Oxidation of heterocyclic thioureas to form benzothiazoles and their copper(II) complexes

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Abstract

N-2-(5-picolyl)-*N′*-methoxyphenylthioureas are oxidized in alkaline ethanol solution by copper(II) to 2-(5-picolylamino)-methoxybenzothiazoles and on air oxidation form [Cu(N,N)$_2$] complexes. Coordination is via the pyridine and thiazole nitrogen atoms. Structural studies show these four-coordinate complexes are closer to tetrahedral than planar and show structural differences based on the position of the methoxy group on the aryl group.
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1. Introduction

Heterocyclic thiosemicarbazones, including those formed from 2-formypyridine [1,2], 2-acetylpyridine [3,4], 2-benzoylpyridine [5], formylpyrazine [6], acetylpyrazine [7], and, most recently, 2-pyridine-formamide [8], have a rich copper(II) chemistry. In addition, there are a number of articles concerned with copper(II) complexes with bis(thiosemicarbazones) with two sulfur donor atoms [9–12]. No reduction of copper(II) is reported for thiosemicarbazones or bis(thiosemicarbazones). However, closely related heterocyclic thioureas are known to reduce copper(II) and form copper(I)

complexes [13,14]; others have reported isolation of copper(II) complexes [15]. Recently, it was reported that slow addition of *N*-(2-pyridyl)-*N′*-ben-zoylthiourea to a solution of copper(II) chloride led to a chloride bridged one-dimensional copper(II) polymer [16]. This polymer involves monodentate coordination of a ligand having a thiadiazole ring with the sulfur bonding to the pyridine nitrogen. Another report indicated that copper(II) ion polarizes the S–C bond of thiourea, thiosemicarbazide, and thiocarbohydrazide to an extent that electron transfer from the ligand to the metal occurs, with simultaneous decomposition of the ligand [17]. More recently, a dimeric copper(II) complex with the anion of 2-formylpyridine *N*(4)-methylthiosemicarbazone has been oxidized with bromate ion to form a coordinated 1,2,4-oxadiazole ring [18].

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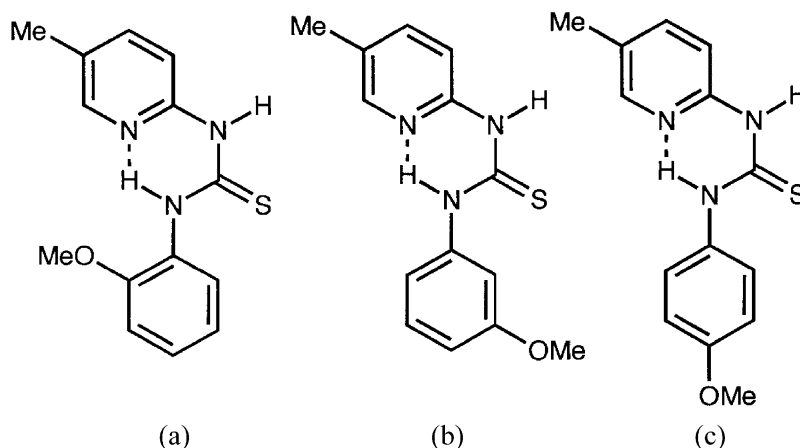*E-mail address:* westdx@hotmail.com (D.X. West).

Fig. 1. (a) *N*-2-(5-picolyl)-*N'*-2-methoxy-, (b) *N*-2-(5-picolyl)-*N'*-3-methoxy-, and (c) *N*-2-(5-picolyl)-*N'*-4-methoxyphenylthiourea.

The oxidative cyclization of arylthioureas (Hugershoff synthesis) can be used to prepare 2-aminobenzothiazoles [19], but *N*-heteroaryl-*N'*-arylthioureas may also produce 1,2,4-thiadiazoles [20]. Use of *N*-bromosuccinamide in H_2SO_4 to oxidize *N*-(2-pyridyl)-*N'*-phenylthiourea produces 2-(2-pyridyl)benzothiazole [21]. We report here our studies of the reaction of copper(II) acetate with *N*-2-(5-picolyl)-*N'*-(2-methoxyphenyl)-, *N*-2-(5-picolyl)-*N'*-(3-methoxyphenyl)- and *N*-2-(5-picolyl)-*N'*-(4-methoxyphenyl)thiourea, 5PicTu2OMePh, 5PicTu3OMePh, and 5PicTu4OMePh, respectively, Fig. 1. The ligands in the copper(II) complexes have been converted to substituted benzothiazole monoanions, 5PicTz2OMePh, 5PicTz3OMePh, and 5PicTz4OMePh.

