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# Variations in the coordination environment of Co<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> complexes prepared from a tridentate (imino)pyridine ligand and their structural comparisons

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#### Abstract

The variations in the coordination environment of Co(II), Cu(II) and Zn(II) complexes with the neutral, tridentate ligand bis[1-(cyclohexylimino)ethyl]pyridine (BCIP) are reported. Analogous syntheses were carried out utilizing either the  $M(BF_{4})_2 \cdot xH_2O$  or  $MCl_2 \cdot xH_2O$  metal salts (where M = Co(II), Cu(II) or Zn(II)) with one equivalent of BCIP. When the hydrated  $BF_4^-$  metal starting material was used, cationic, octahedral complexes of the type  $[M(BCIP)_2]^{2+}$  were isolated as the tetrafluoroborate salt (4, 5). Conversely, when the hydrated chloride metal salt was used as the starting material, only neutral, pentacoordinate  $[M(BCIP)Cl_2]$  complexes (1–3) formed. All complexes were characterized by X-ray diffraction studies. The three complexes that are five coordinate have distortions due mainly to the pyridine di-imine bite angle. The [Cu(BCIP)Cl\_2] (2) also exhibits deviations in the Cu(II)–Cl bond distances with values of 2.4242(9) and 2.2505(9) Å, which are not seen in the analogous Zn(II) and Co(II) structures. Similarly, the two six coordinate complexes (5, 6) are also altered by the ligand frame bite angle giving rise to distorted octahedral geometries in each complex. The [Cu(BCIP)\_2](BF\_4)\_2 (6) also exhibits Cu(II)–N<sub>imine</sub> bond lengths that are on average 0.14 Å longer than those found in the analogous 5 coordinate complex, [Cu(BCIP)Cl\_2]. In addition to X-ray analysis, all complexes were also characterized by UV/Vis and IR spectroscopy with <sup>1</sup>H NMR spectroscopy being used for the analysis of the Zn(II) analogue (3).

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# 1. Introduction

Metal complexes containing substituted (imino)pyridine ligands in their coordination sphere have been of interest for many years [1–3]. This interest has arisen, in part, due to the fact that complexes formed with this motif in the ligand frame are stable and also because the substituents on the ligand periphery can be varied ( $R_1$  and  $R_2$ ) providing a platform for comparison.

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Indeed, (imino)pyridine ligands have been used in the synthesis of some initial model complexes of blue copper proteins [4] and it has been pointed out that many model studies are improved by altering the substituents of the

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ligand frame in order to better replicate the spectroscopic properties of the metalloenzyme. These ligand frames provide an accessible route to structural modifications [5,6].

(Imino)pyridine ligands have also been employed in the synthesis of metal complexes capable of catalyzing ethylene polymerization. Initial studies performed by Brookhart and Gibson revealed that Co(II) and Fe(II) complexes containing (imino)pyridine ligands with bulky any substituents at the imine position  $(R_1)$  are highly active and long lived ethylene polymerization catalysts [7,8]. Subsequent studies have shown that Fe(III) [9] and Cr(III) [10,11] complexes with similar coordination environments also exhibit catalytic behavior and that the catalytic activity is directly related to the identity and steric bulk of the substituents on the periphery of the (imino)pyridine ligand frame [12-15]. These catalysts are all generated from the corresponding  $[M^{n+}LX_n]$  precursor, where L is the substituted (imino)pyridine ligand and X is either chloride or bromide.

More recently ruthenium complexes of an (imino)pyridine ligand with mesityl groups at the  $R_1$  position and methyl groups at the  $R_2$  position were utilized to activate silicon hydride and chloride bonds of tetravalent silanes. The product of activation was then trapped forming a Ru(0) complex which contained the ligated silylene group in a pocket surrounded by the pendant mesityl groups from the (imino)pyridine ligand backbone. This report was the first example of formation of a metal silylene complex via  $\alpha$ -chloride abstraction [16].

The continued interest in (imino)pyridine ligands and their utility in the synthesis and study of metal complexes with varied applications has prompted us to study coordination reactions with bis[1-(cyclohexylimino)ethyl]pyridine (BCIP).



These studies are aimed to (i) provide additional understanding of the coordination behavior of ligands with an (imino)pyridine backbone and (ii) provide a structural comparison of the complexes synthesized from them. In this report we describe the preparation of the Co(II), Cu(II) and Zn(II) complexes of BCIP, their spectroscopic characterization and crystal structures.

