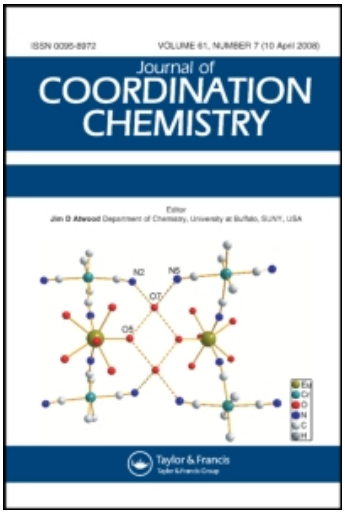

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STRUCTURES OF COPPER(I) AND ZINC(II) COMPLEXES WITH *N,N'*-BIS(2-PYRIDINYL)THIOUREA (BPT)

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STRUCTURES OF COPPER(I) AND ZINC(II) COMPLEXES WITH *N,N'*-BIS(2-PYRIDINYL)THIOUREA (BPT)

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Copper(I) and zinc(II) complexes with *N,N'*-bis(2-pyridinyl)thiourea (BPT), $[Cu(BPT)_2]ClO_4$ (1) and $[Zn(BPT)_2](ClO_4)_2$ (2) were synthesized by reaction of $M(ClO_4)_2$ (M = Cu, Zn) with BPT in methanol solution. The crystal structures of complexes (1) and (2) were characterized by X-ray diffraction: (1) is triclinic, space group $P\bar{1}$, with $a = 10.162(2)$, $b = 14.483(6)$, $c = 9.496(2)$ Å, $\alpha = 105.80(2)°$, $\beta = 106.94(2)°$, $\gamma = 82.71(3)°$, $V = 1284.4(7)$ Å^3, $Z = 2$, and final $R = 0.047$, $R_w = 0.061$; (2) is monoclinic, space group $C2/c$, with $a = 15.15(1)$, $b = 6.299(3)$, $c = 30.16(1)$ Å, $\beta = 93.49(7)°$, $V = 2872(2)$ Å^3, $Z = 4$, and final $R = 0.049$, $R_w = 0.070$. Both of the complexes exhibit novel structures. Two N atoms and two S atoms from two BPT groups coordinate to one M atom. The M atom shows distorted tetrahedral geometry. IR spectra and thermoanalyses of BPT and its complexes (1) and (2) are briefly discussed.

Keywords: Cu(I) and Zn(II) complexes; synthesis; thiourea; crystal structure

INTRODUCTION

Thiourea complexes with transition metal atoms comprise one of the most interesting areas in chemistry because of the special roles played by these kinds of compounds in biological processes.[1–3] The compounds have been studied,[4–6] but pyridinyl thiourea-containing compounds have received little attention.[7] In this paper, we present a new thiourea compound, *N,N'*-bis(2-pyridinyl)thiourea (BPT), and its complexes $[Cu(BPT)_2]ClO_4$ (1)

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and $[Zn(BPT)_2](ClO_4)_2$ (**2**); we have determined the crystal structures of the two complexes. IR spectra and thermoanalyses are discussed.

EXPERIMENTAL

Infrared spectra were recorded with Perkin Elmer 710 spectrophotometer with pressed KBr pellets. Elemental analyses were performed on a Carlo-Erba 1106 analyzer. Thermoanalysis were recorded on a Rigaku instrument. Proton NMR spectra were recorded on a BRUKER FT-80m NMR spectrometer.

$Cu(ClO_4)_2$ was prepared by reaction of CuO with $HClO_4$. Other chemicals were purchased as AR reagents and were used without further purification.