2. Experimental

The thioureas were prepared by warming an equimolar (0.01 mol) mixture of 2-amino-5-picoline (Aldrich) with either 2-, 3-, or 4-methoxyphenyl isothiocyanate (Aldrich) in 30 ml of 95% ethanol. On slow cooling and reducing the volume, white crystals of 5PicTu2OMePh, 5PicTu3OMePh, and 5PicTu4OMePh formed [22–24]. Copper(II) complexes were prepared by slowly adding copper(II) acetate hydrate (0.002 mol) to an ethanol slurry of 5PicTu2OMePh, 5PicTu3OMePh, or 5PicTu4OMePh (0.004 mol). The resulting solutions were refluxed for ca. 3 h and then stirred overnight at room temperature. On reduction of

the volume the resulting green solids were filtered in vacuo, washed with isopropanol followed by diethyl ether to apparent dryness.

Crystals of [Cu(5PicTz2OMePh)$_2$], **1**, [Cu(5PicTz3OMePh)$_2$], **2**, and [Cu(5PicTz4OMePh)$_2$], **3**, were grown by slow evaporation of 1:1 by volume mixtures of methanol and acetonitrile and mounted on glass fibers on a Nonius MACH3 Four Circle (i.e. **1**) and a Nonius Kappa CCD (**2** and **3**) Diffractometers. The structures were solved by direct methods [25] and missing atoms were found by difference-Fourier synthesis. The non-hydrogen atoms were refined with anisotropic temperature factors and all hydrogens attached to nitrogens and aromatic CHs for **1** and **3** were found on a difference Fourier map. The aromatic hydrogens of **2** and the methyl hydrogens were allowed to ride on their carbons and assigned fixed isotropic temperature factors, $U = 1.2$ times U of the aromatic carbon atoms and 1.5 times U of the methyl carbon atoms. Scattering factors are from Wassmaier and Kirfel [26], structure refinement by SHELXL-97 [27] and graphics are Zortep [28]. Table 1 summarizes the crystal data, collection information and refinement data for **1**, **2**, and **3**.

3. Results and discussion

The bond distances for **1**, **2**, and **3** are listed in Table 2 and their bond angles in Table 3. Table 4 lists the mean plane data and angles between planes.

Table 1

Crystal data and structure refinement for [Cu(5PicTz2OMePh)$_2$], **1**, [Cu(5PicTz3OMePh)$_2$], **2**, and [Cu(5PicTz4OMePh)$_2$], **3**

Compound	**1**	**2**	**3**
Empirical formula	C$_{28}$H$_{24}$CuN$_6$O$_2$S$_2$	C$_{28}$H$_{24}$CuN$_6$O$_2$S$_2$	C$_{28}$H$_{24}$CuN$_6$O$_2$S$_2$
Color; habit	Olive green, prism	Green, needle	Red brown; prism
Crystal size (mm^3)	0.20 × 0.17 × 0.15	0.29 × 0.05 × 0.02	0.27 × 0.19 × 0.10
Temperature	293(2)	130(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2/c(#15)	C2/c(#15)	C2/c(#15)
Unit cell dimensions			
a (Å)	13.691(3)	17.699(3)	17.530(2)
b (Å)	13.841(4)	12.8090(19)	12.8470(14)
c (Å)	14.743(4)	11.699(4)	12.1630(7)
β (°)	95.71(2)	94.937(10)	106.355(6)
Volume (Å^3)	2779.9(13)	2642.4(10)	2628.4(4)
Z	4	4	4
Formula weight	604.2	604.2	604.2
Density(calc.) (mg/m^3)	1.448	1.519	1.527
Absorption coefficient (mm^{-1})	0.973	1.024	1.029
F(000)	1244	1244	1244
θ range, data collection (°)	2.09–27.41	3.18–22.46	1.99–24.55
Index ranges	$0 \leq h \leq 17$, $0 \leq k \leq 17$, $-19 \leq 1 \leq 19$	$-18 \leq h \leq 18$, $-13 \leq k \leq 13$, $-12 \leq l \leq 12$	$-20 \leq h \leq 20$, $-14 \leq k \leq 15$, $-12 \leq l \leq 12$
Total reflections/parameters	3806/204	3120/204	2095/204
Unique reflections	2628 ($R_{int} = 0.0000$)	1804 ($R_{int} = 0.1260$)	1473 ($R_{int} = 0.0366$)
Absorption correction	ψ-scan	HKL-Scalepack	HKL-Scalepack
Maximum/minimum transmission	0.8443/0.7859	0.9798/0.7556	0.9041/0.7545
Refinement method (F^2)	Full-matrix least-squares	Full-matrix least-squares	Full-matrix least-squares
Final R indices [$I > 2.0\sigma(I)$]	$R = 0.0293$, $wR = 0.0760$	$R = 0.0630$, $wR = 0.1130$	$R = 0.0363$, $wR = 0.0793$
R indices (all data)	$R = 0.0392$, $wR = 0.0885$	$R = 0.1460$, $wR = 0.1385$	$R = 0.0641$, $wR = 0.0871$
Goodness-of-fit on F^2	1.097	1.002	1.011
Lgst diff. peak/hole (e Å^{-3})	0.313/ − 0.273	0.490/ − 0.572	0.254/ − 0.315

