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Spectroscopic differences between heterocyclic benzothiazoline, -thiazole and imine containing ligands and comparison of the Co and Cu pyridine benzothiazole and imine complexes

Lauren J. Carlson [a], Jenna Welby [a], Kelly A. Zebrowski [a], Matthew M. Wilk [a], Rachel Giroux [c], Nicole Ciancio [c], Joseph M. Tanski [b], Amy Bradley [c], Laurie A. Tyler [a,*]

[a] Department of Chemistry and Biochemistry, Union College, Schenectady, NY 12308, USA
[b] Department of Chemistry, Vassar College, Poughkeepsie, NY 12604, USA
[c] Department of Chemistry, Wilkes University, Wilkes-Barre, PA 18766, USA

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ABSTRACT

Five heterocyclic benzothiazoline and -thiazole analogs have been synthesized and characterized by ^{1}H NMR and IR spectroscopy. The analogs fall into two different classes, (a) those which contain one benzothiazoline group adjacent to the heterocyclic ring system (starting with 2-pyridinecarboxaldehyde, 2-thiophenecarboxaldehyde or 2-furaldehyde), and (b) those which have two benzothiazoline substituents (starting with 2,6-pyridinecarboxaldehyde and 2,5-thiohenecarboxaldehyde). In addition, the imine containing ligands, bis-2-[(pyridin-2-ylmethylene)-imino]-benzenethiol disulfide $(PyIS)_2$ and bis-2-[(thiophen-2-ylmethylene)-imino]-benzenethiol disulfide$(ThIS)_2$, were prepared starting with the disulfide of 2-aminothiophenol. Each species has been characterized by ^{1}H NMR and IR spectroscopies. Ligation reactions with 2-(2-pyridyl)benzothiazoline (Py(Bt)) and $Cu(OAc)_2{\cdot}1H_2O$ resulted in the formation of a dinuclear species containing two copper ions, two ligand frames and two acetate groups, $[Cu(PyAS)(OAc)]_2$ (**1**). Both copper ions are five-coordinate and bonded to one monodentate acetate, one ligand frame (NNS) and one bridging thiolate. Ligation reaction with 2-(2-pyridyl)benzothiazole (Py(oBt)) and $CoCl_2{\cdot}xH_2O$ or $Cu(BF_4)_2{\cdot}xH_2O$ resulted in the formation of a six-coordinate, octahedral Co(II) complex, *cis*-$[Co(Py(oBt)_2Cl_2]$ (**2**) and a five coordinate Cu(II) complex, $[Cu(Py(oBt))_2(OH_2)](BF_4)$ (**3**), respectively. All complexes have been characterized by X-ray crystallography as well as UV–Vis and IR spectroscopy.

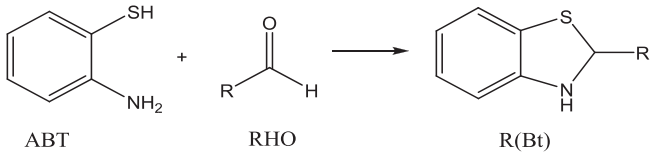
1. Introduction

Heterocyclic systems comprise a fundamental class of organic compounds that continue to be at the forefront of research efforts in catalysts, pharmaceuticals, and photoluminescence [1–3]. Thiazoline heterocyclic moieties have generated renewed interest over the last several years due to their use in organic synthesis [4] as well as in inorganic chemistry as precursors for imine containing ligands.

The synthesis of imine containing ligands can proceed via the condensation of an aldehyde and an amine. In general, these reactions result in formation of the Schiff base except in syntheses which utilize *o*-aminobenzenethiol (ABT) as the amine group. In these cases, it has been established that the condensation reaction results in the formation of the benzothiazoline moiety (Bt) (Scheme 1) [5–8].

The cyclization of the product has an intrinsic advantage because it serves to protect the thiol group from undergoing oxidation to the corresponding disulfide, and the ring easily opens in the presence of base to coordinate the imine nitrogen to a metal ion [9–14].

In our lab, analogous syntheses were carried out with 2-pyridinecarboxaldehyde and 2-thiophenecarboxaldehyde. As expected, we isolated the 2-(2-pyridyl)benzothiazoline (Py(Bt)) in very good yield however the reaction carried out with 2-thiophenecarboxaldehyde was problematic. The synthesis resulted in the formation of two products in approximate equimolar amounts. The first was



Scheme 1. Formation of benzothiazoline from ABT and an aldehyde.

* Corresponding author.
E-mail address: tylerl@union.edu (L.A. Tyler).

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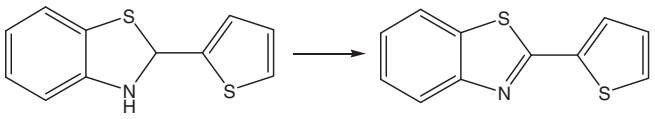

Scheme 2. Oxidation of Th(Bt) to form the corresponding benzothiazole Th(oBt).

identified as the expected product, 2-(2-thienyl)benzothiazoline (Th(Bt)) while the other product was determined to be 2-(2-thienyl)benzothiazole (Th(oBt)) in which the thiazoline ring underwent oxidation to form the corresponding thiazole (oBt) (Scheme 2).

A search of the literature revealed the oxidation of benzothiazoline to -thiazole can occur with several different oxidizing systems (MnO_2 in benzene, $BrCCl_3$/DBU) [15–17], however there is little mention of oxidation during synthesis. As a result, the findings from our lab were somewhat surprising given the fact that very similar syntheses for a variety of benzothiazoline derivatives have been previously reported. Additionally, there are very little ^{1}H NMR and IR data available which distinguish the benzothiazoline form of the molecules from the benzothiazole form. It was also noted that in some cases coordination reactions with the benzothiazolines were problematic and few complexes have been structurally characterized [17–23]. These difficulties could be a result of a mixture of the unoxidized and oxidized forms of the ligand being present in the reaction mixture.

These facts, along with the different outcomes of the ligand syntheses under similar reaction conditions in our lab, prompted us to synthesize and completely characterize a series of benzothiazoline analogs and their corresponding benzothiazole derivatives. In each case, the benzothiazoline moiety is identical and has been denoted (Bt) in the current study. The oxidized benzothiazole derivative of each analog has been denoted (oBt). The varying portion of the molecule (R) is derived from the starting material aldehyde. An acronym for each analog has been systematically assigned to each molecule using an abbreviated form of the starting aldehyde name followed by (Bt) or (oBt).