Preparation of Compounds

N,N'-bis(2-pyridinyl) thiourea (BPT)

Sodium hydroxide (0.5 g) was dissolved in anhydrous ethanol (50 ml), and 2-aminopyridine (9.4 g, 0.1 mol) and carbon disulfide (4.5 g, 0.06 mol) were added. The mixture was refluxed for 6 h. Upon cooling, solid product formed. After recrystallization from anhydrous ethanol, 8 g of white acicular crystals of [PyNHC(S)NHPy] were obtained with a melting point of 160°C. *Anal.* Calcd. for $C_{11}H_{10}N_4S$ (%): C, 57.39; H, 4.35; N, 24.35. Found: C, 57.79; H, 4.45; N, 24.13. ^1H NMR (DMSO): δ 7.09–7.25 (m, 2H), 7.74–7.95 (m, 2H), 8.33–8.42 (m, 2H), 12.69 (br, s, 2H).

$[Cu(BPT)_2]ClO_4$ (1)

$Cu(ClO_4)_2$ (0.01 mol) and BPT (0.03 mol) were dissolved in methanol and the solution of BPT added dropwise to the solution of $Cu(ClO_4)_2$ at room temperature. The mixture was stirred for 30 min and filtered. Red prismatic crystals were obtained several hours later. *Anal.* Calcd. for $C_{22}H_{20}ClCuN_8O_4S_2$ (%): C, 42.34; H, 3.21; N, 17.89. Found: C, 42.44; H, 3.25; N, 17.96.

$[Zn(BPT)_2](ClO_4)_2$ (2)

$Zn(ClO_4)_2$ (0.02 mol) and BPT (0.01 mol) were dissolved in methanol respectively and the solution of BPT added dropwise to the solution of $Zn(ClO_4)_2$ at room temperature. The mixture was stirred for 30 min and filtered. White crystals were obtained after the filtrate was allowed to stand at room

temperature for one day. *Anal.* Calcd. for $C_{22}H_{20}Cl_2N_8O_8S_2Zn$ (%): C, 36.44; H, 2.76; N, 15.46. Found: C, 36.82; H, 2.85; N, 15.70.

X-Ray Crystal Structure Determination

A prismatic crystal was mounted on a glass fibre. All measurements were made on a Rigaku AFC7R diffractometer for complex (1) and a Rigaku RAXIA-IV imaging plate area detector for complex (2) with graphite-monochromated MoKα radiation. Data were collected using the ω–2θ scan technique. A linear correction factor and an empirical absorption correction were applied. Data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods and Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on observed reflections ($I > 3.00\sigma(I)$). All calculations were performed using the teXsan[8] crystallographic software package of the Molecular Structure Corporation. Crystal data for the two complexes are listed in Table I. Table II gives selected bond lengths and bond angles, and lists of atomic positions are given in Tables III and IV.

TABLE I Crystal data and structure refinement details for $[Cu(BPT)_2]ClO_4$ (1) and $[Zn(BPT)_2](ClO_4)_2$ (2)

	Complex (1)	*Complex* (2)
Empirical formula	$C_{22}H_{20}ClCuN_8O_4S_2$	$C_{22}H_{20}Cl_2N_8O_8S_2Zn$
Formula weight	623.57	724.85
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions	$a = 10.160(2)$ Å	$a = 15.15(1)$ Å
	$b = 14.483(6)$ Å	$b = 6.299(3)$ Å
	$c = 9.496(2)$ Å	$c = 30.16(1)$ Å
	$\alpha = 105.80(2)°$	
	$\beta = 106.94(2)°$	$\beta = 93.49(7)°$
	$\gamma = 82.71(3)°$	
Volume, Z	1284.4(7) Å^3, 2	2872(2) Å^3, 4
Density	1.612 g/cm^3	1.676 g/cm^3
$F(000)$	636	1472
Crystal size	0.20 × 0.20 × 0.30 mm	0.50 × 0.30 × 0.30 mm
μ(MoKα)	11.64 cm^{-1}	12.48 cm^{-1}
$2\theta_{max}$	49.9°	55.0°
No. of reflections measured	3710	2606
No. of observations ($I > 3.00\sigma(I)$)	2723	1852
No. of variables	365	196
Reflection/parameter ratio	7.46	9.45
Goodness of fit indicator	2.38	1.21
Residuals: R; R_w	0.047; 0.061	0.049; 0.070
Weights	$w = \sigma^2(F_o)^{-1}$	$w = \sigma^2(F_o)^{-1}$
Max. peak in final diff. map	0.44 eÅ^{-3}	0.48 eÅ^{-3}
Min. peak in final diff. map	−0.47 eÅ^{-3}	−0.46 eÅ^{-3}