Table 5 contains the data for the hydrogen bonding interactions. Figs. 2–4 show perspective views of **1**, **2**, and **3**.

The Cu center in each complex is positioned on a two-fold symmetry axis, and the two ligands in the three complexes are equivalent. The Cu1–N3 bond distance is shorter than the Cu1–N1 bond distance, but these two bonds are significantly different in the three complexes. The difference in these two bond distances is greatest for **1**, 0.163(2) Å, followed by **2**, 0.048(6) Å, and **3** has the smallest difference, 0.033(2) Å; Cu1–N1 decreases in this order and Cu1–N3 increases. However, the bond distances within the ligands in the three complexes are not significantly different, except that the distance of O1 from the phenyl ring in **2** is marginally longer.

Table 2

Selected bond distances (Å) for [Cu(5PicTz2OMePh)$_2$], **1**, [Cu(5PicTz3OMePh)$_2$], **2**, [Cu(5PicTz4OMePh)$_2$], **3**

Bond	**1**	**2**	**3**
Cu1–N1	2.0717(16)	1.972(6)	1.969(2)
Cu1–N3	1.9085(16)	1.924(6)	1.936(2)
N1–C2	1.353(3)	1.358(9)	1.361(3)
C2–N2	1.376(3)	1.379(9)	1.366(4)
N2–C7	1.302(3)	1.298(9)	1.312(4)
C7–N3	1.345(3)	1.343(10)	1.344(3)
C7–S1	1.782(2)	1.772(8)	1.772(3)
N3–C8	1.397(2)	1.409(9)	1.389(4)
S1–C13	1.740(2)	1.750(8)	1.736(3)
C8–C9	1.393(3)	1.407(11)	1.394(4)
C9–O1	1.365(2)	1.397(9) (C10–O1)	1.375(4) (C11–O1)
C8–C13	1.398(3)	1.390(10)	1.395(4)

Table 3
Selected bond angles (°) for [Cu(5PicTz2OMePh)$_2$], **1**, [Cu(5PicTz3OMePh)$_2$], **2**, and [Cu(5PicTz4OMePh)$_2$], **3**

Angle	**1**	**2**	**3**
N1–Cu1–N1′	113.69(9)	106.6(3)	101.41(14)
N1–Cu1–N3	90.95(7)	92.6(3)	93.04(10)
N1–Cu1–N3′	100.89(7)	135.6(2)	135.99(10)
N3–Cu1–N3′	158.34(10)	101.2(4)	104.87(13)
C6–N1–Cu1	118.58(13)	116.4(5)	116.13(19)
C2–N1–Cu1	123.23(13)	123.9(5)	124.7(2)
C7–N3–Cu1	122.80(14)	122.5(5)	121.6(2)
C8–N3–Cu1	123.43(13)	124.8(5)	126.05(17)
C6–N1–C2	117.84(17)	119.4(6)	118.8(3)
N1–C2–N2	124.60(18)	125.2(5)	124.6(3)
N1–C2–C3	119.3(2)	119.8(7)	118.5(3)
N2–C2–C3	116.1(2)	114.9(7)	116.9(3)
C2–N2–C7	123.70(17)	123.5(7)	123.7(2)
N2–C7–N3	132.06(18)	130.7(7)	131.8(3)
N2–C7–S1	115.82(15)	116.9(6)	116.0(2)
N3–C7–S1	112.12(15)	112.4(6)	112.2(2)
C7–N3–C8	112.35(16)	111.8(7)	112.4(2)
C7–S1–C13	90.63(10)	91.0(4)	90.60(14)
N3–C8–C9	124.75(17)	123.1(7)	126.6(3)
N3–C8–C13	115.24(18)	115.8(7)	115.2(3)
C9–C8–C13	119.90(18)	121.0(7)	118.2(3)
C8–C9–O1	114.69(17)	122.0(8)(C9–C10–O1)	114.2(3)(C10–C11–O1)
C10–C9–O1	126.1(2)	116.8(8)(C11–C10–O1)	125.6(3)(C12–C11–O1)
C8–C13–S1	109.65(15)	108.9(6)	109.7(2)
C12–C13–S1	129.25(18)	130.2(7)	128.2(2)
C9–O1–C15	118.71(19)	116.6(6)(C10–O1–C15)	118.8(3)(C11–O1–C15)

