Synthesis and structures of two N,N'-bis(2-pyridinyl)thioureas and N-(2-pyridinyl)-N'-(benzoyl)thiourea

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Abstract

N,N-'bis(4,6-lutidyl)thiourea, $(4,6Lut)_2Tu$, triclinic, P-1, $a = 7.4930(8)$, $b = 8.7210(8)$, $c = 12.6040(14)$ Å, $\alpha = 93.437(5)$, $\beta = 94.919(5)$, $\gamma = 110.246(5)°$, $V = 766.35(14)$ Å^3 and $Z = 2$; N,N'-bis(5-picolyl)thiourea, $(5Pic)_2Tu$, monoclinic, $P2_1/c$, $a = 17.205(2)$, $b = 4.4970(5)$, $c = 17.425(2)$ Å, $\beta = 117.763(5)°$, $V = 1272.6(3)$ Å^3 and $Z = 4$ and N-(2-pyridyl)-N'-benzoylthiourea, PyTubenzo, monoclinic, $P2_1/n$, $a = 5.345(3)$, $b = 20.343(6)$, $c = 11.808(2)$ Å, $\beta = 90.23(3)°$, $V = 1290.8(1)$ Å^3 and $Z = 4$. Intramolecular hydrogen bonding between $N'H$ and the pyridyl nitrogen, intermolecular hydrogen bonding involving the thione sulfur and the NH hydrogen, and the planarity of the molecule is affected by substitution on the pyridine rings of the bis(2-pyridyl)thioureas. PyTubenzo has intramolecular hydrogen bonding to the carbonyl oxygen, intermolecular hydrogen bonding to a thione sulfur and is the least planar of the molecules under study. ^{1}H NMR studies in CDCl$_3$ show the NH$'$ hydrogen resonance considerably downfield from other resonances in the spectrum of the bis(2-pyridyl)thioureas. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bis(2-pyridine); Thiourea; Benzoyl; Crystal structures; Hydrogen bonding; Plane deviation

1. Introduction

A recent report of the preparation of N,N'-bis(2-pyridyl)thiourea, $(Py)_2Tu$, and the structures of its copper(I) and zinc(II) complexes, $[Cu(Py_2Tu)_2]ClO_4$ and $[Zn(Py_2Tu)_2](ClO_4)_2$ has appeared [1]. This prompted us to include representative N,N'-bis(substituted 2-pyridyl)thioureas in our studies of the structures and intramolecular and intermolecular hydrogen bonding interactions of N-(2-pyridyl)-N'-arylthioureas with substituents on either or both rings [2–7]. Further, there have been a number of studies on oxygen containing thioureas [8–14] that feature intramolecular NH···O hydrogen bonding, as well as N'H···S intermolecular hydrogen bonding. However, the structure of N-(2-pyridyl)-N'-benzoylthiourea, PyTubenzo, Fig. 1, has to our knowledge not been reported although a recent report of its reaction with copper(II) chloride has appeared [15]. The structure of the resulting chloride-bridged one-dimensional copper(II) polymer included in that report shows that the thiourea is cyclized at the pyridine nitrogen and coordination is via the resulting imine ring nitrogen. We report here the structures of N,N'-bis(4,6-lutidyl)thiourea and $(4,6Lut)_2Tu$, N,N'-bis(5-picolyl)thiourea, $(5Pic)_2Tu$ in addition to N-(2-pyridyl)-N'-benzoylthiourea, PyTubenzo, Fig. 1.

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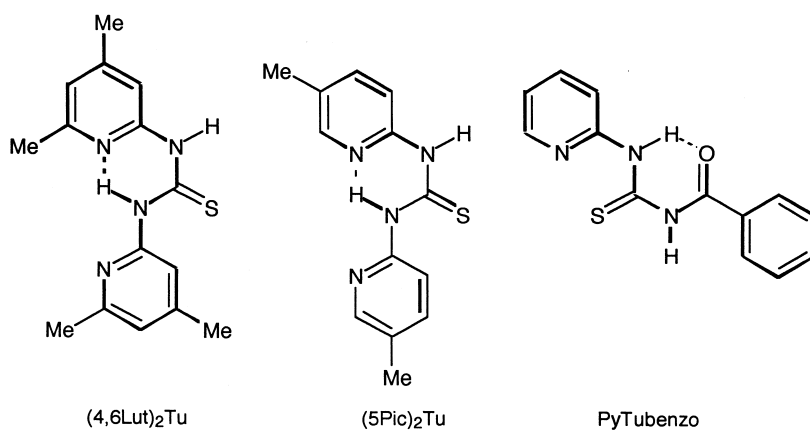*E-mail address:* westdx@chem.washington.edu (D.X. West).