The analogs in this study are separated into two groups as shown in Fig. 1. Group (a) consists of those analogs which contain a heterocyclic R group and one benzothiazoline moiety; group (b) contains those analogs that have a heterocyclic R group and two benzothiazoline groups. Both groups contain heteroatoms which are most commonly used in metal coordination chemistry.

In addition, benzothiazoline containing molecules have been reported to exist as a mixture of the cyclized and imine forms. In order to extend these findings to the current study as well as to provide a spectral comparison of the free imine with the corresponding benzothiazoline and -thiazole analogs, the syntheses and characterizations of the un-cylclized Schiff base ligands (via the disulfide) bis-2-[(pyridin-2-ylmethylene)-imino]-benzenethiol disulfide $(PyIS)_2$ (Fig. 2, R = 2-pyridine) and bis-2-[(thiophen-2-ylmethylene)-imino]-benzenethiol disulfide $(ThIS)_2$ (Fig. 2, R = 2-thiophene) have been carried out.

Finally, in order to elucidate structural and spectroscopic characteristics of metal coordinated benzothiazole compared to Schiff base, coordination reactions of 2-(2-pyridyl)benzothiazoline (Py(Bt)) and 2-(2- pyridyl)benzothiazole ((Py(oBt)) with Cu and Co have been carried out. The results of these studies are presented here.

2. Experimental

2.1. Materials

2-Aminothiophenol 2-pyridinecarboxaldehyde, 2-furaldehyde, 2-thiophenecarboxaldehyde, and 2,5-thiophenedicarboxaldehyde, were purchased from Aldrich Chemical Co., and used without further purification. 2,6-pyridinedicarboxaldehyde was synthesized

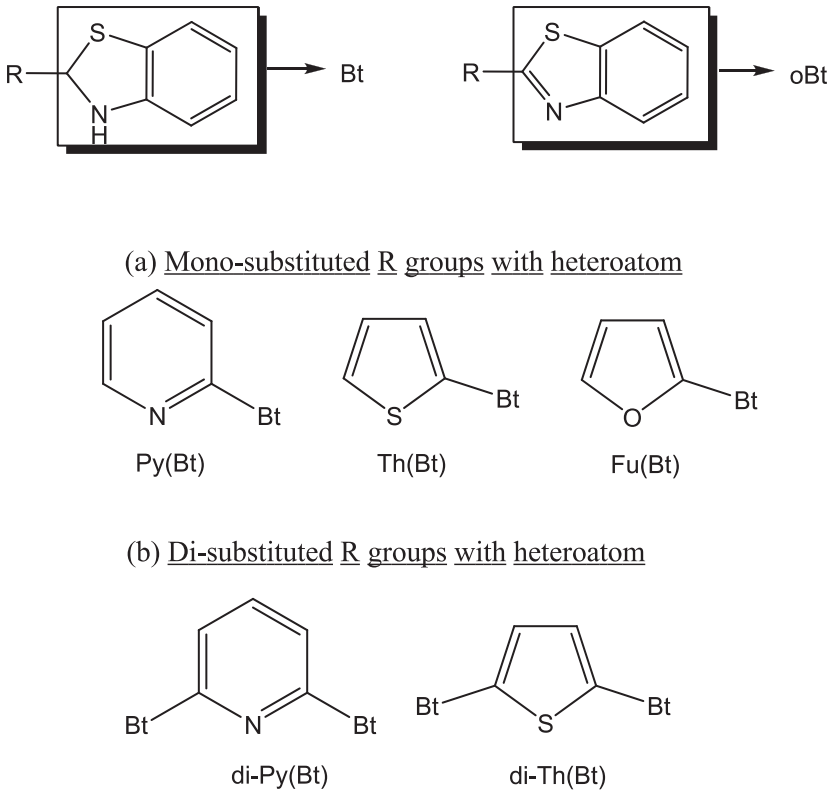

Fig. 1. Benzothiazoline analogs presented in this study and the designated acronym for each.

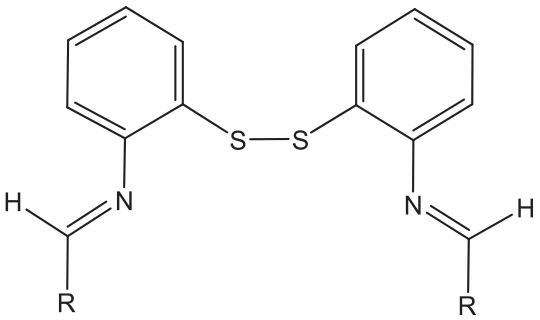

Fig. 2. Disulfide derivatives containing free imine group (R = 2-pyridine $(PyIS)_2$ or 2-thiophene $(ThIS)_2$).

following published procedures [24]. All solvents and chemicals were of reagent grade and used without further purification.

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. ^{1}H NMR spectra were recorded on a Varian 200 MHz spectrometer.

2.3. Preparation of analogs

2.3.1. Benzothiazoline derivatives

A similar method was used to prepare each benzothiazoline derivative; First 1 equiv of the aldehyde was dissolved in 20–25 mL of ethanol (EtOH). The solution was degassed and, under a N_2 atmosphere, 1 equiv of neat ABT was added to it (2 equiv were used for di-Py(Bt) and di-Th(Bt)). The reaction was then refluxed for 2 h and the solvent immediately removed in *vaccuo*. Upon reducing the volume of solvent, the thiazoline product precipitated from solution. When approximately 10 mL of solvent remained the solid was collected, washed with 5 mL of hexanes and dried under vacuum for 10 h. In the case of the furan derivative, Fu(Bt), the procedure resulted in the formation of an oil which formed a solid when triturated with diethyl ether (Et_2O). The solid was collected in a similar manner and dried under vacuum for 24 h. Yields for the ligands ranged from 40–80%. In all cases care was taken to minimize exposure to oxygen. A detailed procedure for Th(Bt) is given below followed by the spectroscopic characterization for each benzothiazoline analog.