TABLE II Selected bond lengths (Å) and bond angles (°) for complexes (1) and (2)

Complex (1)					
Cu–S(1)	2.222(2)	Cu–S(2)	2.292(2)	Cu–N(1)	1.994(4)
Cu–N(5)	2.101(4)	S(1)–C(6)	1.678(5)	S(2)–C(17)	1.679(5)
N(1)–C(1)	1.328(6)	N(1)–C(5)	1.354(7)	N(2)–C(1)	1.404(6)
N(2)–C(6)	1.344(6)	N(3)–C(6)	1.358(6)	N(3)–C(7)	1.401(6)
S(1)–Cu–S(2)	119.85(7)	S(1)–Cu–N(1)	101.6(1)		
S(1)–Cu–N(5)	109.2(1)	S(2)–Cu–N(1)	120.6(1)		
S(2)–Cu–N(5)	90.1(1)	N(1)–Cu–N(5)	115.6(2)		
Cu–S(1)–C(6)	105.0(2)	Cu–S(2)–C(17)	95.0(2)		
Cu–N(1)–C(1)	126.4(3)	Cu–N(1)–C(5)	116.8(4)		
C(1)–N(1)–C(5)	116.8(4)	C(1)–N(2)–C(6)	135.4(4)		
C(6)–N(3)–C(7)	131.0(4)	C(7)–N(4)–C(11)	118.2(5)		
Cu–N(5)–C(12)	120.9(3)	Cu–N(5)–C(16)	122.7(3)		
Complex (2)					
Zn(1)–S(1)	2.263(1)	Zn(1)–S(1)*	2.263(1)	Zn(1)–N(4)	2.029(4)
Zn(1)–N(4)*	2.029(4)	S(1)–C(6)	1.718(4)	N(1)–C(1)	1.362(6)
N(1)–C(5)	1.342(6)	N(2)–C(6)	1.356(6)	N(3)–C(6)	1.342(6)
N(4)–C(7)	1.348(5)	N(3)–C(7)	1.394(6)		
S(1)–Zn(1)–S(1)*	118.70(10)	S(1)–Zn(1)–N(4)	100.1(1)		
S(1)–Zn(1)–N(4)*	116.9(1)	S(1)*–Zn(1)–N(4)*	100.1(1)		
S(1)*–Zn–N(4)	116.9(1)	N(4)–Zn–N(4)*	104.1(2)		
Zn(1)–S(1)–C(6)	104.1(2)	Zn(1)–N(4)–C(7)	126.9(3)		
Zn(1)–N(4)–C(11)	114.6(3)				

RESULTS AND DISCUSSION

Synthesis of $[Cu(BPT)_2]ClO_4$ and $[Zn(BPT)_2](ClO_4)_2$

In the synthesis of complex (1), we found that reaction of $Cu(ClO_4)_2$ with insufficient BPT produced a light orange yellow powder which was not a pure compound. When heated with excess BPT in methanol, the powder dissolved. Upon cooling and standing for several hours at room temperature, shining red crystals were obtained. The compound was identified as (1) by elemental analysis and X-ray crystal structure. Typically, treatment of $Cu(ClO_4)_2$ with an excess of BPT in CH_3OH directly gave red crystals of (1). In the formation of the complex, we observed a change of colour of solution from blackish green to orange red, confirming the existence of oxidation–reduction reactions. Cu(II) ion was reduced to Cu(I) ion. If we used Cu_2O to react with $HClO_4$ and BPT, the same product was obtained. We also found that complex (2) can be conveniently prepared by reaction of $Zn(ClO_4)_2$ with BPT in good yields.