Fig. 1. Representations of $(4,6Lut)_2Tu$, $(5Pic)_2Tu$ and PyTubenzo showing expected intramolecular hydrogen bonding.

Table 1
Crystallographic data and methods of data collection, solution and refinement for $(4,6Lut)_2Tu$, $(5Pic)_2Tu$ and PyTubenzo

| Crystal data	$(4,6Lu)_2Tu$	$(5Pic)_2Tu$	PyTubenzo
Empirical formula	$C_{15}H_{18}N_4S$	$C_{13}H_{14}N_4S$	$C_{13}H_{11}ON_3S$
Crystal color, habit	Colorless, prism	Colorless, prism	Colorless, prism
Crystal size (mm)	$0.30 \times 0.25 \times 0.07$	$0.25 \times 0.18 \times 0.06$	$0.20 \times 0.14 \times 0.10$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/c$	$P2_1/n$
a (Å)	7.4930(8)	17.205(2)	5.345(3)
b (Å)	8.7210(8)	4.4970(5)	20.243(6)
c (Å)	12.6040(14)	17.425(2)	11.808(2)
α (°)	93.437(5)		
β (°)	94.919(5)	117.763(5)	90.23(3)
γ (°)	110.246(5)		
Volume (Å^3)	766.35(14)	1272.6(3)	1290.8(1)
Z	2	4	4
Formula weight	286.39	258.34	257.3
Density (calculated) (g/cm^3)	1.241	1.348	1.324
Absorption coefficient (mm^{-1})	0.207	0.242	0.242
$F(000)$	272	544	536
Reflections for indexing	91	95	25
Index ranges	$-7 \leq h \leq 7$	$-19 \leq h \leq 20$	$0 \leq h \leq 6$
	$-8 \leq k \leq 8$	$-5 \leq k \leq 8$	$0 \leq k \leq 26$
	$-12 \leq l \leq 12$	$-20 \leq l \leq 18$	$-15 \leq l \leq 20$
Reflections collected	2975	3841	3495
Independent reflections	1614 ($R_{int} = 0.0316$)	2166 ($R_{int} = 0.0658$)	2944 ($R_{int} = 0.0491$)
Absorption correction	HKL-Scalepack	HKL-Scalepack	Ψ-scan
Goodness-of-fit	1.047	0.889	1.074
Largest diff. peak (eÅ^{-3})	0.224	0.212	0.249
Largest diff. hole (eÅ^{-3})	-0.196	-0.185	-0.280
R_1, wR_2	0.0432, 0.1129	0.0486, 0.1039	0.0604, 0.0882
R_1, wR_2 (all reflections)	0.0611, 0.1227	0.1200, 0.1275	0.1518, 0.1322
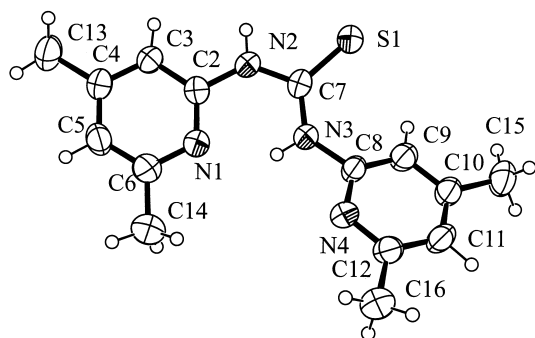
Fig. 2. ORTEP diagram of (4,6Lut)₂Tu with atom numbering scheme and displacement ellipsoids at 50% probability level.

2. Experimental

Representative of the preparative method for the bis(2-pyridyl)thioureas is the following: 2-amino-4,6-lutidine (2-amino-4,6-dimethylpyridine) (6.085 g, 49.9 mmol, Aldrich) and carbon disulfide (2.26 g, 29.7 mmol, Aldrich) were refluxed in 50 ml of MeOH for 8 h. The solution was slowly evaporated to about 20 ml, the white solid filtered off in vacuo, and the resulting solid (4,6Lut)₂Tu dried at 35°C, yield = 17%, mp = 218–219°C; (5Pic)₂Tu, yield = 23%, mp = 188–189°C. PyTubenzo was prepared by mixing equimolar amounts (0.001 mol) of 2-aminopyridine (0.094 g, Aldrich) and benzoyl isothiocyanate (0.163 g, Aldrich) in 40 ml of 95% EtOH. The solution was gently heated (ca. 50°C) and stirred for 2 h, the volume reduced to about 20 ml and the white solid filtered off in vacuo and dried at 35°C, yield, 44%.

