\theta$ range (°)  | 2.21-27.00  |
| Absorption correction   | Multi scan  |
| Reflections collected   | 12100   |
| <i>R</i> <sub>int</sub>   | 0.074   |
| Data/restraints/parameters  | 6579/141/444  |
| Goodness-of-fit on <i>F</i> <sup>2</sup>                                  | 1.01  |
| Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )] <sup>a</sup> | <i>R</i> <sub>1</sub> = 0.086, <i>wR</i> <sub>2</sub> = 0.202   |
| Largest diff. peak and hole (e Å <sup>-3</sup> )                          | -0.83 and 1.93  |

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$$

1.870(5) Å), being comparable to the Co-N<sub>amide</sub> values (Co-N<sub>amide</sub> = 1.892(3) Å) in *trans*-[Co(Mebpb)(prldn)<sub>2</sub>]ClO<sub>4</sub> complex [27], are indicative of strong bonding between the deprotonated amide nitrogens and cobalt center. This is in agreement with the fact that the deprotonated amide nitrogen is a very strong  $\sigma$ -donor. The coordination of the amide in its deprotonated form is also evident from the absence of the amidic proton signals from the <sup>1</sup>H NMR

spectrum of the complex (*vide infra*). The bond distances to the pyridine nitrogens (Co-N1 = 1.968(5) Å and Co-N4 = 1.969(5) Å) are ~0.1 Å longer than those to Co-N2 and Co-N3, confirming the lower donor ability of the pyridine nitrogens [27]. The bond distances to the benzylamine nitrogens (Co-N5 = 1.967(5) Å and Co-N6 = 1.979(5) Å) are in agreement with those in related complexes [19]. The C-O bond distances of the Me<sub>2</sub>bpb<sup>2-</sup> ligand are 1.231(7) and



**Fig. 1.** Molecular structure of (1) with its atom numbering scheme. Hydrogen atoms (except bzlan  $\text{CH}_2\text{-NH}_2$ ) and water oxygen O7w omitted for clarity.

1.235(7) Å.

The nitrogen-cobalt-nitrogen bond angles in the equatorial plane comprise of one angle which is larger than  $90^\circ$  ( $\text{N1-Co1-N4} = 110.1(2)^\circ$ ) and three smaller than  $90^\circ$  ( $\text{N1-Co1-N2} = 82.7(2)^\circ$ ,  $\text{N2-Co1-N3} = 84.4(2)^\circ$ , and  $\text{N3-Co1-N4} = 82.7(2)^\circ$ ). This indicates the existence of some strain in the coordination sphere due to the rigid geometry of the ligand. The trans angles are in the  $167.1(2)$ - $178.6(2)^\circ$  range and deviate from  $180^\circ$  in an ideal octahedral geometry.

The 4,5-dimethylbenzene ring of the  $\text{Me}_2\text{bpb}^{2-}$  ligand is tilted from the  $\text{N1/N2/N3/N4}$  plane, with torsion angles of  $4.2(9)^\circ$  and  $8.4(9)^\circ$  for  $\text{C6-N2-C7-C8}$  and  $\text{C14-N3-C13-C12}$ , respectively. The angle between two pyridyl rings of the ligand is  $8.9^\circ$ . The interplanar angles between the central benzene plane and the two pyridyl rings are  $11.7$  and  $20.1^\circ$ . This observation can be attributed partly to the close intramolecular contact that occurs between the two H atoms ( $\text{H1}\cdots\text{H19}$ ) in the 6-position of the pyridyl rings and partly to other intermolecular contacts. The distance

$\text{H1}\cdots\text{H19}$  of  $2.015$  Å is significantly less than the sum of the van der Waals radii ( $2.40$  Å).

