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# Synthesis, characterization and electrochemistry of carboxamido Co(III) complexes: The crystal structure of [Co<sup>III</sup>(Mebpb)(*N*-MeIm)<sub>2</sub>]BPh<sub>4</sub>·CH<sub>3</sub>OH

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# 1. Introduction

Metal complexes of many amido ligands have been extensively used to mimic the properties of biologically active systems. In this context, metal complexes of a wide variety of picolinamide-based ligands have been studied as structural and/or functional models of several metalloproteins [1]. The number of ligands that can be synthesized using bispyridylamide is practically enormous [2]. The convenient structural variation of the compounds by a modular approach gives access to ligands with varied structures having different electronic and steric properties which show a broad spectrum of affinities for different metal ions. The simple, generic chemistry involved in synthesizing different amido ligands renders them a highly attractive and under-exploited class of ligands for the development of metallamacrocycles [3], molecular devices (logic gates) [4], selective electrodes [5,6], and catalytic applications [7]. Ligands containing one or more amide functionality have proved to be useful in self-assembly, since they give predictable patterns of hydrogen bonding that can add extra dimensionality and helicity to the supramolecular structures and crystal engineering, in a biomimetic fashion [8-11].

Complexes with the neutral ligand show a wide array of geometries. The deprotonated amide nitrogen atom is a strong field li-

# ABSTRACT

Three cobalt(III) complexes of the type *trans*-[Co<sup>III</sup>(Mebpb)(amine)<sub>2</sub>]X {Mebpb<sup>2-</sup> = *N*,*N*'-bis(pyridine-2carboxamido)-4-methylbenzene dianion, and amine = *N*-methylimidazole (*N*-MeIm) (**1**), 3-methylpyridine (3-MePy) (**2**), 3-acetylpyridine (3-AcPy) (**3**), X = BPh<sub>4</sub><sup>-</sup> (**1**), ClO<sub>4</sub><sup>-</sup> (**2**, **3**)} were synthesized and characterized by elemental analyses, IR, UV–Vis, and <sup>1</sup>H NMR spectroscopy. The structure of **1**·CH<sub>3</sub>OH was determined by X-ray crystallography and was found to have a distorted octahedral geometry around Co. The electrochemical behavior of these complexes with the goal of evaluating the effect of axial ligation on the redox properties is also reported. The reduction potential of Co(III), ranging from -0.63 V for (**1**) to -0.20 V for (**3**) shows a relatively good correlation with the  $\sigma$ -donor ability of the axial ligands. © 2010 Elsevier B.V. All rights reserved.

> gand favoring N-coordination of the planar tetradentate ligand, although rare examples of coordination via the oxygen atom of the deprotonated amide group, and deviation from planarity have been encountered [12].

> In continuation of our work devoted to the synthesis and spectroscopic characterization of transition metal complexes utilizing relatively inexpensive and conveniently synthesizable bis(picolinamide) chelating ligands [13–17], we have prepared a group of cobalt(III) complexes of general formula *trans*-[Co(Mebpb)X<sub>2</sub>]<sup>+</sup> (X = monodentate  $\pi$ -acceptor amine) to explore the effect of axial ligand on the spectral properties and redox potentials. The X-ray crystal structure of *trans*-[Co(Mebpb)(*N*-MeIm)<sub>2</sub>]BPh<sub>4</sub>·CH<sub>3</sub>OH complex is also reported.

# 2. Experimental

# 2.1. Materials and general methods

All solvents and chemicals were of commercial reagent grade and used as received from Aldrich and Merck. The H<sub>2</sub>Mebpb ligand was synthesized by a procedure reported in the literature [16]. 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. The <sup>1</sup>H NMR spectra of the complexes were obtained on a BRUKER AVANCE DR X300 (300 MHz) spectrometer. Proton chemical shifts



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are reported in parts per million (ppm) relative to an internal standard of Me<sub>4</sub>Si. Cyclic voltammograms were recorded by using a SAMA 500 Research Analyzer. Three electrodes were utilized in this system, a glassy carbon working electrode, a platinum disk auxiliary electrode and Ag wire as reference electrode. 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. Acetonitrile was dried over CaH<sub>2</sub>. The solutions were deoxygenated by purging with Ar for 5 min. All electrochemical potentials were calibrated versus internal Fc<sup>+/0</sup> ( $E^0$  = 0.40 V versus SCE) couple under the same conditions [18].