#### 2. Experimental

#### 2.1. Materials

Cyclohexylamine, 2,6-diacetylpyridine,  $Co(BF_4)_2 \cdot 6H_2O$ ,  $CoCl_2 \cdot 6H_2O$ ,  $ZnCl_2$ ,  $Zn(BF_4)_2 \cdot xH_2O$ ,  $CuCl_2 \cdot 2H_2O$  and  $Cu(BF_4)_2 \cdot xH_2O$  were purchased from Aldrich Chemical Co. and used without further purification. All solvents were dried and distilled before use.

#### 2.2. Physical measurements

Infrared spectra were obtained with a Thermoelectron, Avatar 330 FT-IR spectrophotometer equipped with a Smart Orbit reflectance insert, diamond window. Absorption spectra were measured on a Hewlett-Packard 8453 diode array spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian 200 MHz spectrometer.

#### 2.3. Preparation of compounds

The ligand Bis[1-(cyclohexylimino)ethyl]pyridine (BCIP) was prepared by following the published procedure [17].

#### 2.3.1. Synthesis of $[Co(BCIP)Cl_2]$ (1)

A batch of 304 mg (0.934 mmol) of BCIP was suspended in 30 mL of CH<sub>3</sub>OH and 222 mg (0.934 mmol) of CoCl<sub>2</sub> · 6H<sub>2</sub>O was added to it. After 10 min, a blue-brown color developed. The reaction was stirred for 8 h and then filtered. Green microcrystalline **1** was obtained by slow evaporation of the mother liquor. The solid was collected via gravity filtration and dried under high vacuum. Yield: 0.20 g (47%). Selected IR bands: (cm<sup>-1</sup>) 1629 (m,  $v_{\rm NC}$ ), 1590 (m), 808 (s). Electronic absorption spectrum in CH<sub>3</sub>CN:  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 305 (403).

# 2.3.2. Synthesis of $[Cu(BCIP)Cl_2]$ (2)

A batch of 270 mg (0.829 mmol) of BCIP was dissolved in 30 mL of CH<sub>3</sub>CN. In a separate flask, 140 mg (0.829 mmol) of CuCl<sub>2</sub> · 2H<sub>2</sub>O was dissolved in 20 mL of CH<sub>3</sub>CN. The copper solution was then added drop wise to the ligand which resulted in immediate precipitate formation. The mixture was stirred for 3 h after which the green precipitate was collected via vacuum filtration and washed with 10 mL of CH<sub>3</sub>CN. The product was further purified by dissolving crude **2** in 20 mL of chloroform and allowing the solution to slowly evaporate in the hood. The green crystals were collected via gravity filtration and dried under high vacuum for 5 h. Yield: 0.38 g (74%). Selected IR bands: (cm<sup>-1</sup>) 1582 (m,  $v_{\rm NC}$ ), 1450 (m), 740 (s). Electronic absorption spectrum in DMF:  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>) 800 (129).

#### 2.3.3. Synthesis of $[Zn(BCIP)Cl_2]$ (3)

A batch of 308 mg (0.945 mmol) of BCIP was dissolved in 30 mL of  $CH_3CN$  and 129 mg (0.945 mmol) of  $ZnCl_2$ , dissolved in 20 mL of  $CH_3CN$  was added to it. Upon addition of the metal salt to the ligand, an off-white precipitate formed. The mixture was stirred for 3 h and the solid collected via gravity filtration. The precipitate was then re-dissolved in CHCl<sub>3</sub> and slow evaporation of this solution yielded **3** as a microcrystalline solid. Yield: 0.30 g (76%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz, 25 °C,  $\delta$  from TMS): 1.33 (m, 8H), 1.94 (m, 8H), 2.39 (m, 4H), 2.48 (s, 6H, CH<sub>3</sub>), 8.00 (d, 2H, py), 8.23 (d, 2H, py), 8.27 (d, 2H, py). Selected IR bands: (cm<sup>-1</sup>) 1633 (m,  $v_{NC}$ ), 1593 (m), 1466 (m), 809 (s). Electronic absorption spectrum in DMF: no absorption between 300 and 900 nm.

# 2.3.4. Synthesis of $[Co(BCIP)_2](BF_4)_2$ (4)

A batch of 290 mg (0.895 mmol) of BCIP was suspended in 30 mL of methanol and 305 mg (0.894 mmol) of Co(BF<sub>4</sub>)<sub>2</sub> · 6H<sub>2</sub>O was added to it. Upon addition of the metal salt, the solution immediately turned a dark redorange color and became homogeneous. The solution was stirred for 20 min and then gravity filtered. Slow evaporation of the filtrate over a period of 24 h afforded pure **4** as red-brown crystals. Yield: 0.30 g (68%). Selected IR bands: (cm<sup>-1</sup>) 1583 (m,  $v_{\rm NC}$ ), 1451, 1046 (s,  $v_{\rm BF}$ ). Electronic absorption spectrum in CH<sub>3</sub>CN:  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 478 (303), 558 (192).