A further interesting feature of the structure of 1 is the inter-molecular hydrogen bonding (Table 3). The structure consists of chains of cations linked by rather strong  $\text{N-H}\cdots\text{O}=\text{C}$  hydrogen bonds along  $[010]$  (Fig. 2). Apart from the contact  $\text{O3}\cdots\text{O7w} = 2.867$  Å where O7w is oxygen of a water molecule, the  $\text{ClO}_4$  anion exhibits only weak  $\text{C-H}\cdots\text{O}$  interactions.

### Spectral Characterization

The FT-IR data of the complex are listed in Section 2. A comparative study of the FT-IR spectral data of the reported complex with those of the free ligand gives meaningful information regarding the coordination mode of the ligand molecule. The absence of the amide  $\nu(\text{N-H})$  band and the shift of the  $\nu(\text{CO})$  band to a lower energy in the spectra of the cobalt complex confirm that the amide nitrogens are

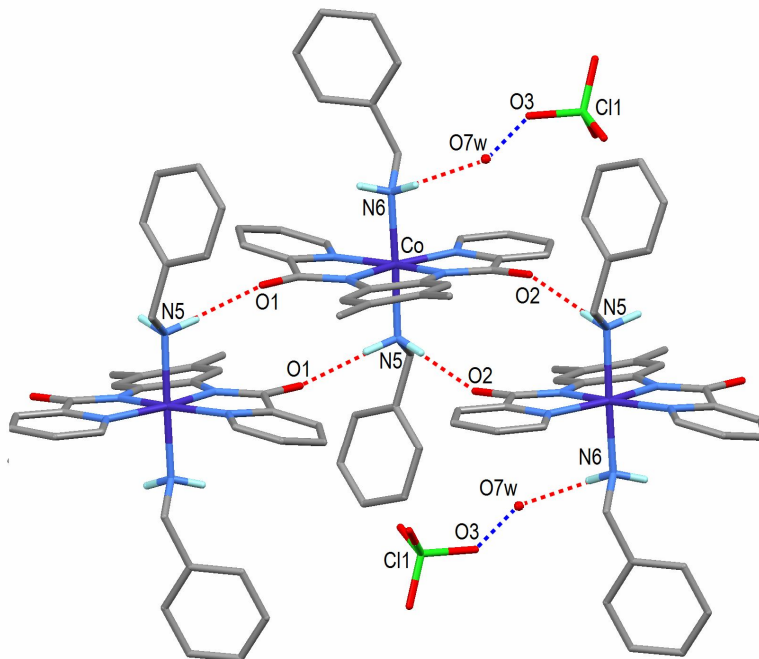
**Table 2.** Selected Bond Lengths (Å) and Angles (°) for (1H<sub>2</sub>O)

| Bond lengths |          |
|--------------|----------|
| Co1-N1       | 1.968(5) |
| Co1-N2       | 1.892(5) |
| Co1-N3       | 1.870(5) |
| Co1-N4       | 1.969(5) |
| Co1-N5       | 1.967(5) |
| Co1-N6       | 1.979(5) |
| Bond angles  |          |
| N1-Co1-N2    | 82.7(2)  |
| N1-Co1-N3    | 167.0(2) |
| N1-Co1-N4    | 110.1(2) |
| N1-Co1-N5    | 90.7(2)  |
| N1-Co1-N6    | 88.5(2)  |
| N2-Co1-N3    | 84.4(2)  |
| N2-Co1-N4    | 167.0(2) |
| N2-Co1-N5    | 88.1(2)  |
| N2-Co1-N6    | 90.7(2)  |
| N3-Co1-N4    | 82.7(2)  |
| N3-Co1-N5    | 90.8(2)  |
| N3-Co1-N6    | 89.8(2)  |
| N4-Co1-N5    | 91.8(2)  |
| N4-Co1-N6    | 89.6(2)  |
| N5-Co1-N6    | 178.6(2) |

coordinated to the Co(III) in their deprotonated form [19]. Also, the bands corresponding to the N-H stretching vibrations of the axially coordinated benzylamine ligands, are shifted to lower frequencies relative to the uncoordinated amine, which is in accord with expectation [27].