*Caution*: Although we have encountered no difficulties, perchlorate salts with organic compounds are potentially explosive and should be handled with care.

#### 2.2. Synthesis of complexes

# 2.2.1. Synthesis of trans-[Co(Mebpb)(N-Melm)<sub>2</sub>]BPh<sub>4</sub>·CH<sub>3</sub>OH (**1**·CH<sub>3</sub>OH)

To a solution of  $Co(CH_3COO)_2$ :4H<sub>2</sub>O (125.4 mg, 0.5 mmol) in methanol (20 mL) was added a boiling solution of H<sub>2</sub>Mebpb (166.2 mg, 0.5 mmol) in methanol (30 mL). To this solution was added dropwise 9.5 mmol (0.75 mL) of N-methylimidazole and air was bubbled through the reaction mixture for 3 h. The final reaction mixture was filtered off and a solution of 0.5 mmol (171.1 mg) of NaBPh<sub>4</sub> in methanol was slowly added to the filtrate. The resulting deep green solution was left undisturbed to give dark green crystals, suitable for X-ray crystallography. The crystals were isolated by filtration and washed with methanol, and dried in vacuum. Yield 95%. Anal. Calc. for C<sub>52</sub>H<sub>50</sub>N<sub>8</sub>O<sub>3</sub>BCo: C, 69.03; H, 5.57; N, 12.38. Found: C, 69.1; H, 5.26; N, 12.74%. FT-IR (KBr, cm<sup>-1</sup>) v<sub>max</sub>: 3606-3296 (w, br, O-H), 1633 (s, C=O), 1598 (s, C=C), 1566 (m, C–N). UV–Vis:  $\lambda_{max}$  (nm) ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>) (CH<sub>3</sub>CN): 577 (211), 412 (7578). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 2.44 (3H, CH<sub>3</sub>, s), 3.07 (6H<sub>i</sub>, s), 6.02, 6.36 (4H<sub>i.k.</sub> s), 6.71 (2H<sub>h</sub>, s), 6.80, 6.93, 7.51 (20H<sub>TPB</sub>), 7.01 (1H<sub>f</sub>, d), 7.17 (2H<sub>b</sub>, dd), 7.94 (2H<sub>d</sub>, dd), 8.10 (2H<sub>c</sub>, dd), 8.60  $(1H_{\sigma} s)$ , 8.62  $(1H_{e} d)$ , 8.77  $(2H_{a}, dd)$ .

#### 2.2.2. Synthesis of trans- $[Co(Mebpb)(3-MePy)_2]ClO_4(2)$

To a solution of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (62.3 mg, 0.25 mmol) in methanol (20 mL) was added a boiling solution of H<sub>2</sub>Mebpb (83.1 mg, 0.25 mmol) in methanol (30 mL). To this solution was added dropwise 7.73 mmol (0.75 mL) of 3-methylpyridine and air was bubbled through the reaction mixture for 3 h. The final reaction mixture was filtered off and a solution of 0.25 mmol (30.6 mg) of NaClO<sub>4</sub>·H<sub>2</sub>O in methanol was slowly added to the filtrate. The resulting deep green solution was left undisturbed to give green crystals. The crystals were isolated by filtration and washed with a mixture of ethanol-ether (1:9 v/v) and dried in vacuum. Yield 40%. Anal. Calc. for C<sub>31</sub>H<sub>28</sub>N<sub>6</sub>O<sub>6</sub>ClCo: C, 55.16; H, 4.18; N, 12.45. Found: C, 54.95; H, 4.34; N, 12.44%. FT-IR (KBr, cm<sup>-1</sup>) v<sub>max</sub>: 1638 (s, C=O), 1602 (s, C=C), 1566 (m, C-N), 1111, 1090 (s, Cl-O). UV-Vis:  $\lambda_{max}$  (nm) ( $\epsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>) (CH<sub>3</sub>CN): 652 (164), 406 (6659). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 2.10 (6H<sub>i</sub>, s), 2.52 (3H, CH<sub>3</sub>, s), 7.02 (2H<sub>k</sub>, dd), 7.13 (1H<sub>f</sub>, d), 7.38 (2H<sub>j</sub>, d), 7.83 (2H<sub>h</sub>, s), 7.94 (2H<sub>l</sub>, d), 8.07 (2H<sub>b</sub>, m), 8.16 (2H<sub>d</sub>, m), 8.38 (2H<sub>c</sub>, m), 8.92 (1H<sub>g</sub>, s), 8.97 (1H<sub>e</sub>, d), 10.27 (2H<sub>a</sub>, dd).