Th(Bt). First, 0.75 mL (8.18 mmol) of 2-thiophenecarboxaldehyde was in dissolved 25 mL of EtOH and 0.88 mL (8.18 mmol) of ABT was added to it. The solution was refluxed for 2 h and then carefully placed under vacuum to slowly reduce the solvent. A light yellow powder began to form as the volume of solvent decreased. When ~10 mL of solvent remained, the solid was quickly collected on a Büchner funnel, washed with ~5 mL of hexane, and immediately dried under high vacuum for 10 h. Yield: 1.36 g (76%). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 4.51 (s, 1H, NH), 6.63 (s, 1H), 6.69 (d, 1H), 6.80 (t, 1H), 6.95 (m, 2H), 7.06 (t, 1H), 7.12 (t, 1H), 7.30 (d, 1H). Selected IR bands: (cm^{-1}) 1583 (m, $\nu_{N=C}$), 1458 (s), 1310 (m), 702 (s).

Py(Bt). Light yellow solid. Yield: 82%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 5.07 (s, 1H, NH), 6.41 (s, 1H), 6.82 (m, 2H), 6.80 (t, 1H), 7.03 (m, 2H), 7.23 (m, 1H), 7.59 (d, 1H), 7.71 (t, 1H), 8.56 (d, 1H). Selected IR bands: (cm^{-1}) 1578 (m), 1468 (s), 1435 (s), 1073 (m), 746(s).

Fu(Bt). Beige solid. Yield: 40%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 4.43 (s, 1H, NH), 6.35 (m, 3H), 6.7 2 (d, 1H), 6.80 (t, 1H), 6.97 (t, 1H), 7.10 (d, 1H), 7.41 (d, 1H). Selected IR bands: (cm^{-1}) 1579 (m), 1458 (m), 1009 (m), 731(s).

di-Py(Bt). Light yellow solid. Yield: 78%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 4.99 (s, 2H, NH), 6.33 (d, 2H), 6.78 (t, 4H), 6.97 (m, 4H), 7.48 (d, 2H), 7.71 (t, 1H). Selected IR bands: (cm^{-1}) 1582 (m), 1474 (s) 1320 (s), 1262 (m), 976 (m), 743 (s).

di-Th(Bt). Beige solid. Yield: 65%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 4.46 (s, 2H, NH), 6.51 (d, 2H), 6.65 (d, 2H), 6.77 (t, 2H), 6.93 (m, 4H), 7.04 (d, 2H). Selected IR bands: (cm^{-1}) 1579 (w), 1471 (s), 1457 (s), 1326 (m), 1250 (m), 1037 (m), 741(s).

2.3.2. Thiazole derivatives

The complete oxidation of the benzothiazoline derivatives was accomplished by vigorously stirring a chloroform solution of each at room temperature in an open flask for ~5 h. The solvent was then removed via rotary evaporation and the residue dried under high vacuum for 10 h. Quantitative yields. A detailed procedure for Th(oBt) is given below followed by the spectroscopic characterization for each benzothiazole analog.

Th(oBt). A batch of 500 mg (2.28 mmol) of Th(Bt) was dissolved in 40 mL $CHCl_3$ and stirred. After 5 h, the solvent was removed via rotary evaporation and the brown-yellow solid dried under high vacuum. Yield: 495 mg (100%). ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 7.15 (d, 1H), 7.45 (m, 3H), 7.67 (d, 1H), 7.86 (d, 1H), 8.04 (d, 1H). Selected IR bands: (cm^{-1}) 1590 (w), 1542 (m), 1478 (m), 1434 (s), 1417 (s), 1311 (m), 911 (m), 695 (s).

Py(oBt). Yellow solid. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 7.42 (m, 3H), 7.85 (t, 1H), 7.97 (d, 1H), 8.11 (d, 1H), 8.38 (d, 1H), 8.71 (d, 1H). Selected IR bands: (cm^{-1}) 1585 (m), 1456 (m), 1433 (s), 1317 (m), 996 (m), 980 (s), 739 (s).

Fu(oBt). Beige solid. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 6.61 (m, 1H), 7.21 (d, 1H), 7.46 (m, 2H), 7.62 (d, 1H), 7.90 (d, 1H), 8.06 (d, 1H). Selected IR bands: (cm^{-1}) 1579 (w), 1502 (s), 1433 (m) 1171 (s), 1312 (m), 1244 (s), 1009 (s), 895 (s), 743 (s), 730 (s).

di-Py(oBt). Light yellow solid. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 7.50 (m, 4H), 8.07 (m, 5H), 8.47 (d, 2H). Selected IR bands: (cm^{-1}) 1565 (m), 1447 (m), 1319 (m), 974 (m), 816 (m), 719 (s).

di-Th(oBt). Beige solid: ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 7.46 (m, 4H), 7.69 (s, 2H), 7.89 (d, 2H), 8.08 (d, 2H). Selected IR bands: (cm^{-1}) 1547 (m), 1429 (s), 1312 (s), 1237 (s), 896 (m), 759 (s), 724 (s).

2.3.3. Disulfide derivatives

The syntheses of $(ThIS)_2$ and $(PyIS)_2$ are analogous and were each carried out in a two step process. First, bis-aminothiophenol disulfide was prepared following published procedure [25]. Next, a batch of the disulfide, (2 equiv, ~2 mmol scale) was dissolved in a minimum amount of EtOH and was then added to one equiv of the corresponding aldehyde dissolved in ~25 mL of EtOH (2-pyridinecarboxaldehyde for $(PyIS)_2$, 2-thiophenecarboxaldehyde for $(ThIS)_2$). The reaction was refluxed for 1.5 h resulting in the formation of a precipitate. The solid was collected on a Büchner funnel and dried under high vacuum for 8 h.

$(PyIS)_2$. Light yellow solid. Yield: 85%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 7.21 (m, 6H), 7.40 (m, 2H), 7.68 (m, 2H), 7.85 (t, 2H), 8.39 (d, 2H), 8.67 (s, 2H, imine), 8.73 (d, 2H). Selected IR bands: (cm^{-1}) 1611 (s, $\nu_{N=C}$), 1581 (m), 1469 (m), 1443 (m), 1298 (m), 743(s, ν_{SS}).

$(ThIS)_2$. Slow evaporation of an ethanolic solution of $(ThIS)_2$ resulted in the formation of yellow microcrystalline $(ThIS)_2$. Yield: 40%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C, δ from TMS): 7.15 (m, 8H), 7.51 (t, 4H), 7.66 (d, 2H), 8.57 (s, 2H, imine-H). Selected IR bands: (cm^{-1}) 1604 (s, $\nu_{N=C}$), 1563 (m), 1421 (s), 1036 (m), 722 (s, ν_{SS}).