Thermoanalyses

The TG-DTA of BPT and its complexes was determined in the air. There is an endothermic peak at 221°C on the DTA curve of complex (1), but

TABLE III Final atomic coordinates for (1)

Atom	*x/a*	*y/b*	*z/c*
Cu()	0.47788(7)	0.24560(4)	0.86781(8)
Cl()	0.8963(1)	0.25567(9)	0.4464(2)
S(1)	0.6537(1)	0.28915(10)	0.8099(2)
S(2)	0.5186(2)	0.1719(1)	1.0627(2)
O(1)	0.8900(9)	0.3087(5)	0.3432(8)
O(2)	0.904(1)	0.1572(4)	0.3944(8)
O(3)	0.764(1)	0.250(2)	0.413(2)
O(3')	0.843(4)	0.286(1)	0.560(4)
O(4)	1.028(1)	0.230(2)	0.457(3)
O(4')	0.967(3)	0.297(1)	0.583(2)
N(1)	0.3492(4)	0.3613(3)	0.8615(5)
N(2)	0.4891(4)	0.4517(3)	0.7894(5)
N(3)	0.6866(4)	0.4323(3)	0.7132(5)
N(4)	0.5660(4)	0.5776(3)	0.6788(5)
N(5)	0.4037(4)	0.1178(3)	0.7106(4)
N(6)	0.5896(4)	0.0310(3)	0.8406(4)
N(7)	0.7295(4)	0.0479(3)	1.0832(4)
N(8)	0.8166(4)	−0.0770(3)	0.9147(5)
C(1)	0.3700(5)	0.4408(3)	0.8287(5)
C(2)	0.2749(6)	0.5185(4)	0.8273(6)
C(3)	0.1538(6)	0.5138(4)	0.8596(7)
C(4)	0.1307(6)	0.4318(5)	0.8939(8)
C(5)	0.2289(7)	0.3587(4)	0.8944(7)
C(6)	0.6021(5)	0.3962(3)	0.7705(6)
C(7)	0.6744(5)	0.5172(4)	0.6655(5)
C(8)	0.7762(6)	0.5341(4)	0.6060(7)
C(9)	0.7619(7)	0.6178(5)	0.5594(7)
C(10)	0.6492(7)	0.6812(4)	0.5719(7)
C(11)	0.5539(6)	0.6581(4)	0.6302(6)
C(12)	0.4691(5)	0.0337(3)	0.7214(5)
C(13)	0.4299(5)	−0.0517(3)	0.6162(6)
C(14)	0.3178(6)	−0.0499(4)	0.4948(6)
C(15)	0.2462(6)	0.0355(4)	0.4824(6)
C(16)	0.2910(6)	0.1165(4)	0.5914(6)
C(17)	0.6147(5)	0.0793(4)	0.9873(6)
C(18)	0.8210(5)	−0.0325(4)	1.0564(6)
C(19)	0.9104(6)	−0.0594(4)	1.1822(6)
C(20)	0.9991(6)	−0.1365(5)	1.1530(9)
C(21)	0.9990(6)	−0.1843(5)	1.0072(9)
C(22)	0.9064(6)	−0.1531(4)	0.8931(7)

without corresponding weight loss in the TG curve (melting point). Two strong exothermic peaks at 261°C and 600°C on the DTA curve have corresponding weight losses of 62.5% and 27.5%. The residue is thus Cu_2O. In the DTA curve of complex (2), there are one weak exothermic peak at 230°C, two moderate exothermic peaks at 260°C and 310°C, and one strong exothermic peak at 598°C. Complex (2) keeps losing weight from 230°C to 800°C. BPT melts endothermally at 160°C, then decomposes endothermally at 197°C.