## 2.2.3. Synthesis of trans- $[Co(Mebpb)(3-AcPy)_2]ClO_4$ (3)

To a solution of  $Co(CH_3COO)_2$ ·4H<sub>2</sub>O (62.3 mg, 0.25 mmol) in methanol (20 mL) was added a boiling solution of H<sub>2</sub>Mebpb (83.1 mg, 0.25 mmol) in methanol (30 mL). To this solution was added dropwise 6.87 mmol (0.75 mL) of 3-acetylpyridine and air was bubbled through the reaction mixture for 3 h. The final reac-

tion mixture was filtered off and a solution of 0.25 mmol (30.6 mg) of NaClO<sub>4</sub>·H<sub>2</sub>O in methanol was slowly added to the filtrate. The resulting deep green solution was left undisturbed to give dark green crystals. The crystals were isolated by filtration and washed with a mixture of ethanol–ether (1:9 v/v) and dried in vacuum. Yield 45%. *Anal.* Calc. for C<sub>33</sub>H<sub>28</sub>N<sub>6</sub>O<sub>8</sub>ClCo: C, 54.22; H, 3.86; N, 11.5. Found: C, 53.91; H, 3.93; N, 11.53%. FT-IR (KBr, cm<sup>-1</sup>) v<sub>max</sub>: 1703, 1637 (s, C=O), 1602 (s, C=C), 1567 (m, C–N), 1119, 1090 (s, Cl–O). UV–Vis:  $\lambda_{max}$  (nm) ( $\varepsilon$ , L mol<sup>-1</sup> cm<sup>-1</sup>) (CH<sub>3</sub>CN): 680 (136), 402 (7639). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  = 2.19 (6H<sub>i</sub>, s), 2.99 (3H, CH<sub>3</sub>, s), 7.25 (1H<sub>5</sub>, d), 7.42 (2H<sub>k</sub>, dd), 8.09–8.15 (4H<sub>b</sub>, j, m), 8.25 (2H<sub>d</sub>, dd), 8.46 (2H<sub>c</sub>, dd), 8.55 (2H<sub>1</sub>, d), 8.69 (2H<sub>h</sub>, s), 9.04 (1H<sub>g</sub>, s), 9.08 (1H<sub>e</sub>, d), 10.44 (2H<sub>a</sub>, dd).

#### 2.3. X-ray crystallography

Dark green crystals of 1 CH<sub>3</sub>OH suitable for X-ray crystallography were obtained by crystallization from methanol. X-ray data of **1**·CH<sub>3</sub>OH were collected at T = 100 K on a Bruker Smart APEX CCD diffractometer with graphite monochromated Mo Kα  $(\lambda = 0.71073 \text{ Å})$  radiation and  $0.3^{\circ} \text{ }\omega$ -scan frames. Cell refinement and data reduction were performed with the help of program SAINT [19]. Correction for absorption was carried out with the multi-scan method and program sADABS [19]. The structure was solved with direct methods using program SHELXS97 and structure refinement on  $F^2$  was carried out with program SHELXL97 [20]. 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. The methanol solvent molecule was refined in population (result 0.81(1)) and its OH group with distance restraints. Since the methanol deficit was probably due to sample storage prior to measurement, chemical formula and quantities derived thereof are given for the idealized methanol content of one molecule per formula unit. Crystal data, together with other relevant information on structure determination, are listed in Table 1.