Table 4
Mean plane deviations and angles between planes for [Cu(5PicTz2OMePh)$_2$], **1**, [Cu(5PicTz3OMePh)$_2$], **2**, and [Cu(5PicTz4OMePh)$_2$], **3**

Compound	Plane	RMS dev.	Largest dev.	∠, °[a]
1	N1–C2–C3–C4–C5–C6	0.0029	C2, 0.0047(0.0016)	
	N1–C2–N2–C7–N3	0.0171	C2, 0.0259(0.0014)	2.21(0.15)
	C7–N3–C8–C13–S1	0.0036	N3, 0.0052(0.0012)	1.72(0.13)
	C8–C9–C10–C11–C12–C13	0.0043	C8, 0.0061(0.0014)	3.65(0.13)
2	N1–C2–C3–C4–C5–C6	0.0122	C5, 0.0168(0.0050)	
	N1–C2–N2–C7–N3	0.0207	C2, 0.0335(0.0048)	3.49(0.40)
	C7–N3–C8–C13–S1	0.0060	C13, 0.0084(0.0040)	1.08(0.44)
	C8–C9–C10–C11–C12–C13	0.0062	C9, 0.0093(0.0052)	0.68(0.46)
3	N1–C2–C3–C4–C5–C6	0.0092	C6, 0.0147(0.0021)	
	N1–C2–N2–C7–N3	0.0144	C2, 0.0177(0.0024)	2.43(0.14)
	C7–N3–C8–C13–S1	0.0041	C7, 0.0053(0.0016)	2.13(0.15)
	C8–C9–C10–C11–C12–C13	0.0027	C10, 0.0039(0.0025)	1.24(0.17)

[a] Angle with previous plane.

Table 5
Intramolecular and intermolecular interactions for [Cu(5PicTz2OMePh)$_2$], **1**, [Cu(5PicTz3OMePh)$_2$], **2**, and [Cu(5PicTz4OMePh)$_2$], **3**

Compound	D	A	D–H	H···A (Å)	D–H···A (Å)	∠(D–H···A) (°)
Intramolecular						
2	C6	N1$'$	0.95	2.87	3.360(9)	113.5
	C9	N3$'$	0.95	2.71	3.220(9)	114.1
3	C6	N1$'$	0.96(3)	2.66(3)	3.220(4)	118(2)
	C9	N3$'$	0.96(3)	2.66(3)	3.330(5)	127(3)
Intermolecular						
1[a]	C6	N3#1	0.92(2)	2.59(2)	3.170(3)	121(2)
	C11	N2#2	0.94(3)	2.88(3)	3.566(4)	131(2)
	C14	N1#3	0.96	2.96	3.890(3)	163.2
2[b]	C3	O1#1	0.95	2.74	3.431(10)	130.5
	C6	N2#2	0.95	2.48	3.363(10)	155.4
3[c]	C3	O1#1	0.97(3)	2.86(3)	3.578(4)	132(2)
	C6	N2#2	0.96(3)	2.73(3)	3.639(4)	157(2)
	C14	N2#2	0.96	2.82	3.743(4)	161.4