TABLE IV Final atomic coordinates for (2)

Atom	*x/a*	*y/b*	*z/c*
Zn(1)	1.0000	0.3569(1)	0.2500
Cl(1)	1.33762(8)	0.4989(2)	0.11181(4)
S(1)	0.9511(1)	0.5401(3)	0.18880(5)
O(1)	1.3022(3)	0.6965(7)	0.0965(2)
O(2)	1.3405(3)	0.3517(8)	0.0759(2)
O(3)	1.4274(3)	0.5202(8)	0.1297(2)
O(4)	1.2846(3)	0.4196(7)	0.1458(1)
N(1)	1.1054(3)	0.3990(7)	0.0650(1)
N(2)	1.0168(3)	0.5942(7)	0.1126(1)
N(3)	1.0827(2)	0.3128(6)	0.1497(1)
N(4)	1.0876(2)	0.1587(6)	0.2229(1)
C(1)	1.1463(4)	0.3846(9)	0.0262(2)
C(2)	1.1453(4)	0.546(1)	−0.0047(2)
C(3)	1.1026(4)	0.732(1)	0.0049(2)
C(4)	1.0583(4)	0.7517(9)	0.0436(2)
C(5)	1.0622(3)	0.5798(9)	0.0729(1)
C(6)	1.0229(3)	0.4699(7)	0.1494(1)
C(7)	1.1110(3)	0.1582(7)	0.1805(1)
C(8)	1.1690(3)	0.0022(8)	0.1650(2)
C(9)	1.2023(3)	−0.1529(8)	0.1940(2)
C(10)	1.1781(3)	−0.1510(8)	0.2378(2)
C(11)	1.1210(3)	0.0039(8)	0.2509(2)

TABLE V Selected IR data (cm^{-1}) for BPT, $[Cu(BPT)_2]ClO_4$ and $[Zn(BPT)_2](ClO_4)_2$

Compound	ν_{N-H}	$\nu_{C=N(ring)}$	$\nu_{ClO_4^-}$
BPT	3224, 3195	1603	
$[Cu(BPT)_2]ClO_4$	3274	1630, 1602	1096
$[Zn(BPT)_2](ClO_4)_2$	3253, 3120	1645, 1610	1096

IR Spectra

Selected IR data for BPT, complexes (1) and (2) are given in Table V. Vibrations around 3200 cm^{-1} are associated with N–H stretching. The $\nu_{C=N(ring)}$ vibration is observed at 1603 cm^{-1} for BPT, 1630, 1602 cm^{-1} for complex (1) and 1645, 1610 cm^{-1} for complex (2). Both complexes exhibit two $\nu_{C=N}$ peaks, indicating that only one pyridine ring participates in the formation of the complexes. In addition, there is a strong peak at 1096 cm^{-1} from ClO_4^- in the IR spectra of complexes (1) and (2), entirely consistent with free ClO_4^-.

Crystal Structures of $[Cu(BPT)_2]ClO_4$ and $[Zn(BPT)_2](ClO_4)_2$

The structure of the complex ion $Cu(BPT)_2^+$ is shown in Figure 1. Two S atoms and two N atoms from two BPT units, respectively, coordinate to