Prismatic crystals of the thioureas were grown by slow evaporation of acetone–ethanol solutions
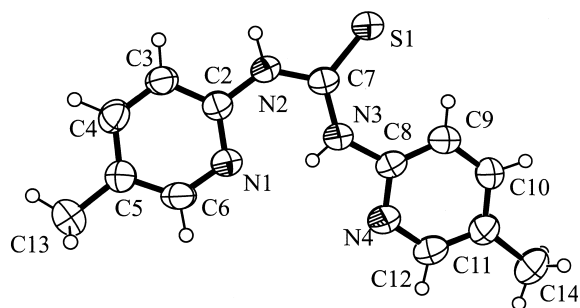

Fig. 3. ORTEP diagram of (5Pic)₂Tu with atom numbering scheme and displacement ellipsoids at 50% probability level.

Table 2
Selected bond distances (Å) and angles (°) for (4,6Lut)₂Tu, (5Pic)₂Tu and PyTubenzo

Distances (Å)	(4,6Lut)₂Tu	(5Pic)₂Tu	PyTubenzo
S1–C7	1.677(3)	1.674(3)	1.658(3)
N1–C2	1.328(4)	1.334(2)	1.325(5)
N1–C6	1.347(4)	1.346(4)	1.343(6)
C2–N2	1.399(4)	1.404(4)	1.417(4)
N2–C7	1.363(4)	1.371(4)	1.329(4)
N3–C7	1.337(4)	1.341(4)	1.382(4)
N3–C8	1.415(4)	1.413(4)	1.388(4)
C8–N4	1.328(4)	1.326(4)	1.220(4) (C8–O1)
N4–C12	1.337(4)	1.344(4)	1.470(5) (C8–C9)
Angles (°)			
C2–N1–C6	117.7(3)	116.8(3)	117.0(4)
N1–C2–C3	123.4(3)	122.4(3)	123.2(4)
N1–C2–N2	117.9(3)	119.0(3)	109.9(3)
N2–C2–C3	118.7(3)	118.6(3)	126.9(4)
C2–N2–C7	131.9(3)	131.8(3)	133.1(3)
S1–C7–N2	117.8(2)	118.0(2)	126.8(3)
N2–C7–N3	116.4(3)	114.9(3)	114.7(3)
S1–C7–N3	125.7(2)	127.1(3)	118.6(3)
C7–N3–C8	131.0(3)	131.2(3)	128.5(3)
N3–C8–C9	124.2(3)	126.7(3)	116.8(3)
N3–C8–N4	112.1(3)	111.1(3)	121.5(3) (N3–C8–O1)
N4–C8–C9	123.7(3)	122.2(3)	121.7(3) (C9–C8–O1)
C8–N4–C12	117.6(2)	116.9(3)	

(1:1 by volume) at room temperature. Crystals were mounted on glass fibers and used for data collection at 293 K on a Nonius CCD {(4,6Lut)₂Tu and (5Pic)₂Tu} or Nonius MACH3 (PyTubenzo) automatic diffractometer, Mo Kα (λ = 0.71073 Å). Cell constants and an orientation matrix for data collections were obtained by least squares refinements of the diffraction data from 25 reflections for PyTubenzo. The structures were solved with direct methods and missing atoms were found by difference-Fourier synthesis. All non-hydrogen atoms were refined with anisotropic temperature factors and hydrogens attached to nitrogens were found on the difference map. The H atoms on carbons in PyTubenzo were fixed at $d = 0.96$ Å, allowed to ride on the C atoms and assigned fixed isotropic temperature factor, $U = 0.05$ Å². The coordinates of the H atoms attached to N and N' and hydrogens on carbons in (4,6Lut)₂Tu and (5Pic)₂Tu were refined isotropically. Refinement of the structures was made by full-matrix least-squares on F^2. Scattering factors

Table 3
Intramolecular and intermolecular hydrogen bond distances (Å) and angles (°) for (4,6Lut)₂Tu, (5Pic)₂Tu and PyTubenzo