2.4. Preparation of metal complexes

2.4.1. Synthesis of [Cu(PyAS)(OAc)]$_2$·CH$_3$OH (**1**·CH$_3$OH)

First, 245 mg (1.15 mmol) of Py(Bt) was dissolved in 20 mL of CH_3OH. Separately, 458 mg (2.30 mmol) of $Cu(OAc)_2{\cdot}1H_2O$ was dissolved in 20 mL of CH_3OH. Upon addition of the metal salt to the ligand solution a deep purple color developed. The solution was stirred for 1 h and gravity filtered. Slow diffusion of Et_2O into the solution over 12 h resulted in the formation of dark purple crystals of 1. Yield: 0.31 g (40%). Selected IR bands: (cm^{-1}) 1580 (s, $\nu_{N=C}$), 1473 (m), 1380 (s), 1327 (s), 1019 (w), 760 (s).

2.4.2. Synthesis of [Co(Py(oBt))$_2$Cl$_2$]·THF (**2**·THF)

A batch of 250 mg (1.18 mmol) of Py(oBt) was suspended in 20 mL of CH_3OH. Next, 140 mg (0.59 mmol) of $CoCl_2{\cdot}6H_2O$ was dissolved in 15 mL of CH_3OH and was added to the Py(oBt) suspension. The resulting mixture was stirred for 1.5 h until a homogeneous orange solution appeared. The solution was then gravity filtered and the solvent removed via rotary evaporation. The olive green residue was then dissolved in 40 mL of CH_3CN and the solution was filtered to isolate **2** as an orange powder. Yield: 0.15 g (41%). Selected IR bands: (cm^{-1}) 1601 (m, $\nu_{N=C}$), 1492 (m), 771 (s). Electronic absorption spectrum in CH_3OH: λ_{max} (nm) (ε, M^{-1} cm^{-1}) 346 (1956).

2.4.3. Synthesis of [Cu(Py(oBt))$_2$H$_2$O](BF$_4$)$_2$ (**3**)

A similar synthetic procedure as that described for complex **2** was used to obtain complex **3**. First, 281 mg (1.32 mmol) of Py(oBt) was suspended in 20 mL of CH_3OH and 157 mg (0.66 mmol) of $Cu(BF_4)_2{\cdot}xH_2O$ dissolved in 15 mL of CH_3OH was added to it. The solution was stirred for 8 h and then gravity filtered. Slow diffusion of Et_2O into the methanolic solution resulted in the formation of light green crystalline **3** within 4 h. Yield: 0.24 g (56%). Selected IR bands: (cm^{-1}) 1608 (m, $\nu_{N=C}$), 1497 (s), 1029 (s, ν_{BF}), 785 (s). Electronic absorption spectrum in CH_3OH: λ_{max} (nm) (ε, M^{-1} cm^{-1}) 356 (4595), 433 (203).

2.5. X-ray data collection and structure solution and refinement

Crystals suitable for X-ray analysis were obtained using the following procedures: Slow evaporation of an ethanolic solution of $(ThIS)_2$ yielded yellow needles after 24 h. Purple plates of [Cu(PyAS)(OAc)]$_2$·CH$_3$OH (**1**·CH$_3$OH) and green plates of [Cu(Py(oBt))$_2$OH$_2$](BF$_4$)$_2$ (**3**) were obtained by slow diffusion of Et_2O into separate solutions of **1** and **3** dissolved in methanol. Orange blocks of [Co(Py(oBt))$_2$Cl$_2$]·THF (**2**·THF) were obtained by slow diffusion of THF into an acetonitrile solution of **2**. X-ray diffraction data were collected on a Bruker APEX 2 CCD platform diffractometer (Mo Kα (λ = 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) [26]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were included in calculated positions and were refined using a riding model. Crystal data and refinement details are presented in Table 1 for all complexes while selected bond distances and angles are listed in Table 2 and Table 3, respectively. All crystallographic data for $(ThIS)_2$ has been submitted as supplementary material.

3. Results and discussion

3.1. Synthesis and characterization of benzothiazoline, -thiazole and disulfide analogs

Although the mono- [13,18,21,22] and di-benzothiazoline [27–29] analogs in the current study have been previously reported, much of the spectroscopic characterization is incomplete and ^{1}H NMR data is mostly unavailable. The lack of data could be the result of oxidation products forming in tandem with the desired product complicating the analyses. In the current study, we found that all analogs could be prepared without benzothiazole formation however precautions to exclude air during the syntheses were essential. We also aimed to include a pyrrole analog starting with pyrrole-2-carboxaldehyde but all attempts to obtain the pure product were unsuccessful. The oxidized benzothiazole products were obtained by vigorously stirring the benzothiazoline derivatives in air over a 2–5 h period. This process was complete in ~1 h with heat however the longer stirring time resulted in consistently pure product. Interestingly, the analogs differ in their

Table 1
Summary of crystal data and intensity collection and structure refinement parameters for complexes.