Table 1	
Crystal data and structure refinement for 1.CH_OH	

Chemical formula C <sub>51</sub> H <sub>46</sub> BCoN <sub>8</sub> O <sub>2</sub> ·CH <sub>3</sub> OH	
Formula weight 904.74	
Temperature (K) 100(2)	
Crystal system triclinic	
Space group $P\bar{1}$	
a (Å) 12.4711(14)	
b (Å) 14.2143(15)	
c (Å) 14.8115(16)	
α (°) 69.210(2)	
β (°) 75.133(2)	
γ (°) 65.999(2)	
V (Å <sup>3</sup> ) 2223.0(4)	
Z, calculated density (g/cm <sup>3</sup> ) 2, 1.352	
Crystal size (mm) $0.58 \times 0.36 \times 0.16$	
$\mu$ (mm <sup>-1</sup> ) 0.441	
F (0 0 0) 948	
<i>θ</i> Ranges (°) 2.48–27.00	
Index ranges $-15 \le h \le 15, -18 \le k \le 18$	3,
$-18 \leqslant l \leqslant 18$	
Absorption correction multi-scan	
Reflections collected 28 709	
Independent reflections $(R_{int})$ 9646 (0.0281)	
Minimum and maximum 0.76, 0.93 transmission	
Data/restraints/parameters 9646/2/594	
Goodness-of-fit (GOF) on $F^2$ 1.066	
Final <i>R</i> indices $[I > 2\sigma(I)]$ $R_1 = 0.0408, wR_2 = 0.1046$	
<i>R</i> indices (all data) $R_1 = 0.0537, wR_2 = 0.1146$	
Maximum/minimum $\Delta \rho$ (e Å <sup>-3</sup> ) 0.65 and -0.53	



Fig. 1. ORTEP diagram of compound 1 CH<sub>3</sub>OH with the atom labeling scheme.

## 3. Results and discussion

## 3.1. Description of the structure of $(1 \cdot CH_3OH)$

An ORTEP diagram of the complex with the atomic numbering is presented in Fig. 1. Selected bond distances and angles are listed in Table 2. Hydrogen-bonding data are listed in Table 3.

The cobalt(III) center resides in a distorted octahedral environment with the Mebpb<sup>2–</sup> ligand occupying the equatorial plane of the octahedron. The remaining coordination sites are occupied by two *N*-methylimidazole ligands in *trans* position relative to each other.

#### Table 2

Table 2

Selected bond lengths (Å) and angles (°) for 1-CH<sub>3</sub>OH.

Bond lengths	
Co(1)-N(1)	1.9822(17)
Co(1)-N(2)	1.8771(16)
Co(1)-N(3)	1.8797(17)
Co(1)-N(4)	1.9802(16)
Co(1)-N(5)	1.9316(16)
Co(1)-N(7)	1.9410(17)
Bond angles	
N(1)-Co(1)-N(2)	82.96(7)
N(1)-Co(1)-N(3)	167.32(7)
N(1)-Co(1)-N(4)	109.57(7)
N(1)-Co(1)-N(5)	87.44(7)
N(1)-Co(1)-N(7)	91.02(7)
N(2)-Co(1)-N(3)	84.73(7)
N(2)-Co(1)-N(4)	166.85(7)
N(2)-Co(1)-N(5)	92.44(7)
N(2)-Co(1)-N(7)	89.48(7)
N(3)-Co(1)-N(4)	82.94(7)
N(3)-Co(1)-N(5)	90.09(7)
N(3)-Co(1)-N(7)	91.86(7)
N(4)-Co(1)-N(5)	92.12(7)
N(4)-Co(1)-N(7)	86.40(7)
N(5)-Co(1)-N(7)	177.38(7)
	. ,

Table 5		
Hydrogen bon	d lengths (Å) and angles ( $)$ for <b>1</b> ·CH <sub>3</sub> OH.	