Two C=O sharp stretching bands of the H<sub>2</sub>Me<sub>2</sub>bpb ligand at 1678 and 1666 cm<sup>-1</sup> are red shifted in complex 1 and appear at 1627 and 1599 cm<sup>-1</sup> [27]. The C-N stretching vibration of the H<sub>2</sub>Me<sub>2</sub>bpb appearing at 1511 cm<sup>-1</sup> for the

free ligand undergoes a significant shift to higher frequencies in the corresponding complex and appears at 1566 cm<sup>-1</sup>. This might be expected due to the resonance enhancement in the deprotonated amide which in turn leads to the strengthening of the C-N bond [28]. The stretching vibration due to the perchlorate anion appears at 1091 cm<sup>-1</sup>. The UV-Vis spectral data in CH<sub>3</sub>CN solvent are presented in the Experimental Section. The electronic spectrum of this complex consists of an absorption band at 611 nm with low intensity ( $\epsilon = 208 \text{ M}^{-1} \text{ cm}^{-1}$ ) corresponding to the first ligand



**Fig. 2.** N-H $\cdots$ O Hydrogen bonding (dashed red) in (1) along *b*. Only N-bonded hydrogen atoms are shown. O7w is a water oxygen with a hydrogen bond to ClO<sub>4</sub> (dashed blue).

**Table 3.** Hydrogen Bond Lengths (Å) and Angles (°) in (1H<sub>2</sub>O)

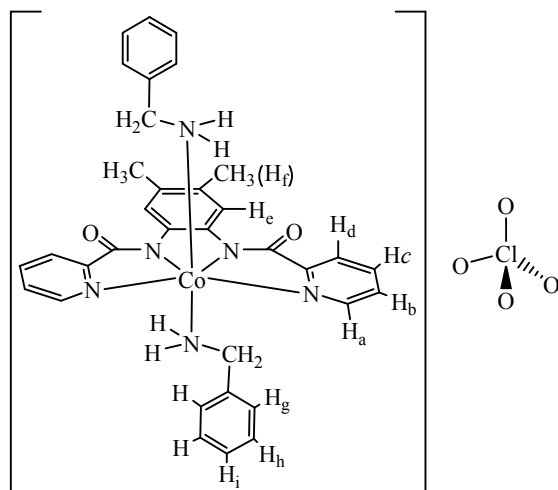
| D-H $\cdots$ A                   | D $\cdots$ A | H $\cdots$ A | D-H      | D-H $\cdots$ A |
|----------------------------------|--------------|--------------|----------|----------------|
| N5-H5A $\cdots$ O2 <sup>i</sup>  | 0.92         | 2.02         | 2.930(6) | 171.4          |
| N5-H5B $\cdots$ O1 <sup>ii</sup> | 0.92         | 1.99         | 2.901(7) | 172.9          |
| N6-H6B $\cdots$ O7w              | 0.92         | 2.12         | 2.983(8) | 156.4          |

Symmetry codes: (i)  $-x+1, -y+1, -z+1$ ; (ii)  $-x+1, -y, -z+1$ .

field ( $^1A_1 \rightarrow ^1T_1$ ) transition. However the  $^1A_1 \rightarrow ^1T_2$  band is masked by the intense charge-transfer band which appears at 419 nm ( $\epsilon = 8796 \text{ M}^{-1} \text{ cm}^{-1}$ ) [19,27]. Two additional strong intraligand absorption bands are observed at 273 ( $\epsilon = 26910 \text{ M}^{-1} \text{ cm}^{-1}$ ), and 314 ( $\epsilon = 16920 \text{ M}^{-1} \text{ cm}^{-1}$ ) [27].