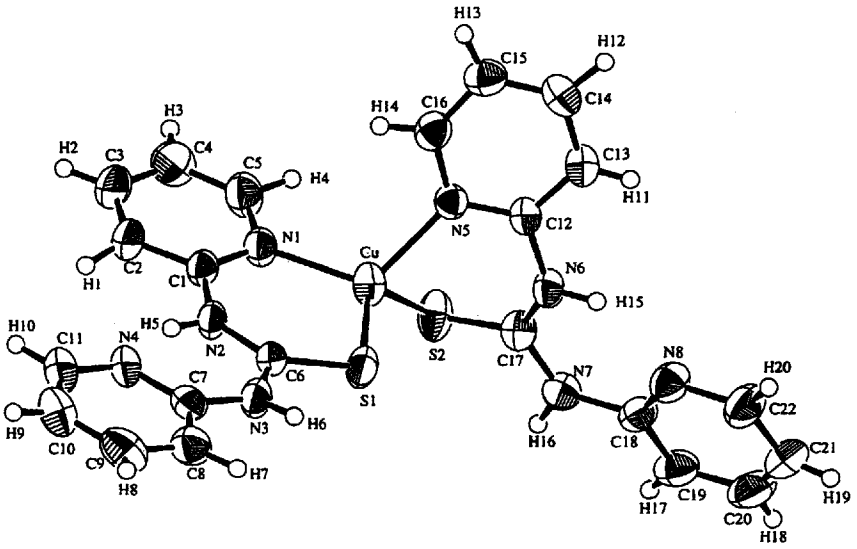

FIGURE 1 The molecular structure of (1) showing the atom numbering scheme.

the Cu atom and form two six-membered rings. Cu exhibits a distorted tetrahedral coordination environment. The Cu atom deviates from one coordination ring plane [ring I: N(1), C(1), N(2), C(6), S(1), Cu] by about 0.154 Å, and from the other [ring II: N(5), C(12), N(6), C(17), S(2), Cu] by about 1.338 Å. The dihedral angle between the two distorted ring planes is 77.85°.

The bond lengths Cu–N(5) (2.101 Å) and Cu–S(2) (2.292 Å) are much longer than Cu–N(1) (1.994 Å) and Cu–S(1) (2.222 Å). Moreover, the bond angle N(5)–Cu–S(2) (90.1°) is much smaller than N(1)–Cu–S(1) (101.6°). This may result from steric tension between the two BPT ligands.

Two BPT units contain four N atoms, N(1), N(4), N(5) and N(8). N(1) and N(5) coordinate with Cu. N(4) and N(8) form hydrogen bonds, N(4)···H(5)–N(2) or N(8)···H(15)–N(6). N(4)···H(5) and N(8)···H(15) distances are 1.972 and 1.894 Å, respectively. The two Py rings from one BPT unit have a torsion angle of 9.28°. The torsion angle of the other two Py rings is 37.41°.

Complex (2) has a similar structure to (1); its skeleton is depicted in Figure 2. The Zn atom also lies in a tetrahedral coordination environment. Zn–S(1) and Zn–N(4) bond lengths are the same as those of Zn–S(1)* and Zn–N(4)*, and the six bond angles S(N)–Zn–N(S) range from 100.1° to 118.7°. There is no hydrogen bond in the complex.

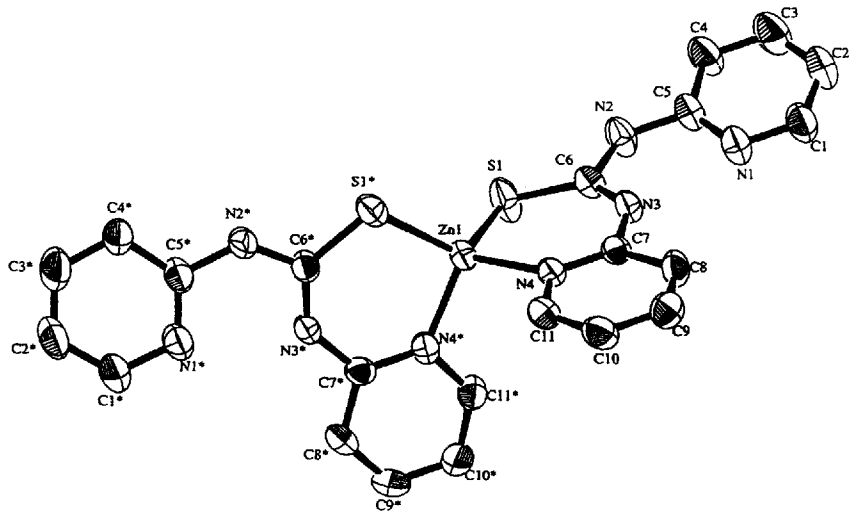

FIGURE 2 The molecular structure of (2) showing the atom numbering scheme.

Acknowledgements

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Supplementary Data

Full lists of crystallographic data are available from the authors upon request.

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