	D	A	D–H	H···A	D–H···A	∠(D–H···A)
Intramolecular thiourea						
(4,6Lut)₂Tu	N3	N1	0.850(3)	1.961(3)	2.666(4)	139.7(2)
(5Pic)₂Tu	N3	N1	0.82(3)	1.99(3)	2.666(4)	139.6(29)
PyTubenzo	N2	O1	0.88(3)	1.89(3)	2.598(4)	136(3)
Intermolecular thiourea						
(4,6Lut)₂Tu	N2	S1	0.871(3)	2.540(1)	3.393(3)	166.6(2)
(5Pic)₂Tu	N2	S1	0.88(3)	2.62(3)	3.474(3)	165.0(23)
PyTubenzo	N3	S1	0.91(3)	2.71(3)	3.587(3)	161(3)

are from Wassmaire and Kirfel [16], calculations were done by maXus, version 2.0 [17], and graphics are Platon for Windows [18].

3. Results and discussion

3.1. Structural studies of (4,6Lut)₂Tu and (5Pic)₂Tu

The crystallographic data, as well as the solution and refinement information for these thioureas, are shown in and Table 1, and the atomic coordinates and equivalent isotropic displacement coefficients are included in the deposited material (CCDC), as are a complete list of bond distances and angles (Table 2, Figs. 2 and 3).

There are no significant differences in the bond distances of (4,6Lut)₂Tu and (5Pic)₂Tu (Table 2); all distances are within twice their combined estimated standard deviations. N2–C7 is longer than C7–N3 by 0.02–0.03 Å, which is probably due to N2–C7 being involved in the ring resulting from N3–H3···N1 hydrogen bonding. There are small differences in a few of the bond angles between the two; the largest difference involves N3–C8–C9.

A comparison of the bond distances of (5Pic)₂Tu to *N*-(5-picolyl)-*N′*-phenyl thiourea, 5PicTuPh [14], and (4,6Lut)₂Tu to *N*-(4,6-lutidyl)-*N′*-phenylthiourea, 4,6LutTuPh [14], shows no significant differences for either pair of compounds. Similarly, the bond angles in the two pairs of compounds are within twice their combined e.s.d. values.

Like other 2-pyridyl thioureas, these bis(2-pyridyl)thioureas possess intramolecular and intermolecular hydrogen bonding interactions, Table 3. The intramolecular N3–H3···N1 interactions of (4,6Lut)₂Tu and (5Pic)₂Tu are equivalent, but the intermolecular N2–H2···S1 interactions are different. The bulkier (4,6Lut)₂Tu has a shorter N2···S1 non-bonding distance, as well as a shorter H2···S1 distance. The intramolecular hydrogen bonding interaction of (4,6Lut)₂Tu is substantially weaker than found for 4,6LutTuPh [14]; H3···N1 distance is 1.961(3) Å and the N3–H3···N1 distance and angle are 2.666(4) Å and 139.7(2)° for (4,6Lut)₂Tu compared to 1.83(4), 2.633(4) Å and 152(3)° for 4,6LutTuPh [7]. However, the intermolecular interaction of (4,6Lut)₂Tu is stronger than 4,6LutTuPh, the H2···S1 and N2···S1 distances are 2.540(1), 3.393(3) and 2.66(4), 3.462(3) Å, respectively. In contrast, (5Pic)₂Tu has a longer H2···S1 distance and N2···S1 non-bonding distance than 5PicTuPh, an average of 2.62(3), 3.474(3) Å for the former compared to 2.47, 3.433(7) Å for the latter, but their intramolecular interactions are essentially equivalent. The N2–H2···S1 angles are also different; (5Pic)₂Tu = 165.0(23)° and 5PicTuPh averages 156.1°.

The most significant difference between (4,6Lut)₂Tu and (5Pic)₂Tu is their planarity; the angle between the two pyridyl rings in (4,6Lut)₂Tu is 24.48(0.82)° compared to 10.55(0.43)° for (5Pic)₂Tu (Table 4). The pyridine ring involved in hydrogen bonding is almost coplanar with the thiourea moiety in the two compounds, but the other pyridine ring is significantly out of its plane. The analogous phenyl derivatives have the following angles between the mean plane of the pyridyl and phenyl rings: 13.91(0.17)° for 4,6LutTuPh and 5PicTuPh averages 28.75(0.97)°. Since the relationship for this angle is 5PicTuPh > 4, 6LutTuPh, but

Table 4
Mean plane data and angles between planes for $(4,6Lut)_2Tu$, $(5Pic)_2Tu$ and PyTubenzo