The  $^1\text{H}$  NMR spectroscopic measurements were performed in  $\text{CDCl}_3$  solution. Scheme 1 displays the labeling system. The assignments are based on comparison with related cobalt(III) complexes [19]. The absence of the

amido N-H resonance in the spectra of the complex indicates that the ligand is coordinated to cobalt in its deprotonated form. The proton signals of the equatorial amide ligand in the complex are generally shifted downfield relative to the free ligand. As expected, the most significant downfield shift corresponds to the protons *ortho* to the pyridyl nitrogen,  $H_a$ , and *ortho* to the nitrogen substituent on the diamido benzene group,  $H_c$ . The broad doublet of doublet at *ca.*  $\delta = 9.39$  is assigned to  $H_a$ , and the broad siglet



Scheme 1. Chemical formula of  $trans\text{-}[\text{Co}^{\text{III}}(\text{Me}_2\text{bpb})(\text{bzlan})_2]\text{ClO}_4$

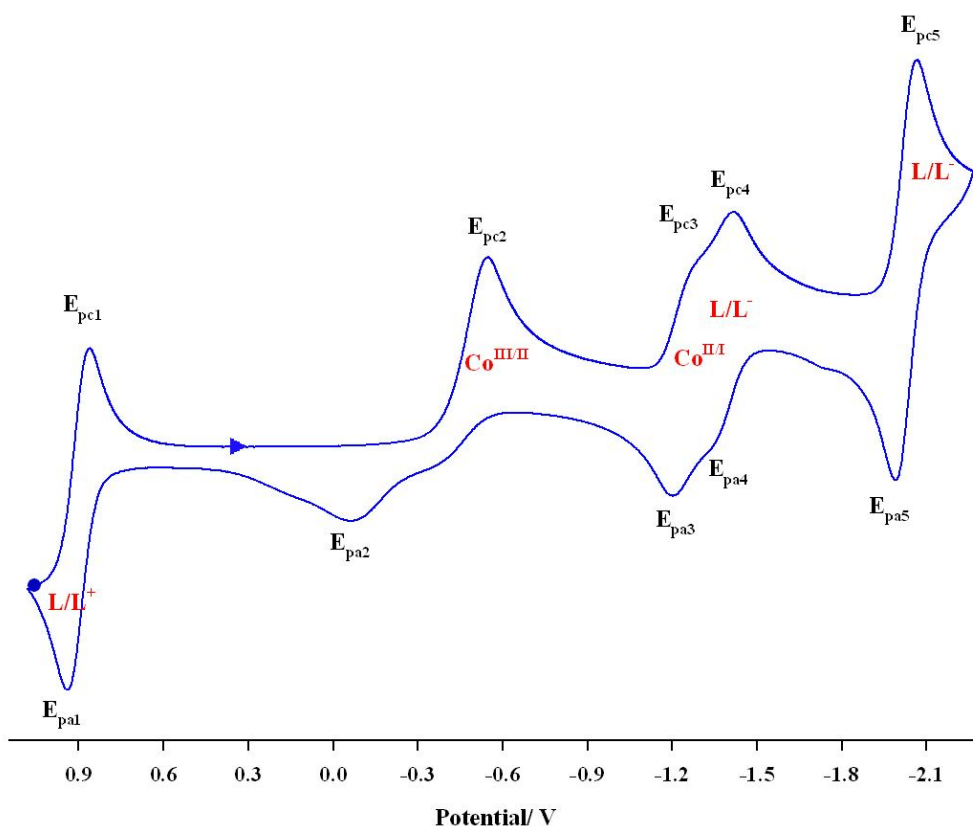
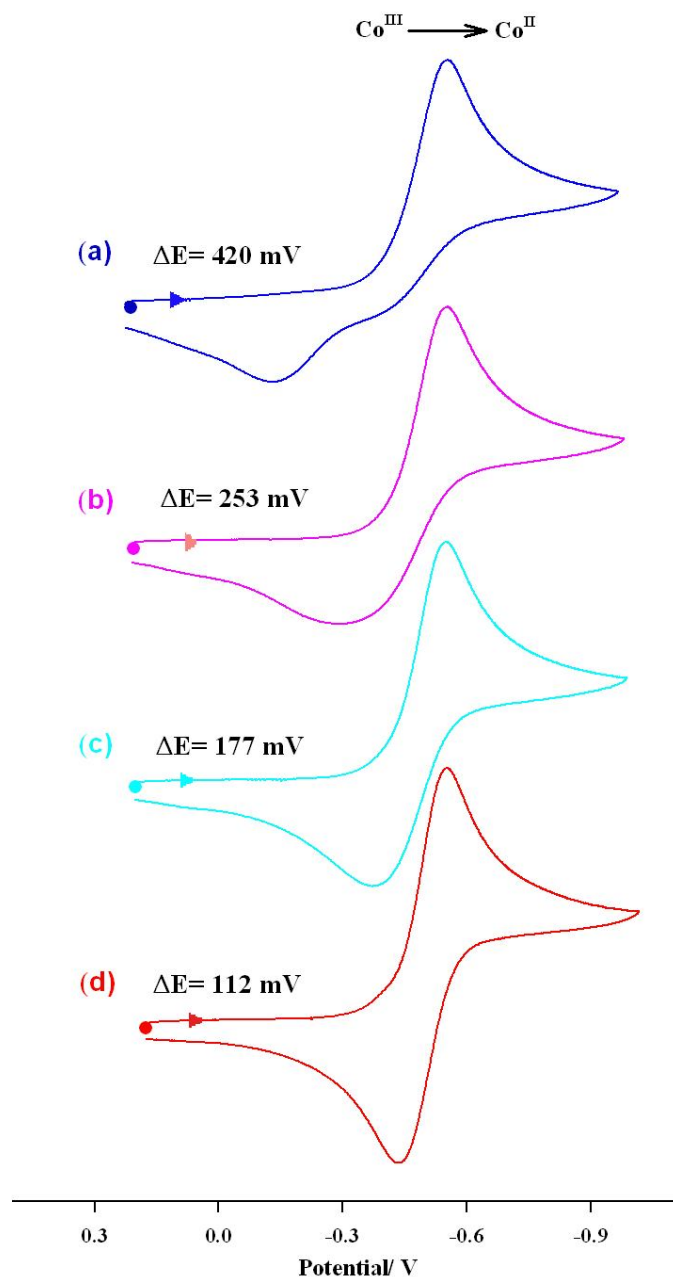