D−H···A	D–H (Å)	H· · ·A (Å)	D···A (Å)	$D-H\cdots A$ (°)
$O(3)-H(30)\cdots O(2)$	0.80	1.88	2.672(3)	168

The Co–N<sub>amide</sub> (Co–N2 = 1.8771(16) Å and Co–N3 = 1.8797(17) Å) and Co–N<sub>pyridine</sub> (Co–N1 = 1.9822(17) Å and Co–N4 = 1.9802(16) Å) bond distances of [Co(Mebpb)(*N*-MeIm)<sub>2</sub>]<sup>+</sup> are similar to those in [Co(Me<sub>2</sub>bpb)(py)<sub>2</sub>]<sup>+</sup> [21], and [Co(Mebpb)-(Prldn)<sub>2</sub>]<sup>+</sup> [16]. The Co–N<sub>amide</sub> bond is significantly shorter than that to the pyridyl N atom, the former being comparable to Co–N<sub>peptide</sub> bonds, 1.87(1) Å [22]. The somewhat shorter Co–N<sub>axial</sub> (Co–N5 = 1.9316(16) Å and Co–N7 = 1.9410(17) Å) bond lengths of **1**·CH<sub>3</sub>OH versus those reported for the pyridine complex (1.960(4) and 1.981(4) Å) reflect the higher basicity of the *N*-MeIm ligand (pK<sub>a</sub> = 6.95) versus py (pK<sub>a</sub> = 5.23) [23]. The C–O = 1.24 ± 0.01 Å, C<sub>pyridine</sub>–N = 1.35 ± 0.01 Å, and C<sub>carboxy</sub>–N = 1.34 ± 0.01 Å bond distances, agree well with those reported for related complexes [22,24–26].

The *trans*-N5–Co–N7 unit with a bond angle of  $177.38(7)^{\circ}$  is almost linear. The two axial ligands are perpendicular to the Mebpb<sup>2–</sup> ligand. However, the planes of the two *N*-MeIm rings form a dihedral angle of  $83.0(1)^{\circ}$  with each other.

All *cis* angles around the Co center deviate from 90°, indicating a distortion from regular octahedron. The N–Co–N bond angles in the equatorial planes consist of one angle that is distinctly larger than 90° (N1–Co1–N4 = 109.57(7)). The Co atom is displaced slightly out of the mean plane of the four N atoms of the planar Mebpb<sup>2–</sup> ligand, 0.015 Å toward the N5 atom. The dihedral angle between the Co/N2/N3 and Co/N1/N4 planes is  $4.8(1)^\circ$  at the cobalt atom. The angles between the pyridine rings and the N1/N2/N3/N4 plane are 3.2(1) and  $12.9(1)^\circ$ . The dihedral angle between the two pyridine portions is  $16.0(1)^\circ$ . Steric congestion between the H atoms H1 and H18 of the pyridine moieties is the major reason for these distortions. The H1…H18 contact distance of 2.06 Å is less than the sum of van der Waals radii (2.20 Å) [27].

#### 3.2. Spectral characterization

The newly prepared metal complexes are all air-stable solids and have satisfactory elemental analyses. The octahedral geometry of complex **1** in **1**·CH<sub>3</sub>OH is evident from the X-ray structure analysis (Fig. 1). An octahedral *trans*-structure for other complexes (**2**, **3**) can be inferred based on the similarity of the spectral data of these complexes with those of complex **1**. The FT-IR data of the complexes are listed in Section 2. Differences between the spectra of H<sub>2</sub>Mebpb and its cobalt compounds are readily noticeable in the regions of the  $v_{NH}$ ,  $v_{CO}$ , and  $v_{CN}$  of the amide ligand vibrations. 1590