# 2.3.5. Synthesis of $[Cu(BCIP)_2](BF_4)_2(5)$

The synthesis of **5** was carried out in a similar procedure used to obtain complex **4**. BCIP (166 mg, 0.51 mmol) was dissolved in 20 mL of CH<sub>3</sub>OH. In a separate vial, 163 mg of Cu(BF<sub>4</sub>)<sub>2</sub> · xH<sub>2</sub>O (19–22% Cu) was dissolved in 10 mL of CH<sub>3</sub>OH and added to the ligand solution. The addition resulted in an immediate color change to dark green-blue and the solution became homogenous within 5 min. The solution was stirred for 3 h and then concentrated to 7 mL and cooled to 0 °C. Microcrystalline **5** was collected after 2 h via gravity filtration and dried under high vacuum. Yield: 0.15 g (66%). Selected IR bands: (cm<sup>-1</sup>) 1588 (m,  $v_{\rm NC}$ ), 1051 (s,  $v_{\rm BF}$ ). Electronic absorption spectrum in CH<sub>3</sub>CN:  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 756 (169).

# 2.4. X-ray data collection and structure solution and refinement

Crystals suitable for X-ray analysis were obtained using the following procedures: Purple plates of  $[Co(BCIP)Cl_2]$ (1) were obtained by slow diffusion of Et<sub>2</sub>O into a methanolic solution of 1. Slow evaporation of a separate solution of  $[Cu(BCIP)Cl_2]$  (2) in CH<sub>3</sub>OH and  $[Zn(BCIP)Cl_2]$  (3) in  $CHCl_3$  yielded yellow-green and colorless blocks of 2 and 3, respectively. Red blocks of  $[Co(BCIP)_2](BF_4)_2 \cdot CH_3OH$  $(4 \cdot CH_3OH)$  and blue-green blocks of  $[Cu(BCIP)_2]$  $(BF_4)_2 \cdot CH_3OH (5 \cdot CH_3OH)$  were obtained by slow evaporation of separate solutions of 4 and 5 in methanol. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo K $\alpha$  ( $\lambda = 0.71073$  Å)) equipped with an Oxford liquid nitrogen cryostream. Crystals were mounted in a nylon loop with Paratone-N cryoprotectant oil. The structures were solved using direct methods and standard difference map techniques, and were refined by full-matrix least-squares procedures on  $F^2$  with SHELXTL (Version 6.14) [18]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included

Table 1

building of eristal and intensity concentric function parameters for complexes 1 of	Summary of crystal	data and intensity	v collection and	structure refinement	parameters for complexe	es 1–3
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	$[Co(BCIP)Cl_2](1)$	$[Cu(BCIP)Cl_2]$ (2)	$[Zn(BCIP)Cl_2](3)$
Empirical formula	$C_{21}H_{31}Cl_2CoN_3$	$C_{21}H_{31}Cl_2CuN_3$	$C_{21}H_{31}Cl_2N_3Zn$
Molecular weight	455.32	459.93	461.76
Crystal color, habit	purple, plate	yellow-green, block	colorless, block
Crystal size (mm)	$0.32 \times 0.26 \times 0.10$	$0.13 \times 0.10 \times 0.06$	$0.35 \times 0.18 \times 0.18$
Temperature (K)	125(2)	115(2)	115(2)
Crystal system	orthorhombic	monoclinic	orthorhombic
Space group	Pbca	$P2_1/c$	Pbca
Unit cell dimensions			
<i>a</i> (Å)	10.2293(4)	12.9820(8)	10.2180(5)
b (Å)	16.8746(7)	9.9698(6)	16.8895(8)
c (Å)	24.539(1)	17.046(1)	24.674(1)
α (°)	90	90	90
β (°)	90	98.485(1)	90
γ (°)	90	90	90
$V(\text{\AA}^3), Z$	4235.9(3), 8	2182.1(2), 4	4258.2(3), 8
$D_{\rm calc} ({\rm mg}{\rm m}^{-3})$	1.428	1.400	1.441
Absorption coefficient ( $\mu$ , mm <sup>-1</sup> )	1.074	1.257	1.416
$\Phi$ Range collected (°)	1.66-28.12	1.59-28.25	1.65-28.29
Completeness to $\Phi_{\max}$ (%)	97.7	93.8	96.4
Reflections collected/unique $(R_{int})$	46871/5063 (0.042)	23870/5075 (0.0578)	45518/5102 (0.0259)
Data/restraints/parameters	5063/0/244	5075/0/246	5102/0/246
$R_1, wR_2 (I > 2\sigma I)$	0.0273, 0.0663	0.0480, 0.1237	0.0218, 0.0565
$R_1$ , $wR_2$ (all data)	0.0355, 0.0709	0.0734, 0.1364	0.0257, 0.0584
Goodness-of-fit on $F^2$	1.021	1.050	1.044
Largest difference in peak/hole (e/Å <sup>3</sup> )	0.114, -0.217	1.835, -0.536	0.461, -0.222