	[Cu(PyAS)(OAc)]$_2$·CH$_3$OH (**1**·CH$_3$OH)	[Co(PyBt)$_2$Cl$_2$]·THF (**2**·THF)	[Cu(Py(oBt))$_2$H$_2$O](BF$_4$)$_2$·(**3**)
Empirical formula	$C_{29}H_{28}Cu_2N_4O_5S_2$	$C_{28}H_{24}Cl_2CoN_4OS_2$	$C_{24}H_{18}B_2CuF_8N_4OS_2$
Molecular weight	703.75	626.46	679.70
Crystal color, habit	purple, plate	orange, block	green, plate
Crystal size (mm)	0.24 x 0.17 x 0.05	0.24 x 0.19 x 0.17	0.28 x 0.25 x 0.18
Temperature (K)	125(2)	125(2)	125(2)
Crystal system	monoclinic	monoclinic	tetragonal
Space group	*C*2/*c*	*C*2/*c*	$I4_1cd$
Unit cell dimensions			
a (Å)	24.574(6)	18.2218(12)	14.5775(4)
b (Å)	9.327(2)	14.5762(9)	14.5775(4)
c (Å)	13.086(3)	13.0337(8)	25.0238(16)
α (°)	90	90	90
β (°)	105.131(3)	117.4180(10)	90
γ (°)	90	90	90
V (Å^3), *Z*	2895.3(1), 4	3072.9(3), 4	5317.6(4), 8
D_{calc} (mg m^{-3})	1.614	1.354	1.698
Absorption coefficient (μ, mm^{-1})	1.660	0.895	1.063
Φ range collected (deg.)	1.72–27.48	1.88–30.46	2.56–30.31
Completeness to Φ max (%)	99.9	94.9	97.1
Reflns collected/unique ($R_{(int)}$)	17203/3300 (0.0566)	21330/4436 (0.0282)	34489/3826 (0.0312)
Data/restraints/parameters	3300/0/196	4436/0/150	3826/7/229
R_1, $wR_2(I > 2\sigma I)$	0.0391, 0.0866	0.0278, 0.0713	0.0414, 0.1011
R_1, wR_2(all data)	0.0709, 0.1004	0.0324, 0.0728	0.0606, 0.1154
Goodness of fit on F^2	1.085	1.075	1.065
Largest diff peak/hole (e Å^3)	1.208, −0.435	0.334, −0.323	0.741, −0.330

Table 2
Selected bond distances (Å) for metal complexes.

*[Cu(PyAS)(OAc)]$_2$·CH$_3$OH (**1**·CH$_3$OH)*			
Cu–N(1)	1.981(3)	Cu–N(2)	2.042(3)
Cu–S(0A)	2.278(1)	Cu–S(1)	2.792(1)
Cu–O(1)	1.928(2)	N(1)–C(6)	1.286(4)
O(1)–C(13)	1.274(4)	O(2)–C(13)	1.241(4)
*[Co(Py(oBt)$_2$Cl$_2$]·THF (**2**·THF)*			
Co–N(1)	2.1510(1)	N(2)–C(6)	1.3062(2)
Co–N(2)	2.1830(1)	C(6)–C(5)	1.4652(2)
Co–Cl(1)	2.4082(3)	C(5)–C(4)	1.3841(2)
*[Cu(Py(oBt))$_2$H$_2$O](BF$_4$)$_2$·(**3**)*			
Cu–N(1)	2.063(1)	Cu–N(2)	1.970(2)
Cu–N(1A)	2. 063(1)	Cu–N(2A)	1.970(2)
Cu–O(1)	2.126(4)	N(2)–C(6)	1.315(4)
C(6)–C(5)	1.448(5)	C(5)–C(4)	1.386(5)

Table 3
Selected bond angles (°) for metal complexes.

*[Cu(PyAS)(OAc)]$_2$·CH$_3$OH (**1**·CH$_3$OH)*			
O(1)–Cu–N(1)	169.39(9)	O(1)–Cu–N(2)	95.57(9)
N(1)–Cu–N(2)	80.93(11)	O(1)–Cu–S	5.97(8)
N(1)–Cu–S	86.38(8)	N(1)–Cu–S(OA)	98.59(7)
N(2)–Cu–S	66.25(8)	N(2)–Cu–S(OA)	91.67(7)
O(1)–Cu–S(OA)	91.50(7)	S–Cu–S(OA)	95.47(3)
Cu–S–Cu(A)	84.53(3)	C(12)–S–Cu	97.38(11)
*[Co(Py(oBt)$_2$Cl$_2$]·THF (**2**·THF)*			
N(1)–Co–N(1A)	177.62(5)	N(1)–Co–N(2)	76.32(4)
N(2)–Co–N(2A)	87.53(5)	N(2)–Co–Cl	168.02(3)
Cl–Co–Cl(A)	97.496(2)	N(1)–Co–N(2A)	101.92(4)
*[Cu(Py(oBt))$_2$H$_2$O](BF$_4$)$_2$·(**3**)*			
N(2)–Cu–N(2A)	172.34(2)	N(2)–Cu–N(1A)	102.11(2)
N(2)–Cu–O	86.17(9)	N(2)–Cu–N(1)	81.17(11)
N(1)–Cu–N(1A)	130.04(2)	N(1)–Cu–O 114.98(9)	114.98(9)

susceptibility towards oxidation; we found the pyridine derivative quite resistant while the thiophene and furan analogs were much more susceptible toward oxidation. It was also found that once the pure benzothiazoline solid had been isolated, they too oxidized albeit slower than in solution. This suggests that if these types of ligands are to be used to obtain imine coordination in inorganic syntheses, they should be freshly prepared or kept under an inert atmosphere.

There is little difference noted between the IR spectra of the benzothiazoline and the corresponding thiazole derivative and there is no strong frequency that can be attributed to the thiazole $\nu_{N=C}$. On the contrary, the IR spectra of $(ThIS)_2$ and $(PyIS)_2$ clearly show strong bands that are assigned the imine $\nu_{N=C}$ at 1611 and 1604 cm^{-1}, respectively.

The molecular formula of the benzothiazoline and -thiazole forms of the molecule differ by two hydrogen atoms however there are other prominent features present in the ^{1}H NMR ($CDCl_3$) spectra that can be used to distinguish the two forms. First, the –NH of the benzothiazoline group resonates between ~4.4 and 5.1 ppm as confirmed by the D_2O exchange reaction. Because this peak can often times be broad, a more definite distinction is identification of the thiazoline CH. This hydrogen is found as a singlet between 6.3 and 6.7 ppm. The resonances for the NH and thiazoline CH atoms for each analog are listed in Table 1. An additional feature of the ^{1}H NMR spectrum of the benzothiazole compared to the benzothiazoline is a downfield shift in the ring resonances for the benzothiazole analogs with all peaks appearing above 7 ppm (the only exception to this is Fu(oBt) which contains one resonance below 7 ppm). This shift is most likely the result of the conjugation of the two ring systems upon oxidation.