Compound **1** CH<sub>3</sub>OH exhibits a broad band at 3418 cm<sup>-1</sup>, which is due to the presence of a methanol molecule, as solvent of crystallization. The absence of the  $v_{N-H}$  band and the shift of the  $v_{CO}$  band to a lower energy in the spectra of metal complexes confirm that the amide nitrogens are coordinated to the Co in their deprotonated form [28]. All three complexes display strong carbonyl stretching frequencies ( $v_{CO}$ ) in the range 1633–1638 cm<sup>-1</sup> which are red shifted compared to the  $v_{CO}$  values of the free ligands (for H<sub>2</sub>Mebpb,  $v_{CO}$  = 1659, 1689 cm<sup>-1</sup>). The band, generally considered to be a combination of C-N stretch and N-H band, undergoes a sizable shift to higher frequencies in the deprotonated complexes (from 1520 cm<sup>-1</sup> in H<sub>2</sub>Mebpb to 1566 cm<sup>-1</sup> in the complexes). This might be expected since on removal of the amide proton this band becomes a pure C-N stretch. The perchlorate stretching vibrations for the perchlorate salts 2-3 are observed in the 1090 and 1119 cm<sup>-1</sup> region [29].

The UV–Vis data of **1–3** in MeCN are presented in Section 2. The electronic spectra of these complexes show a low intensity ligand field band (136 <  $\varepsilon$  < 211) which, depending on the axial amine ligand field strength, appears in the region between 577 and 680 nm. In most cases however [30], the expected  ${}^{1}A_{1} \rightarrow {}^{1}T_{2}$  band is masked by the intense charge-transfer bands. In addition, a strong absorption with  $\lambda_{max}$  in the 402–412 nm region was seen. The high extinction coefficient (6659–7639  $M^{-1}$ cm<sup>-1</sup>) of this absorption band suggests a CT transition [31]. All three complexes exhibit one strong intraligand absorption band with  $\lambda_{max}$  at ~320 nm [32].

Proton NMR spectral measurements were performed in CDCl<sub>3</sub> solution to throw light on the solution structure of these complexes. Scheme. 1 shows the numbering system for **1–3**. The results are given in Section 2. On formation of the deprotonated cobalt complexes, the benzene and pyridyl protons show chemical shifts similar to those found for analogous complexes [13,30,33–37].

<sup>1</sup>H NMR spectral studies reveal that most tetradentate ligands are generally coordinating in a planar manner so that the two monodentate ligands are *trans* to each other [30]. The appearance of the amine signals indicates the coordination of two amine ligands to the metal center [13]. The absence of the amide N–H signal in the spectrum of these complexes, clearly demonstrate coordination of the amide ligand in its deprotonated form [36,37]. Due to the electron withdrawing nature of the Co(III) center, all proton resonances of the ligand shift downfield upon coordination to cobalt, as compared to those of the free ligand [38]. The only exceptions are the meta protons on the pyridine moiety, H<sub>d</sub>,

which exhibit a slight upfield shift upon coordination.  $H_a$  is also the most downfield broad doublet by virtue of its proximity to electron withdrawing pyridyl nitrogen. The next most downfield shifted signals correspond to  $H_{e,g}$ . This is presumably due to the magnetic anisotropy induced by the ring current.

It is interesting to note that a good correlation between the chemical shifts of the equatorial ligand protons, the UV–Vis spectral data, and electrochemistry of these complexes exists. The trend in the chemical shifts of  $H_{a-g}$  and  $CH_3$  protons is inversely related to the donorability of the axial ligands, (*N*-MeIm > 3-MePy > 3-AcPy). This in turn is evident from the electronic spectra and electrochemical data of these complexes (Table 4).