Table 3

Table 2
Summary of crystal data and intensity collection and structure refinement
parameters for complexes 4 and 5

	$\begin{matrix} [Co(BCIP)_2](BF_4)_2 \cdot CH_3OH \\ (\textbf{4} \cdot CH_3OH) \end{matrix}$	$\begin{array}{l} [Cu(BCIP)_2](BF_4)_2 \\ (\textbf{5}\cdot CH_3OH) \end{array}$
Empirical formula	$C_{43}H_{66}B_2CoF_8N_6O$	C43H66B2CuF8N6O
Molecular weight	915.57	920.18
Crystal color, habit	red, block	blue-green, block
Crystal size (mm)	$0.20\times0.20\times0.20$	$0.17\times0.17\times0.12$
Temperature	115(2)	125(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions		
a (Å)	11.4820(6)	11.4925(9)
b (Å)	18.0443(9)	18.103(2)
c (Å)	22.752(1)	22.427(2)
α (°)	90	90
β (°)	103.693(1)	102.111(1)
γ (°)	90	90
$V(Å^3), Z$	4579.9(4), 4	4562.2(6), 4
$D_{\rm calc} ({\rm mg}{\rm m}^{-3})$	1.328	1.340
Absorption coefficient $(\mu mm^{-1})$	0.447	0.552
$\Phi$ Range collected (°)	1.84–28.30	1.46–23.81
Completeness to $\Phi_{\max}$ (%)	93.8	100.0
Reflections are collected/unique $(R_{int})$	51073/10683 (0.0338)	41276/7005 (0.0549)
Data/restraints/ parameters	10683/0/555	7005/0/536
$R_1, wR_2 (I \ge 2\sigma I)$	0.0526, 0.1502	0.0553, 0.1449
$R_1$ , $wR_2$ (all data)	0.0701, 0.1643	0.0776, 0.1554
Goodness-of-fit on $F^{2a}$	1.020	1.099
Largest difference in peak/hole (e/Å <sup>3</sup> )	0.965, -0.772	0.512, -0.405

in calculated positions and were refined using a riding model. The methanol solvent of crystallization in  $(5 \cdot CH_3OH)$  is disordered. The atoms of the solvent were included in the refinement as a diffuse contribution to the scattering using the program SQUEEZE in the PLATON suite of programs [19]. Crystal data and refinement details are presented in Table 1 for complexes 1–3 and Table 2 for complexes 4 and 5. Selected bond distances for complexes 1 – 5 are listed in Table 3. Bond angles are given in Table 4 for complexes 1–3 and Table 5 for complexes 4 and 5.

#### 3. Results and discussion

In many cases the synthesis of metal imine complexes involves the use of *in situ* condensation of the amine and aldehyde in the presence of the metal starting material [20–22]. However, in this study, the ligand was synthesized and characterized before addition to the metal salt. We employed the use of either  $M(BF_4)_2 \cdot xH_2O$  or  $MCl_2 \cdot xH_2O$  (where M = Cu(II), Co(II) or Zn(II)), and found that the ligand to metal ratio in the isolated product was dependent on the identity of the starting metal salt. The