Fig. 3. Cyclic voltammogram of  $trans\text{-}[\text{Co}^{\text{III}}(\text{Me}_2\text{bpb})(\text{bzlan})_2]^+$  in acetonitrile at 298 K,  $c = 5.9 \times 10^{-4}$  M, scan rate =  $100 \text{ mV s}^{-1}$ .



**Fig. 4.** Cyclic voltammograms of  $\text{trans-}[\text{Co}^{\text{III}}(\text{Me}_2\text{bpb})(\text{bzlan})_2]^+$  in acetonitrile in the presence of excess benzylamine at 298 K. Amine/complex molar ratio: a = 0, b = 50, c = 70, d = 100, scan rate =  $100 \text{ mV s}^{-1}$ .

of  $\delta = 8.64$  is attributed to  $\text{H}_c$ . Other aromatic protons of the equatorial ligand appear in the 7.92-8.31 ppm range. The appearance of the signals due to the amine protons indicates the coordination of two amine ligands in the axial positions.

Aside from the aromatic protons of benzylamine appearing in the 6.72-7.14 ppm region, the benzylic proton resonances of the axial amine appear as a multiplet centered at 2.72 ppm, and the  $\text{NH}_2$  proton resonances appear as a broad



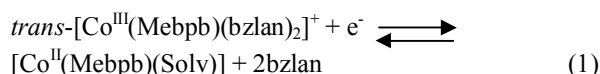
signal at 2.93 ppm.