#### 3.3. Electrochemistry

The electrochemical behavior of these complexes has been studied by cyclic voltammetry in acetonitrile with 0.1 M TBAH as the supporting electrolyte at a glassy carbon working electrode under argon atmosphere at 25 °C. Ferrocene (Fc) was used as the internal standard, and all redox potentials are referenced to the Fc<sup>+/0</sup> couple. The electrochemical data are presented in Table 4 and the voltammetric behavior of a representative complex [Co(Mebpb)(3-MePy)<sub>2</sub>]ClO<sub>4</sub> is shown in Fig. 2. The approximate concentrations of the compounds were  $2 \times 10^{-3}$ - $10^{-6}$  M.

#### 3.3.1. Electrochemistry of the complexes in the absence of amines

It has been demonstrated that transition metal complexes of dianionic bis(amide) ligands, derived from picolinic acid and 2,6-pyridinedicarboxylic acid, are subject to electrochemical oxidation at both the metal and the ligand to form metal- and ligand-centered oxidation products, respectively [39]. The purpose of electrochemical studies on these cobalt(III) complexes was to investigate the sensitivity of the Co<sup>III</sup>/Co<sup>II</sup> redox potentials with a change in the donor strength of the axial ligands.

For all redox couples, the peak-to-peak separation,  $\Delta E_{p}$ , is relatively independent of the scan rate, v, typical of diffusion-controlled experiments with fast simple one electron transfer at the electrode [33]. As previously mentioned [16], the ligand is electroactive over a range of 1.5 to -2.2 V. For the [Co(Mebpb)(amine)<sub>2</sub>]<sup>+</sup> complexes, the first oxidation couples have virtually identical potentials in the range 1.01–1.1 V. Thus, the first oxidation couple is suggested to be mainly ligand-centered (Fig. 2) [26]. This is also supported by the results reported by Che and co-workers [22].



Scheme 1. Structural formulas of the complexes and ligands.

# Table 4 Redox potentials of cobalt complexes 1, 2, and 3 in acetonitrile.<sup>a</sup>

No.	Compound	Epc1	Epa1	Epc2	Epa2	Epc3	Epa3	Epc4	Epa4	Epc5	Epa5
1	$[Co(Mebpb)(N-MeIm)_2]B(Ph)_4$ $[Co(Mebpb)(3-MePy)_2]ClO_4$	0.97 1.04	1.04	-0.63 -0.31	-0.02	-1.32 -1.30	-1.26	-1.42	-1.36 -1.33	-2.07 -2.06	-1.99 -1.99
3	$[Co(Mebpb)(3-AcPy)_2]ClO_4$	1.04	1.12	-0.20	0.14	-1.29	-1.22	-1.41	-1.31	-2.06	-1.99

<sup>a</sup> Potentials are vs.  $Fe^{+/0}$  in 0.1 M TBAH, T = 298 K. Scan rate 100 mV/s. Approximate concentrations:  $2 \times 10^{-3} - 10^{-6}$  M.



**Fig. 2.** Cyclic voltammogram of  $[Co^{III}(Mebpb)(3-MePy)_2]ClO_4$ , **2**,  $c = 2 \times 10^{-3}$  M, in acetonitrile at 298 K. Scan rate, 100 mV s<sup>-1</sup>.

In addition, complexes **1–3** each display an irreversible reduction wave at -0.2 to -0.63 V. As an example, the cyclic voltammograms of **2** (Fig. 2) show an electrochemically irreversible Co<sup>III</sup>/Co<sup>II</sup> reductive response ( $\Delta E_p = 450$  mV) with  $E_{pc}$  value of -0.31 V, and the occurrence of a structural change due to the reduction is implied [16]. The axial ligands have a profound effect on the  $E_{pc}$  value of the reduction process indicating that the reduction processes are presumably metal centered. From the  $E_{pc}$  values (Table 4) it is evident that stronger axial ligands shift the potential to more negative values.

All complexes display an additional reduction process (Table 4). We assign this as resulting from the combination of  $Co^{II}/Co^{I}$  couple [40] and the redox couple corresponding to one of the pyridyl rings (Fig. 2), based on our previous observations [16,17]. The reduced sensitivity of the  $Co^{II}/Co^{I}$  reductive potential to the change in the axial ligands suggests that the species being reduced at this stage have almost the same structure for the three complexes, [ $Co^{II}$ (-Mebpb)(MeCN)], resulting from the solvolysis of the  $Co^{II}/Co^{I}$  reduction product [30].