Selected bond distances (Å) of complexes 1–5					
Bond distances					
$[Co(BCIP)Cl_2]$ (1)					
Co-N(1)	2.022(1)	Co-N(2)	2.261(1)		
Co-N(3)	2.196(1)	Co-Cl(2)	2.2790(4)		
Co-Cl(1)	2.3070(4)	N(2)-C(13)	1.281(2)		
$[Cu(BCIP)Cl_2]$ (2)					
Cu–N(1)	1.954(3)	Cu-N(2)	2.120(3)		
Cu-N(3)	2.132(3)	Cu–Cl(2)	2.2505(9)		
Cu-Cl(1)	2.4242(9)	N(2)-C(13)	1.285(4)		
$[Zn(BCIP)Cl_2]$ (3)					
Zn-N(1)	2.063(1)	Zn-N(2)	2.230(1)		
Zn-N(3)	2.323(1)	Zn-Cl(2)	2.2542(3)		
Zn-Cl(1)	2.2828(3)	N(2)-C(13)	1.280(2)		
$[Co(BCIP)_2](BF_4)$	<sub>2</sub> ( <b>4</b> )				
Co-N(11)	2.008(2)	Co-N(21)	2.008(2)		
Co-N(12)	2.221(2)	Co-N(22)	2.219(2)		
Co-N(13)	2.273(2)	Co-N(23)	2.250(2)		
N(13)-C(16)	1.280(3)	N(23)-C(26)	1.283(3)		
$[Cu(BCIP)_2](BF_4)$	<sub>2</sub> ( <b>5</b> )				
Cu-N(11)	1.940(3)	Cu-N(21)	1.937(3)		
Cu-N(12)	2.243(3)	Cu-N(22)	2.266(3)		
Cu-N(13)	2.300(3)	Cu-N(23)	2.266(3)		
N(13)-C(16)	1.269(5)	N(23)-C(26)	1.279(5)		

Selected bond angles for complexes 1–3 with the average  $N_{\rm py}\text{-}M(II)\text{-}N_{\rm imine}$  reported

	[Co(BCIP)Cl <sub>2</sub> ] (1)	[Cu(BCIP)Cl <sub>2</sub> ] ( <b>2</b> )	[Zn(BCIP)Cl <sub>2</sub> ] ( <b>3</b> )
N <sub>imine</sub> -M(II)-N <sub>imine</sub>	151.86(4)	155.53(1)	149.35(4)
N <sub>py</sub> -M(II)-N <sub>imine</sub>	75.95(5)	78.07(1)	74.68(4)
Cl(2)-M(II)-Cl(1)	128.09(2)	115.50(3)	126.28(1)

Table 5

Table 4

Selected bond angles and average  $N_{py}\mbox{-}M(II)\mbox{-}N_{imine}$  and  $N_{imine}\mbox{-}M(II)\mbox{-}N_{imine}$  bond angles for complexes 4 and 5

	[Co(BCIP) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub> ( <b>4</b> )	$[Cu(BCIP)_2](BF_4)_2$ (5)
N <sub>py</sub> -M(II)-N <sub>imine</sub> (intraligand)	76.22(8)	77.38(1)
N <sub>py</sub> -M(II)-N <sub>imine</sub> (interligand)	103.83(8)	102.61(1)
N <sub>imine</sub> -M(II)-N <sub>imine</sub> (interligand)	93.27(8)	92.74(1)
N <sub>imine</sub> -M(II)-N <sub>imine</sub> (trans)	152.31(8)	154.74(1)
$N_{py}-M(II)-N_{py}$	176.24(8)	178.04(1)

synthesis of both complexes 4 and 5 were carried out using the tetrafluoroborate salt of the hydrated metal(II) starting material. Only the bis complexes were isolated from these reactions even though in both cases a 1:1 metal to ligand ratio was used. The yields for these reactions were: 4 – 68% and 5 – 64%, which confirm that each is the major product for the reactions. In no case was a 5 coordinate hydrated complex formed when the starting material contained the non-coordinating  $BF_4^-$  anion. This latter result could be due to the use of dry CH<sub>3</sub>OH as solvent for these reactions as 5-coordinate M(II) complexes with coordinated water have been reported [23,24]. These findings suggest that, under the reaction conditions reported here, coordination of other N-type donor atoms is preferable over water when the coordination sphere of the metal contains other nitrogen atoms. A similar Cu(II) complex has been reported (substitution of methyl imine group for hydrogen) however, attempts to isolate the corresponding  $[Cu(L)_2]^{2+}$  complex starting with the tetrafluoroborate salt were unsuccessful [25]. These attempts resulted in brown solutions from which no pure product was obtained. The authors suggested that perhaps the hydrated  $Cu(BF_4)_2$  salt was undergoing spontaneous reduction to the Cu(I) species which was confirmed by their investigation of the reactivity of the ligand with the corresponding Cu(I) starting material. We however did not see similar reactivity in the synthesis and isolation of 5 and only obtained blue solutions. Attempts were made to isolate the analogous Zn(II) complex using  $Zn(BF_4)_2 \cdot xH_2O$ , however no pure product was isolated from these attempts.