Compound	Plane	Plane #	Mean plane deviation	Atom with greatest deviation	Plane/plane	Angle
$(4,6Lut)_2Tu$	N1–C2–C3–C4–C5–C6	1	0.0004	N1, 0.0031(0.0019)	1/2	1.09(0.04)
	N2–C7–S1–N3	2	0.0013	C7, 0.0078(0.0024)	2/3	25.48(0.87)
	C8–C9–C10–C11–C12–C13	3	0.0008	C12, 0.0177(0.0019)	3/1	24.41(0.82)
$(5Pic)_2Tu$	N1–C2–C3–C4–C5–C6	1	0.0002	C5, 0.0105(0.0030)	1/2	1.15(0.05)
	N2–C7–S1–N3	2	0.0002	C7, 0.0032(0.0030)	2/3	9.50(0.31)
	C8–C9–C10–C11–C12–C13	3	0.0015	C9, 0.0138(0.0047)	3/1	10.35(0.43)
PyTubenzo	N1–C2–C3–C4–C5–C6	1	0.0064	C6, 0.0110(0.0044)	1/2	2.09(0.29)
	N2–C7–S1–N3	2	0.0030	C7, 0.0053(0.0029)	2/3	30.34(0.17)
	C9–C10–C11–C12–C13–C14	3	0.0039	C9, 0.0056(0.0025)	3/1	31.74(0.18)
	N2–C7–N3–S1–C8–O1	4	0.0375	N3, 0.0529(0.0025)	3/4	28.59(0.16)

$(4,6Lut)_2Tu > (5Pic)_2Tu$, substitution on the second ring is a significant factor in the packing of these molecules.

Although bond distances, bond angles and intramolecular hydrogen bonding parameters of bis(2-pyridyl)thioureas are not significantly affected by position of substitution on the pyridyl rings, intermolecular hydrogen bonding and planarity of the molecules are different. Further, a comparison of the bis(2-pyridyl)thioureas with their (2-pyridyl)phenylthiourea analogs [14] shows differences in all of the above except for bond distances. Based on angles between the pyridine and tolyl rings of 67.4(1), 79.4(1) and 58.7(1)° for *N*-(2-pyridyl)-*N'*-*o*-tolylthiourea, PyTuoT; *N*-(2-pyridyl)-*N'*-*m*-tolylthiourea, PyTumT and *N*-(2-pyridyl)-*N'*-*p*-tolylthiourea, PyTupT, compared to the angles for 5PicTuPh and 4,6LutTuPh [14], it was suggested that substitution on the hydrogen bonding pyridine ring increased the planarity of the molecule, but substitution on the phenyl ring decreased the planarity [3]. The greater substitution on the pyridine ring not involved in hydrogen bonding in $(4,6Lut)_2Tu$ compared $(5Pic)_2Tu$ may help to explain the larger angle between the mean planes of the pyridine rings.

Since bond distances, bond angles and intramolecular hydrogen bonding are not significantly different in $(4,6Lut)_2Tu$ and $(5Pic)_2Tu$, it is reasonable to compare these parameters to the coordinated $(Py)_2Tu$ in the complexes $[Cu\{(Py)_2Tu\}_2]ClO_4$ and $[Zn\{(Py)_2Tu\}_2](ClO_4)_2$ [1]. In both complexes, the coordination of $(Py)_2Tu$ is via a pyridine nitrogen and the thione sulfur. The two ligands in $[Zn\{(Py)_2$ $Tu\}_2](ClO_4)_2$ are identical and S1–C7 is 1.718(4) Å and N1–C2 is 1.362(6) Å; both are significantly longer than found for $(5Pic)_2Tu$, 1.677(3) and 1.328(4) Å, respectively. In addition, N2–C7, 1.342(6) Å, and N3–C7, 1.356(6) Å, in $[Zn\{(Py)_2$ $Tu\}_2](ClO_4)_2$ are different from $(5Pic)_2Tu$, 1.371(4) and 1.341(4) Å, respectively. Only angles involving the zinc center are listed and the authors indicate that no hydrogen bonding is present in $[Zn\{(Py)_2$ $Tu\}_2](ClO_4)_2$ [1]. Consistent with the lower charge on the metal center in $[Cu\{(Py)_2Tu\}_2]ClO_4$, the S1–C7 and N1–C2 distances are essentially the same as those of $(5Pic)_2Tu$. However, N2–C7 and N3–C7 are substantially different and have essentially the same distances as found for $[Zn\{(Py)_2Tu\}_2](ClO_4)_2$ [1]. The ligands in the copper(I) complex show N2–H2···N4 hydrogen bonding interactions with H···N distances of 1.972 and 1.894 Å, which is shorter than the 1.99(3) Å found for $(5Pic)_2Tu$. Therefore, the formation of the chelate ring and the hydrogen bonding interaction with the second pyridine ring in $Cu\{(Py)_2$ $Tu\}_2]ClO_4$ cause the difference in N2–C7 and N3–C7 distances. Bond angles that would allow a comparison between the coordinated and non-coordinated thioureas are not listed [1]. The planes of the two pyridine rings in a ligand are at an angle of 9.28°, which is similar to 10.35(0.43)° found for $(5Pic)_2Tu$.