An earlier study identified three possible stereoisomers for di-Th(Bt) arising from the two chiral thiazoline carbon atoms and reported that the ^{1}H NMR spectrum contained a 1:1 mixture of two of the three isomers [29]. In the current study, we see no such separation of stereoisomers in the ^{1}H NMR spectrum, and the previous observations may be attributed to both the -thiazoline and -thiazole forms being present. Additionally, it has been postulated that in solution, the benzothiazoline is in equilibrium with the open, imine form of the molecule [30,31]. In the current study, no imine ligand was detected by ^{1}H NMR in $CDCl_3$, CD_3OH or d_6-DMSO. To further clarify this point, as well as to provide a basis for spectroscopic comparison between the free (un-cyclized) and ligated imine, we synthesized $(PyIS)_2$ and $(ThIS)_2$. These two analogs were prepared using the disulfide of ABT and then reacting it with either 2-pyridinecarboxaldehyde or 2-thiophenecarboxaldehyde ($(PyIS)_2$ and $(ThIS)_2$, respectively). Cyclization to the corresponding benzothiazoline is therefore prohibited and the 'open' forms of Py(Bt) and Th(Bt) which contain the Schiff base nitrogen are obtained. The imine hydrogen in $(PyIS)_2$ and $(ThIS)_2$ is noted as a singlet at 8.67 and 8.57 ppm respectively ($CDCl_3$), and is not present in the ^{1}H NMR spectrum of Py(Bt) or Th(Bt).

The ^{1}H NMR spectra of Py(Bt), Py(oBt) and $(PyIS)_2$ are shown in Fig. 3.

3.2. Synthesis, characterization and structure of complexes

The synthesis and isolation of the Cu and Co complexes of Py(oBt) were relatively straight forward. The cobalt chloride salt yielded complex **2** in which both chloride ions and two Py(oBt) ligand frames bond to the metal center. Analogous reactions were carried out with copper chloride however no pure product could be isolated from these attempts. A change to the hydrated BF_4^- salt resulted in isolation of **3** which contains two Py(oBt) ligand frames and one water in the coordination sphere. The IR spectra of **2** and **3** both have a medium intensity band ~1600 cm^{-1} that is assigned to the thiazole $\nu_{N=C}$.

Mascharak and coworkers previously reported the Co(III) complex of Py(Bt) [11]. This reaction was carried out in DMF using NaH as base and $[Co(NH_3)_5Cl]Cl_2$ as the starting metal salt and yielded $[Co(PyAS)_2]Cl$ with a 2:1 metal to ligand ratio (Note: the un-cyclized ligand *N*-2-mercaptophenyl-2′-pyridylmethyl-enimine is denoted PyASH where $PyAS^-$ is the deprotonated form of the ligand). The synthesis of the analogous Cu complex utilized $Cu(OAc)_2·H_2O$ with two equiv of Py(Bt) in CH_3OH. Unlike the Co complex, this reaction yielded the dimeric species **1** with a 1:1 ligand to metal ratio in a 40% yield (based on Cu). One acetate from the starting material serves to deprotonate the thiol while the other remains coordinated to the metal center in an end-on fashion. Interestingly, performing the reaction with one equivalent of Py(Bt) also yields **1** albeit with a much lower yield (19%). Upon dissolution of complex **1** in various solvents, a color change from purple to brown was noted. This color change is presumably due to the instability of the complex in solution. As a result, no UV–Vis data is reported. The IR spectrum for **1** exhibits the $\nu_{N=C}$ at 1580 cm^{-1} while in $[Co(PyAS)_2]Cl$ it was reported to appear at 1572 cm^{-1}. Both $\nu_{N=C}$ shift to lower energy by ~30 cm^{-1} compared to $(PyIS)_2$ as expected upon complexation [33].

For comparison purposes, complexation reactions with the furan and thiophene benzothiazoline and -thiazole analogs were also carried out with Co and Cu salts. These reactions were problematic and no pure product was isolated from these attempts. These results are most likely due to the poor ligating ability of O-furan and S-thiophene donor atoms to first row transition metals.

3.2.1. Structure of *[Cu(Py(Bt)(OAc)]$_2$·CH$_3$OH (**1**·CH$_3$OH)*

The dimeric structure of complex **1** is shown in Fig. 4. Each five coordinate Cu(II) center consists of an N_2S_2O coordination sphere comprised of one monodentate acetate ion and one $PyAS^-$ ligand

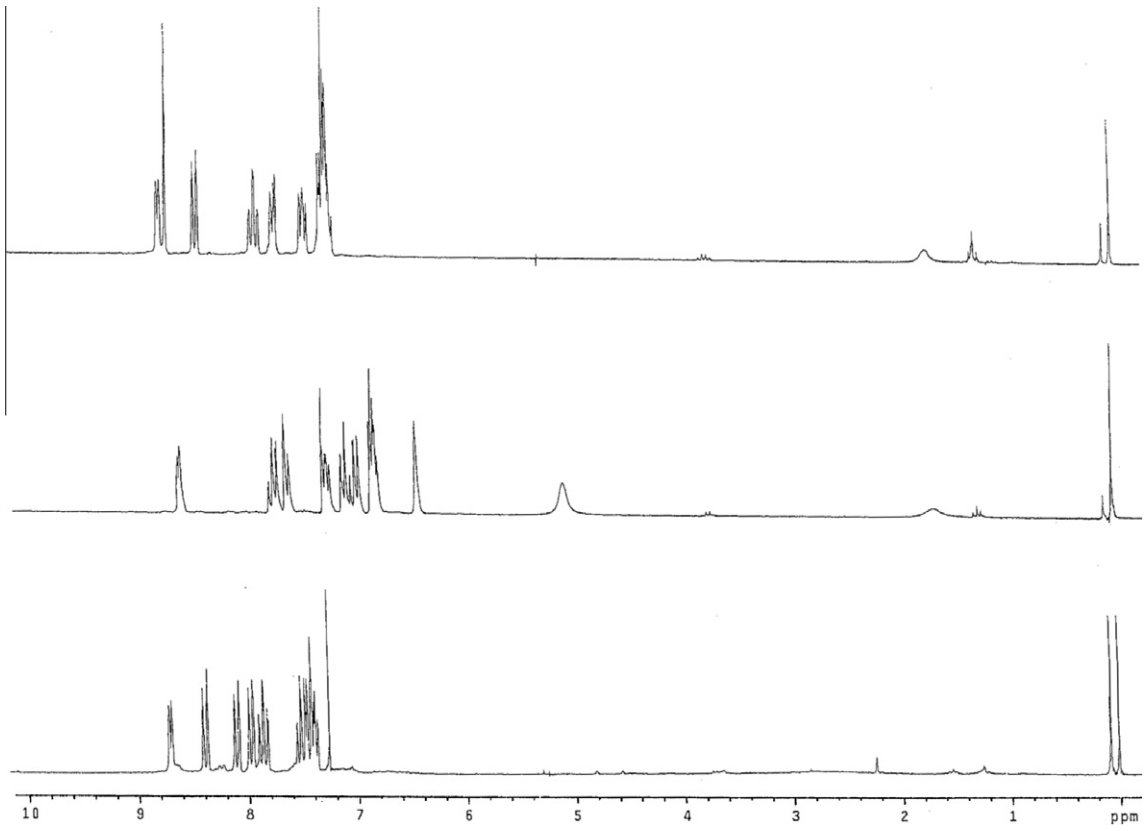

Fig. 3. ^{1}H NMR spectra (0–10 ppm) of Py(oBt) (bottom), Py(Bt) (middle) and $(PyIS)_2$ (top) in $CDCl_3$. The extra peak at ~0.07 ppm is attributed to silicon vacuum grease [32].