Unlike the syntheses that resulted in the formation of bis complexes 4 and 5, no bis complexes were isolated from analogous syntheses utilizing one equiv. of BCIP and starting metal salts that contain chloride ion,  $MCl_2 \cdot xH_2O$ , (where M = Cu, Zn, or Co). These syntheses resulted in coordination of the two chloride ions and the formation of one of the five coordinate complexes 1-3 as the major product in each reaction. None of the syntheses resulted in the formation of the corresponding agua complex which suggests that under these conditions, Cl<sup>-</sup> is a better ligand than water in these complexes when the coordination sphere contains N-donor atoms. Two syntheses for complex 1 have been reported previously however, one method was not detailed [26] and no crystallographic analysis was included in either report [27]. In the first report, the complex was isolated as a grey-green solid which showed no propensity to air oxidize. We report complex 1 as a green solid which is air stable but does undergo air oxidation over the course of 24 h in MeOH to give an orange-brown solution.

We were interested to know if bis complexes could be obtained from reactions with 1:2 metal-to-ligand ratios in the presence of chloride ion. In the case of using 2.1 equiv. of BCIP with  $CoCl_2 \cdot 6H_2O$ , the reaction yielded a solution which had a similar color (dark red-brown) to the solution which yielded the bis complex 4. However upon crystallization, only complex 1 was isolated, albeit in lower yield. This result, combined with the lower yield, suggested that at high ligand-to-metal ratios the Co(II) bis complex can form in the presence of chloride ion. In order to confirm this hypothesis, a reaction was carried out using a 1:5 metal-to-ligand ratio. These reactions produced only redorange solutions from which  $[Co(BCIP)_2]^{2+}$  was identified using UV/Vis spectroscopy. Similar reactions were carried out with  $CuCl_2 \cdot 2H_2O$ , however only complex 2 was isolated. The reaction produced a light green precipitate in similar yield as reported for the 1:1 metal-to-ligand synthesis. The isolation of **2** as the only product may be a result of the insolubility of the product in CH<sub>3</sub>CN and it preferentially precipitating out of solution before the bis complex can form. To confirm that the Cu(II) bis complex can also form in the presence of chloride ion, [Cu(BCIP)Cl<sub>2</sub>] was dissolved in CH<sub>3</sub>OH and excess BCIP was added to it. After 5 min the color of the solution changed from light green to blue-green in color and a shift in  $\lambda_{max}$  from 800 nm to 756 nm confirmed that [Cu(BCIP)<sub>2</sub>]<sup>2+</sup> also forms under high ligand to metal ratios.

#### 3.1. Structure of complexes

# 3.1.1. Structure of $[Co(BCIP)Cl_2]$ (1)

The structure of  $[Co(BCIP)Cl_2]$  is shown in Fig. 1. The five coordinate Co(II) complex is comprised of one BCIP ligand coordinated in a *mer* fashion, with the N<sub>py</sub> and the two chloride ions positioned in the equatorial plane and the imine nitrogen donors in the axial positions. The distortion of the complex arises mainly from the 2,6-pyridine di-imine bite angle, with an N(2)–Co–N(3) bond angle of 151.86(4)°. The N(1)–Co–Cl(2) bond angle is 120.52(4)° while the Cl(2)–Co–Cl(1) bond angle is 128.09(2)°, with the difference most likely due to the larger size of the chloride ions. The Co(II)–N<sub>py</sub> bond distance is 2.022(1) Å which is shorter than the corresponding Co(II)–N<sub>imine</sub> average bond distance of 2.2286(12) Å. The average Co(II)–Cl bond distance is 2.2930(4) Å. The reported bond distances are similar to other Co(II)–N bond lengths [28].

#### 3.1.2. Structure of $[Cu(BCIP)Cl_2]$ (2)

The structure of  $[Cu(BCIP)Cl_2]$  is shown in Fig. 2. The distortion in this complex can be seen not only in the bite



Fig. 1. Thermal ellipsoid plot (30% probability level) of complex **1** showing the numbering scheme. H atoms have been omitted for clarity.

angle of the tridentate ligand, but also in the Cu(II)–Cl bond lengths. The Cu(II)–Cl bond distances are 2.2505(9) Å and 2.4242(9) Å, a difference of approximately 0.17 Å. Comparatively, Co(II)–Cl bonds have nearly identical lengths with a difference of 0.028 Å. Overall, the Cu(II)–N bond lengths are slightly shorter than the analogous Co(II)–N distances. The Cu–N<sub>py</sub> and average Cu–N<sub>imine</sub> bond lengths in **2** are 1.954(3) Å and 2.126(3) Å, respectively. The N(2)–Cu–N(3) angle is 155.5(1)° which is somewhat larger than the analogous angle in complex **1**. These differences are most likely due to Cu(II) having a slightly smaller radius than Co(II) [29]. The bond distances reported are within the range of previously reported Cu(II)–N and Cu(II)–Cl bond distances [30,31].