3.2. Structural studies of PyTubenzo

Like the bis(2-pyridyl)thioureas PyTubenzo crystallized with one unique molecule in the unit cell, (Fig. 4). The intramolecular hydrogen bonding is
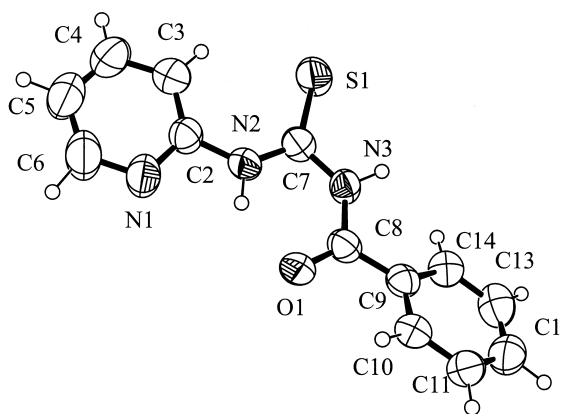
Fig. 4. ORTEP diagram of PyTurbenzo with atom numbering acheme and displacement ellipsoids at 50% probability level.

between N2H2 and the benzoyl oxygen and the nonbonding N2···O1 distance, 2.598(4) Å, is shorter than the N2···N1 distance of the bis(2-pyridyl)thioureas indicating a stronger interaction. This distance is also shorter than the N···O distance found for *N*-benzoyl-*N'*-*p*-nitrophenylthiourea, 2.635(3) Å [12] and *N*-benzoyl-*N'*-*p*-methoxyphenylthiourea, 2.618(9) Å [13]. The N2–H2···O angle of PyTubenzo is smaller than the N3–H3···N1 angle of (4,6Lut)$_2$Tu and (5Pic)$_2$Tu, as is the intermolecular angle of N3H3···S1 compared to N2H2···S1 for the bis(2-pyridyl)thioureas. The intermolecular hydrogen bonding for PyTubenzo, however, appears to be weaker compared to the bis(2-pyridyl)thioureas based on longer N3H3···S1 nonbonding distance.

There are small differences in the bond distances in the thiourea moiety of PyTubenzo compared to the bis(2-pyridyl)thioureas. The difference in N2–C7 and N3–C7 bond distances, >0.05 Å, is larger for PyTubenzo than the bis(2-pyridyl)thioureas; the electron withdrawing effect of the carbonyl group increases this difference. The angles about the thiosemicarbazone moiety are similar to those of the bis(2-pyridyl)thioureas based on the hydrogen bonding patterns. Although not involved in intramolecular hydrogen bonding like other 2-pyridyl thioureas, the pyridine ring is nearly coplanar with the thiourea moiety, but the phenyl ring is at a larger angle to the thiourea moiety.

Reaction with copper(II) chloride causes PyTu-

benzo to be cyclized at the pyridine nitrogen resulting in a thiadiazole ring and coordination of the ring's imine nitrogen [15]. Also, N3–C7 formally becomes a double bond so that bond distances for what was the thiourea moiety should undergo significant change. N2–C7, formally a single bond in both, is not significantly different, 1.341(4) Å in PyTubenzo and 1.334(8) Å in the complex. However, N3–C7 decreases from 1.387(7) to 1.356(8) Å, consistent with the complex having greater double bond character, but still is longer than N2–C7, which is formally a single bond [15]. No other information is provided that allows comparison between PyTubenzo and the cyclized ligand in the copper(II) complex.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no CCDC-157695 for (4,6Lut)$_2$Tu, CCDC-157694 for (5Pic)$_2$Tu, and CCDC-154846 for PyTubenzo. Copies of available material can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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