### Electrochemical Studies

The electrochemical studies of the H<sub>2</sub>Me<sub>2</sub>bpb ligand and its cobalt complex in acetonitrile solutions with 0.1 M [N(n-Bu)<sub>4</sub>]PF<sub>6</sub> as the supporting electrolyte were recorded at a glassy carbon working electrode under argon atmosphere. The approximate concentrations were 5 × 10<sup>-3</sup>-10<sup>-4</sup> M.

As reported in our previous studies, the carboxamide ligands are electroactive in the potential range of 1.5 to -2.5 V in different solvents [18,19]. Three redox processes in the cyclic voltammogram of H<sub>2</sub>Me<sub>2</sub>bpb ligand has been observed. An electrochemically irreversible oxidation at +1.336 V that is assigned to the oxidation of the 4,5-dimethylorthophenylenediamine ring [29], and two consecutive reduction peaks observed at -1.96 and -2.34 V that are attributed to the pyridyl rings. These peaks are shifted to more positive values in the cobalt complex due to the transfer of electron density from the ligand to the metal center [30].

The cyclic voltammogram of the *trans*-[Co<sup>III</sup>(Me<sub>2</sub>bpb)(bzlan)<sub>2</sub>]<sup>+</sup> complex in acetonitrile solution is shown in Fig. 3. The electrochemically reversible oxidation process observed at E<sub>1/2</sub> = + 0.90 V (ΔV = 80 mV), is suggested to be mainly ligand-centered, and is presumably due to the increased delocalization of electrons in the more planar conformation, acquired by the coordinated ligand. The observation of a similar redox process in the CV's of the [Co<sup>III</sup>(Mebpb)(amine)<sub>2</sub>]<sup>+</sup> complexes [19] gives further support to this assignment. An irreversible reduction wave observed at -0.55 V is assigned to the Co<sup>III/II</sup> redox process (ΔE = 490 mV). Due to the addition of an electron to antibonding d<sub>z<sup>2</sup></sub> orbital, the reduction process is accompanied by loss of axial ligands as shown in Eq. (1) [19,29]. This process becomes quasi-reversible (ΔE = 112 mV) in the presence of excess amine (Fig. 4).



The two consecutive reversible reduction processes observed at E<sub>pc3&4</sub> = -1.29 V - -1.46 V are attributed to Co<sup>II</sup>/Co<sup>I</sup> and one of the pyridyl rings of the coordinated carboxamide ligand respectively. The final reversible wave

at E<sub>pc5</sub> = -2.06 V (ΔE = 70 mV) corresponds to the second pyridyl ring. Similar redox processes have been observed in our previous investigation of related cobalt(III) carboxamide complexes [19].

### CONCLUSIONS

A cobalt(III) complex of Me<sub>2</sub>bpb<sup>2-</sup> ligand with two ancillary amine ligands in the *trans* positions have been prepared. The coordination geometry around Co(III) center in *trans*-[Co<sup>III</sup>(Me<sub>2</sub>bpb)(bzlan)<sub>2</sub>]ClO<sub>4</sub> complex is a distorted octahedron. The electrochemical behavior of this complex in acetonitrile solution indicates that the axial amine ligand is replaced by acetonitrile solvent leading to [Co<sup>II</sup>(Me<sub>2</sub>bpb)(ACN)<sub>2</sub>] species. The redox potentials of the coordinated ligand are shifted to more positive values and the redox processes become reversible upon coordination. The metal centered redox process (Co<sup>III</sup>/Co<sup>II</sup>) becomes quasi-reversible in the presence of excess amine.

### Appendix A. Supplementary Data

Crystallographic data for *trans*-[Co<sup>III</sup>(Me<sub>2</sub>bpb)(bzlan)<sub>2</sub>]ClO<sub>4</sub> have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 1033273. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data\_request/cif.

### ACKNOWLEDGEMENTS

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