The final electrochemically reversible reduction couple observed in the voltammograms is attributed to the second pyridyl ring. These reductions were also observed in the cyclic voltammogram of the free ligand though only the reduction at more negative potential was reversible [16,17]. These two reductions probably involve the pyridyl rings in Mebpb ligand as no reductions, either reversible or irreversible, were observed in the CVs of the pyrrolidine-based carboxamido ligands [41].

# 3.3.2. *Electrochemistry of the complexes in the presence of amines*

It is well established that in many *trans*- $[Co^{III}(N_2O_2)(L)_2]^+$  Schiff base complexes, the first irreversible reduction process (Co<sup>III</sup>/Co<sup>II</sup>) can become quasi-reversible under controlled concentration conditions [42,43]. In an attempt to examine the possibility of reversible electrochemical behavior in analogous amido complexes, the electrochemistry of  $[Co^{III}(Mebpb)(3-MePy)_2]ClO_4$  was carried out in the presence of excess 3-methylpyridine. Fig. 3 shows the cyclic voltammogram of *trans*- $[Co^{III}(Mebpb)(3-MePy)_2]ClO_4$  (**2**) at different 3-Mepy concentrations. In the absence of additional amine the first reduction processes of  $(Co^{III}/Co^{II})$  is electrochemically irreversible ( $\Delta E$  = 450 mV). Upon addition of excess amine, the oxida-



**Fig. 3.** Cyclic voltammograms of  $[Co^{III}(Mebpb)(3-MePy)_2]CIO_4$ , **2**, in acetonitrile solution ( $c = 2 \times 10^{-3}$  M) in the presence of excess 3-methylpyridine concentrations ratios: (a) 0, (b) 20, (c) 60, (d) 100 at 298 K. Scan rate: 100 mV s<sup>-1</sup>.

tion wave of Co(II) is shifted towards more negative potentials (Fig. 3) ( $\Delta E = 220 \text{ mV}$ ), indicating the increased formation of sixcoordinated adducts; i.e. the electrode process is preceded by a reversible chemical reaction (Eq. (1));

$$[CoII(Mebpb)] + excess amine \rightarrow [CoIII(Mebpb)(amine)_2]^+ + e^-$$
(1)

The redox potential of the Co(II/I) couple is not significantly changed by the addition of excess amine and can be regarded as approximately independent.

#### 4. Conclusion

We have reported the synthesis and characterization of several trans-[Co<sup>III</sup>(Mebpb)(amine)<sub>2</sub>]X complexes and part of our characterization included the single-crystal X-ray structure analysis of trans-[Co(Mebpb)(N-MeIm)<sub>2</sub>]BPh<sub>4</sub>·CH<sub>3</sub>OH (1·CH<sub>3</sub>OH). The fused methyl group in the structure of Mebpb, increases the  $\sigma$  donating character of Mebpb. Consequently, contrary to [Co<sup>II</sup>(bpb)], which is not reactive towards oxidative addition of  $\pi$ -acceptor amines, the reactivity of Co(II) in [Co<sup>II</sup>(Mebpb)] towards  $\pi$ -acceptor amines is increased and  $\pi$  acceptor ligands are suitable for addition to the axial positions in an oxidative process. The coordination geometry around Co(III) center in these complexes is a distorted octahedron. Electrochemical studies revealed that the first reduction process Co(III/II) is irreversible and strongly influenced by the nature of the axial amines. When the axial ligands are changed from 1 to 3 a change in the Co(III/II) cathodic peak of 450 mV is observed. This process shows a tendency towards becoming quasi-reversible upon the addition of excess amine.

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# Appendix A. Supplementary material

CCDC 737919 contains the supplementary crystallographic data for 1-CH<sub>3</sub>OH. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam. ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2010.01.007.

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