# 3.1.3. Structure of $[Zn(BCIP)Cl_2]$ (3)

The structure of  $[Zn(BCIP)Cl_2]$  has been submitted as supporting information. Unlike [Cu(BCIP)Cl<sub>2</sub>], the Zn analogue exhibits little distortion and is remarkably similar to complex 1, with the same orthorhombic crystal system and space group (Pbca) as the Co(II) complex. The  $Zn(II)-N_{py}$  bond length is 2.063(1) Å while the average Zn(II)-N<sub>imine</sub> and Zn(II)-Cl bond distances are 2.2761(1) and 2.2685(3) Å, respectively. All distances are within the range of previously reported Zn(II)-N and Zn-Cl bond distances [32]. The bond lengths in complex 3 are somewhat longer than analogous Co(II) bond lengths and the deviation is most likely due to the slightly larger size of the Zn(II) ion [28]. This is supported by the slight decrease in the N(2)-M(II)-N(3) bond angle from  $151.86(4)^{\circ}$  in the Co(II) complex to  $149.35(4)^{\circ}$  in the Zn(II) species as well.

# 3.1.4. Structure of $[Co(BCIP)_2](BF_4)_2 \cdot CH_3OH$ $(4 \cdot CH_3OH)$

The monoclinic crystals of  $[Co(BCIP)_2](BF_4)_2$  co-crystallized with one methanol molecule. The structure of the cation,  $[Co(BCIP)_2]^{2+}$ , is shown in Fig. 3. The octahedral geometry around the Co(II) center is comprised of 2 BCIP ligands coordinated in a *mer* fashion with the N<sub>py</sub> groups positioned trans to each other. The average Co–N<sub>py</sub> bond distance is 2.008(2) Å, a value that is slightly shorter than the corresponding bond lengths in complex **1**. All the Co(II)–N<sub>imine</sub> bond distances are within 0.05 Å with an average distance of 2.239(2) Å. The N(22)–Co–N(23) bond angle is 152.05(8)° while the N(11)–Co–N(21) bond angle is 176.24(8)° which suggests that the distortion is due to the BCIP bite angle. All the Co–N bond distances are similar to those previously reported [28].

# 3.1.5. Structure of $[Cu(BCIP)_2](BF_4)_2(5 \cdot CH_3OH)$

Like complex 4, complex 5 also co-crystallized with one solvent methanol in the same crystal system (monoclinic) and space group as complex 4. The structure of the cation is shown in Fig. 4. The average Cu(II)-N<sub>py</sub> bond length is 1.939(3) Å which is slightly longer than the analogous bond length in complex 2 and slightly shorter than the corresponding Co(II)-N<sub>pv</sub> bond distance in complex 4. The average Cu(II)-N(12)<sub>imine</sub> and Cu(II)-N(13)<sub>imine</sub> bond distance is 2.272(3) Å while the average Cu(II)–N(22)<sub>imine</sub> and Cu(II)-N(23)<sub>imine</sub> is 2.266(3) Å. The combined average of the Cu(II)-N<sub>imine</sub> distances is 0.143 Å longer than the average Cu(II)-N<sub>imine</sub> distance found in complex 2. The N(11)-Cu-N(21) is 178.0(1)° which is approximately 2° larger than the analogous Co(II) bond angle while the N(22)-Cu-N(23) is 3° larger at 155.1(1)°. Similar to complex 2, all Cu(II)-N bond lengths are comparable to other reported values [30,31].



Fig. 2. Thermal ellipsoid plot (30% probability level) of complex 2 showing the numbering scheme. H atoms have been omitted for clarity.



Fig. 3. Thermal ellipsoid plot (30% probability level) of the cation of **4** showing the numbering scheme. H atoms have been omitted for clarity.

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The differences between similar bonds lengths within each complex 1-5 are given in Table 6.