frame (NNS) with the thiolate from each ligand bridging to the other Cu. One CH_3OH of crystallization is also present. The Cu–N_{py} and Cu–N_{imine} bond lengths are 2.042(3) and 1.981(3) Å, respectively. The Cu–thiolate bond distances are 2.2777(1) Å for Cu–S and 2.791(1) Å Cu–S(0A). As expected the bridging Cu–S bond length is ~0.5 Å longer than the terminal Cu–S distance. The N(2)–Cu–S bond angle is 166.25(8) giving rise to an overall distorted trigonal bi-pyramid geometry around each Cu center. All distances are within the range of those observed for similar compounds [34,35].

3.2.2. Structure of $[Co(Py(oBt))_2Cl_2]\cdot THF$ (**2**·THF)

The structure of $[Co(Py(oBt))_2Cl_2]$ is shown in Fig. 5 without the THF of crystallization. The cobalt center contains two Cl^- ions ligated in a *cis* conformation and two bidentate Py(oBt) (N,N) ligand frames which give rise to a slightly distorted octahedral coordination sphere around the metal. The N_{py} atoms are oriented *trans* to each other while the $N_{thiazole}$ groups adopt a *cis* conformation. The bond lengths between the donor atoms in both ligand frames and the cobalt are identical for analogous bonds with the Co–N_{py} bond length measuring 2.1510(1) Å with the Co–$N_{thiazole}$ bond distances slightly longer at 2.1830(1) Å. These bond lengths are similar to previously reported Co(II)–N_{py} and Co(II)–N_{imine} distances [34,36]. The bite angle for the thiazole ligand is the same for each Py(oBt) unit with the N_{py}–Co–$N_{thiazole}$ angle measuring 76.32(4)°.

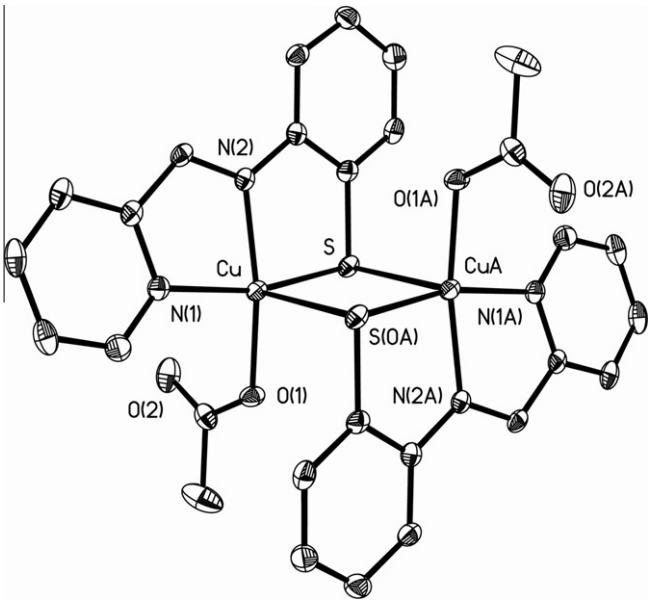

Fig. 4. Thermal ellipsoid plot (30% probability level) of complex **1** showing the numbering scheme. H atoms have been omitted for clarity.

3.2.3. Structure of $[Cu(Py(oBt))_2(H_2O)](BF_4)_2$ (**3**)

The structure of **3** is shown in Fig. 6. The Cu complex is comprised of two N,N coordinated Py(oBt) ligand frames and one water molecule which give rise to an overall distorted trigonal bi-pyramidal geometry around the metal center. The analogous metal–ligand bond lengths and ligand–metal–ligand bond angles are the same for both the Py(oBt) ligand frames bound to the copper. The Cu–N_{py} bond lengths and $N_{thiazole}$ bond lengths measure 2.063(3) and 1.970(2) Å, respectively. The Cu–O bond length is 2.126(4) Å while the N_{py}–Cu–$N_{thiazole}$ bite angle measures 81.17(1)°. All distances are within the range of previously reported Cu complexes containing N and O type donor atoms [34].

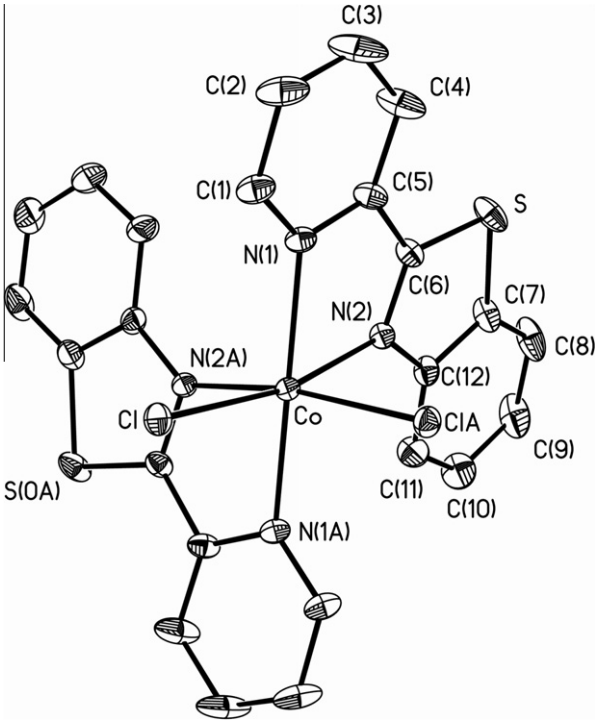

Fig. 5. Thermal ellipsoid plot (30% probability level) of complex **2** showing the numbering scheme. H atoms have been omitted for clarity.