[a] #1: $1 - x, y, 0.5 - z$; #2: $0.5 - x, 0.5 + y, 0.5 - z$; #3: $1.5 - x, 0.5 - y, 1 - z$.
[b] #1: $0.5 + x, 0.5 - y, 0.5 + z$; #2: $x, -y, -0.5 + z$.
[c] #1: $-0.5 + x, 0.5 - y, -0.5 + z$; #2: $-x, 1 - y, 0.5 - z$.
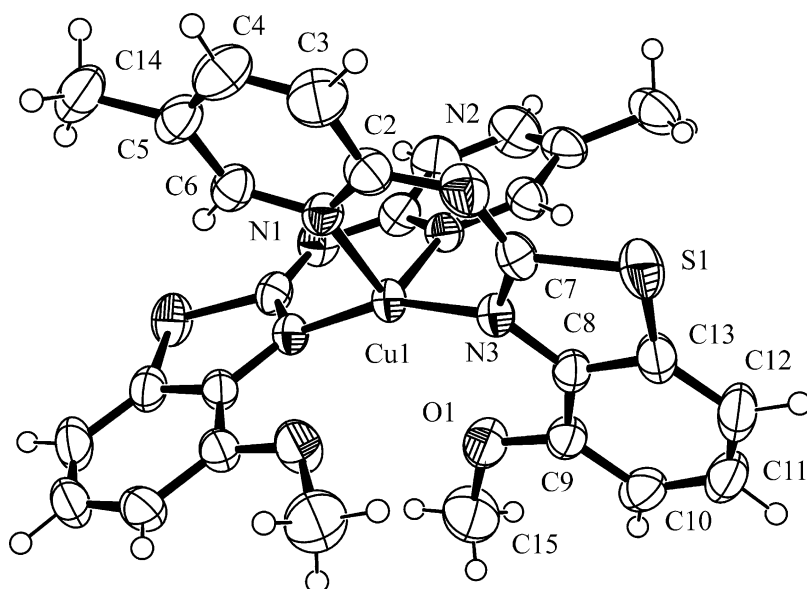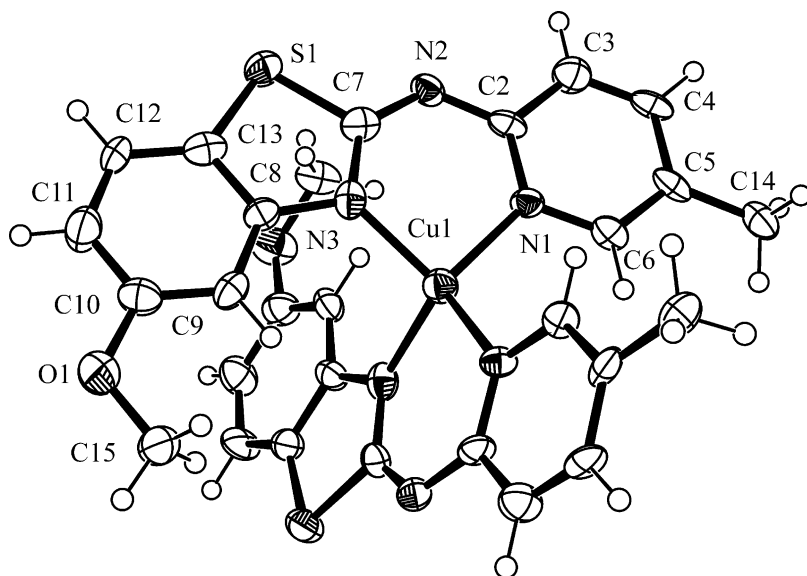

Fig. 2. ORTEP diagram of [Cu(5PicTz2OMePh)$_2$] at 50% probability.

Fig. 3. ORTEP diagram of [Cu(5PicTz3OMePh)$_2$] at 50% probability.

Like the bond distances, the bond angles about the copper(II) centers in the three complexes are also different, Table 3. The N1–Cu1–N1$'$ angle is in the order **1** > **2** > **3** with the difference between the former and latter being > 12°. More significantly, the N3–Cu1–N3$'$ angle is more than 50° larger for **1** than for the other two complexes. The 2-methoxy oxygens are ca. 2.70 Å away from the copper(II) center in **1**, too far to be considered as coordinated, but these oxygens likely contribute to differences in