Both Cu(II) and Co(II) (high-spin) complexes are expected to exhibit Jahn-Teller distortion, however the distinction between the degeneracy in the  $e_g$  set (Cu(II)) versus the  $t_{2g}$  set (Co(II)) would expectedly give rise to greater distortion in octahedral Cu complexes. Complex 4 is slightly compressed along the  $N_{\rm py}\text{-}M\text{-}N_{\rm py}$  axis with a decrease in the average Co(II)-N<sub>py</sub> bond length of 0.0138 Å and a lengthening of the Co(II)-N<sub>imine</sub> average bond length by 0.040 Å compared to complex 1. A similar comparison between complexes 2 and 5 reveals a variance of 0.015 Å in the of the Cu(II)-N<sub>py</sub> bond lengths, a value that is comparable to the difference between the cobalt complexes. However, the average Cu(II)-N<sub>imine</sub> distance in complex **5** is 0.143 Å longer than those in complex **2**. There is very little difference between the average of the two sets of axial M(II)–N<sub>imine</sub> bond lengths (from the two BCIP ligands L1 and L2) within complexes 4 and 5 with values of only 0.0055 Å in complex 5 and 0.0125(2) Å in complex 4. These results suggest that the distortion in these complexes is dictated by the limited flexibility of the ligand frame and by the shorter M(II)-N<sub>py</sub> bonds lengths compared to M(II)-N<sub>imine</sub> distances in these complexes. Both of these factors



Fig. 4. Thermal ellipsoid plot (20% probability level) of the cation of **5** showing the numbering scheme. H atoms have been omitted for clarity.

Table 6 Differences in the M–Cl and M– $N_{imine}$  bond lengths within each complex 1–5

	1 (Co)	<b>2</b> (Cu)	3 (Zn)	<b>4</b> (Co)	5 (Cu)
$\begin{array}{l} \Delta M(II) - Cl \\ \Delta M(II) - N(L1)_{imine} \\ \Delta M(II) - N(L2)_{imine} \end{array}$	0.028(4)	0.1737(9)	0.0286(3)	0.052(2)	0.057(3)
	0.065(1)	0.012(3)	0.093(1)	0.031(2)	0

combine to afford distorted complexes which minimize the strain energy [33].

The differences in bond lengths for the pentacoordinate  $[M(II)(BCIP)Cl_2]$  complexes, 1–3, are not as straightforward. The two M(II)-Cl bond distances are nearly identical to each other in the Co complex 1 and Zn complex 3 structures (2.2790(4) and 2.3070(4) Å and2.2542(3) and 2.2828(3), respectively) while the Cu analogue (2) has greater than a 0.17 Å difference between the two. There are two possibilities that may explain the deviation in the Cu(II)-Cl bond lengths in complex 2 which arise from its assignment as either a distorted square pyramid (SP) or a distorted trigonal bipyramid (TBP) [34]. The assignment to these geometries can be made using the continuous symmetry approach developed by Pinsky and Avnir [33] or by using the parameter  $\tau$ , introduced by Addison, Reedijk and co-workers [35], both of which provide a measure of the degree of SP versus TBP geometry. However, neither approach gives a clear assignment of the Cu(II) structure, with the calculated values of the parameters falling between the two geometries. Therefore, if the structure is assigned as distorted SP, then one of the chloride groups occupies the axial site which would result in a natural lengthening of this bond compared to the Cu(II)-Cl bond in the equatorial plane. However, if the assignment is made as distorted TBP, then the results suggest that the distortion is due to the electron configuration of the Cu(II) center indicating that it is Jahn-Teller in nature. Additionally, there is no clear trend for the M(II)-Nimine bond distances. The two Cu(II)-Nimine bond distances are nearly identical to each other (2.120(3) and 2.132(3) Å) while the two bonds differ by greater 0.06 Å in the Co analogue and nearly 0.1 Å in the Zn analogue.

#### 4. Concluding remarks

This work has described the synthesis and characterization of five imino(pyridine) metal complexes and their crystallographic analysis. The product isolated from each synthesis is directly related to the starting metal salt that was used. The structural analysis of the octahedral complexes showed both complexes **4** and **5** exhibit distortion. The structural analysis of the five coordinate complexes showed no clear trend in metal-ligand bond lengths however the Cu(II) analogue (**2**) showed the greatest distortion. Work on obtaining the corresponding tris complexes with the analogous bidentate ligand is currently underway.

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#### Appendix A. Supplementary material

CCDC 629360, 629359, 629358, 629356 and 629357 contain the supplementary crystallographic data for 1, 2, 3, 4 and 5. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2007.03.002.

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