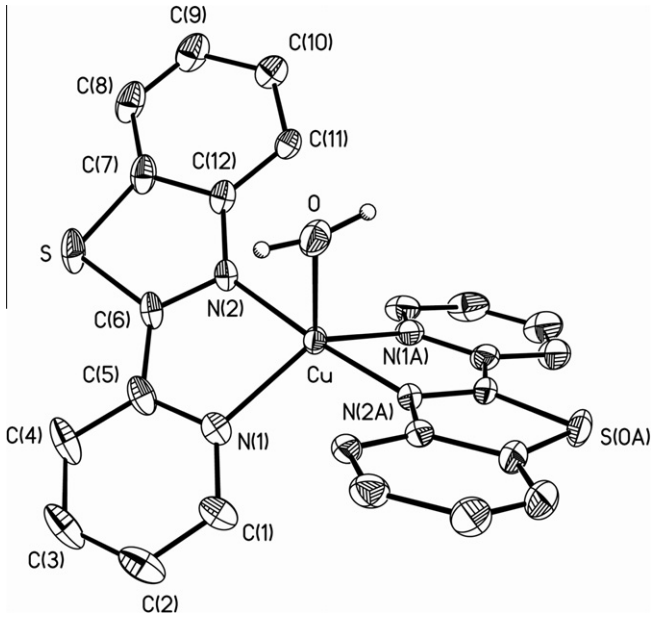

Fig. 6. Thermal ellipsoid plot (30% probability level) of complex **3** showing the numbering scheme. H atoms have been omitted for clarity.

A variety of first row transition metal complexes with the benzothiazoline ligands Th(Bt), Py(Bt) and Fu(Bt) have been reported. Characterization of these complexes included UV–Vis and IR spectroscopies as well as magnetic susceptibility measurements [22,23,29–31], but only limited structural information is available [11]. As such, complexes **1**–**3** provide a basis for comparison between coordinated imine ($PyAS^-$) and the corresponding ligated benzothiazole analogs (Py(oBt)). In addition to complexes **1**–**3**, the structure of $(ThIS)_2$ was also determined (submitted as supplementary material) and provides a direct correlation between free and coordinated imine.

Both complexes **1** and **3** contain a Cu(II) metal center in a distorted TBP geometry however the coordination spheres are comprised of N_2S_2O and N_4O, respectively. The $Cu–O_{OAc}$ in complex **1** is approximately 0.355(2) Å shorter than the $Cu–O_{H2O}$ in **3** which is attributed to the charge on the acetate ion. The $Cu–N_{py}$ bond lengths in complexes **1** and **3** are somewhat similar (1.981(3) and 2.063(1) Å, respectively), differing by ~0.08 Å. These bond lengths are also similar to the $Cu–N_{thiazole}$ distances. This suggests that the strength of $M–N_{thiazole}$ bonds is comparable to $M–N_{py}$ in these copper complexes. A similar direct comparison between $Co–N_{py}$ and $Co–N_{thiazole}$ in $[Co(PyAS)_2]BF_4$ and complex **2** is complicated by the fact that the two metal centers have different oxidation states. The $Co–N_{py}$ is approximately 0.17 Å shorter in $[Co(PyAS)_2]BF_4$ compared to the analogs $Co–N_{py}$ bond distance in **2** while the $Co–N_{imine}$ is ~0.28 Å longer than the $Co–N_{thiazole}$ length. The shorter bonds observed for $[Co(PyAS)_2]BF_4$ is most likely due to the +3 oxidation state of the metal center and the low spin configuration which leaves the d_{x2-y2} and d_{z2} orbital set empty.

Both the octahedral Co(II) and distorted trigonal bipyramid Cu(II) thiazole complexes (**2** and **3**, respectively) are expected to exhibit Jahn–Teller distortion. The distinction between the degeneracy in the higher energy orbital set (Cu(II)) versus the t_{2g} set (h.s. Co(II)) is expected to give rise to greater distortion in **3**. This is observed in the apparent differences between the $Cu–N_{py}$ and $Cu–N_{thiazole}$ bond lengths. These bond distances differ by only ~0.032 Å in the Co complex while there is approximately 0.167 Å difference between the $Cu–N_{thiazole}$ and $Cu–N_{py}$ lengths.

It is also noted that there is a slight lengthening of the N=C bond upon complexation to the metal center in complexes **1** and $[Co(PyAS)_2]Cl$ when compared to the structure of $(ThIS)_2$ which is in agreement with the shift of the $\nu_{N=C}$ in the IR spectrum to lower energy upon coordination of imine to a metal center.

4. Concluding remarks

This work describes the synthesis and characterization of benzothiazoline and -thiazole analogs. We have identified unique spectral features of each which include the –NH of the benzothiazoline group between ~4.4 and 5.1 ppm and the thiazoline hydrogen between 6.3 and 6.7 ppm in the ^1H NMR spectrum ($CDCl_3$). Additionally, comparison of the ^1H NMR spectra of $(PyIS)_2$ and $(ThIS)_2$ suggest that the free imine is not present in these solutions. Overall, there is clear indication that the benzothiazoline moiety is susceptible toward oxidation during synthesis as well as ambient conditions after isolation. Accordingly, care should be taken to avoid prolonged exposure to air when working with these types of ligands. Coordination reactions with Py(oBt) and Py(Bt) resulted in the isolation of complexes **1**–**3** and structural analyses suggest $N_{thiazole}$ binds to metal centers similar to pyridine type donors. Work on identifying key features responsible for the differences in the susceptibility toward oxidation (benzothiazoline to -thiazole) for the analogs is currently under way.

Acknowledgements

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Appendix A. Supplementary material

CCDC 784987, 784988, 784989 and 785391 contain the supplementary crystallographic data for $[Cu(Py(Bt)(OAc)]_2{\cdot}CH_3OH$ (**1**·CH_3OH), $[Co(Py(oBt))_2Cl_2]{\cdot}THF$ (**2**·THF), $[Cu(Py(oBt))_2(H_2O)]$-

$(BF_4)_2\cdot$(**3**) and $(ThIS)_2$, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre 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.2010.09.002.

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