bond angles for **1**. The chelating N1–Cu1–N3 angles are similar for the three complexes, but the interligand N1–Cu1–N3$'$ angles are also different. These differences in bond angles result in part from differences in intramolecular interactions between the two ligands in a complex (e.g. the potential steric interaction between the methoxy groups in **1**). The bond angles within the ligands are essentially the same except that the angles involving the methoxy group are somewhat different in **2**.
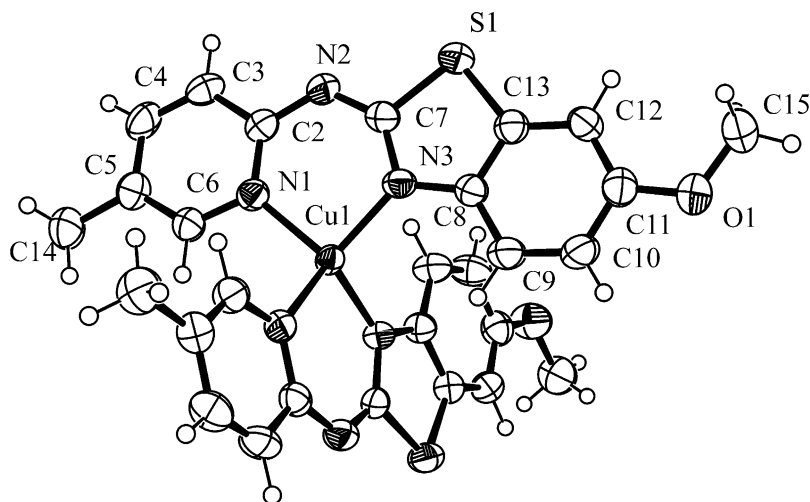

Fig. 4. ORTEP diagram of [Cu(5PicTz4OMePh)$_2$] at 50% probability.

The ligands in the three complexes are nearly planar, Table 4; the angle between the mean planes of the pyridine ring and aryl ring in a ligand is 6.98(0.15)° for **1**, 4.80(0.24)° for **2**, and 2.84(0.16)° for **3**. In contrast to the similarity of many of the bond distances, bond angles and planarity of the chelate rings in the three complexes, Cu1 is 0.3249(0.0023), 0.2569(0.0077), and 0.1340(0.0033) Å out of the N1–C2–N2–C7–N3 plane for **1**,**2**, and **3**, respectively. Also, the angle between N1–C2–N2–C7–N3 and N1′–C2′–N2′–C7′–N3′ planes is 83.40(0.06), 59.29(0.20), and 63.08(0.05)° for **1**,**2**, and **3**; the steric requirement of the methoxy groups probably contributes to the larger angle and more tetrahedral stereochemistry for **1**.

Although these molecules lack functional groups capable of traditional hydrogen bonding (i.e. O–H, N–H, etc.), the above differences suggested a close look at intramolecular and intermolecular interactions by the hydrogens attached to carbons, Table 5. In **2** and **3** there are weak C–H···N interligand interactions within a molecule which probably contribute to the similarity of their stereochemistry. The C6H6···N1′ (and C6′H6′···N1) and C9–H9···N3′ (and C9′–H9′···N3) interactions likely contribute to the N1–Cu1–N1′ and N3–Cu1–N3′ angles being significantly smaller in these two complexes than in **1**, Table 3. The weak interactions with neighboring molecules are different in the three complexes although the strongest interaction for each based on H6···X distance involves C6H6, Table 5. In **2** and **3** O1 is involved in intermolecular interactions with C3–H3, but not in **1**.

The reaction proceeds by an initial polarization and oxidation of the C=S bond by the addition of copper(II) acetate in agreement with recent studies [17]. We suggest that transfer of electron density from the electron rich aromatic ring to the sulfur occurs, which results in formation of the thiazole ring. A methoxy group on the aryl ring appears to be required for this reaction; N-2-pyridyl-N′-arylthioureas lacking a methoxy group on the aryl ring have not formed copper(II) complexes to date. Once formed the benzothiazoles coordinate to copper(I) since the color of the reaction mixture remains beige, but changes on stirring overnight to green indicating air (and dissolved oxygen) oxidation to the final copper(II) complexes, **1**, **2**, and **3**.

4. Conclusion

In contrast to the reaction of copper(II) with N-(2-pyridyl)-N′-benzoylthiourea in which the sulfur bonds to the pyridine nitrogen [16], the present thioureas react by sulfur forming a bond with the aryl carbon ortho to the thiourea moiety. Thus, use of a weakly coordinating oxidizing agent should allow formation of metal complexes of a number of modified heterocyclic ligands formed from substituted thioureas and related sulfur compounds. The ease of formation of thioureas makes this an attractive approach to new metal complexes.

5. Supplementary material

Crystallographic data for the structures reported in this paper (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Center as Supplementary Publication No. CCDC-181297, [Cu(5PicTz2OMePh)₂]; CCDC-185899, [Cu(5PicTz3OMePh)₂];CCDC-181298, [Cu(5PicTz4OMePh)₂]. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

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