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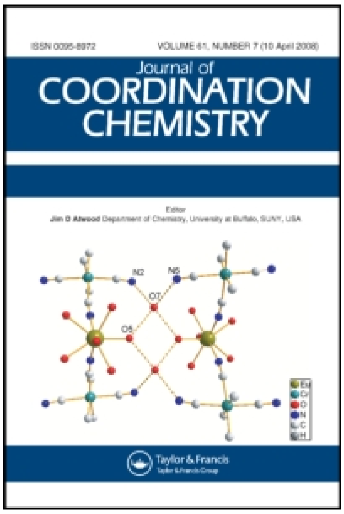

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Synthesis, characterization, and antibacterial activity of metal complexes of phenylthiourea: the X-ray single crystal structure of $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$

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First published on: 19 August 2010

To cite this Article Ajibade, Peter A. and Zulu, Nonkululeko H.(2010) 'Synthesis, characterization, and antibacterial activity of metal complexes of phenylthiourea: the X-ray single crystal structure of $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$', Journal of Coordination Chemistry, 63: 18, 3229 — 3239, First published on: 19 August 2010 (iFirst)
To link to this Article: DOI: 10.1080/00958972.2010.510558
URL: http://dx.doi.org/10.1080/00958972.2010.510558

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Journal of Coordination Chemistry
Vol. 63, No. 18, 20 September 2010, 3229–3239

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Synthesis, characterization, and antibacterial activity of metal complexes of phenylthiourea: the X-ray single crystal structure of $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$

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(*Received 19 April 2010; in final form 23 June 2010*)

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Co(II), Cu(II), Zn(II), and Fe(III) complexes of phenylthiourea have been synthesized and characterized by elemental analyses, molar conductivity, magnetic susceptibility, FT-IR, and electronic spectroscopy. The spectroscopic data of the complexes are consistent with four-coordinate geometry for the metal(II) complexes and six-coordinate octahedral for the Fe(III) complex. Single crystal X-ray analysis of the Zn(II) complex revealed distorted tetrahedral geometry around the metal ion with two molecules of phenylthiourea and two acetate ions. The *in vitro* antibacterial activity of the complexes was studied against six bacterial strains using disc diffusion and broth microdilution methods. The complexes showed selective antibacterial activity against *Staphylococcus aureus* and *Bacillus pumilus* when compared to standard antibiotic ampicillin. The minimum inhibitory concentrations of the sensitive compounds are between 0.625 and 5.0 $mg\,mL^{-1}$.

Keywords: Metal complexes; Phenylthiourea; Crystal structure; Antibacterial; Drug resistant

1. Introduction

Infectious diseases are the major causes of death especially in developing countries. These diseases kill about 15 million people every year, which corresponds to about one-third of the number of deaths [1, 2]. The development of antimicrobial drugs, particularly antibiotics, has long been touted as one of the great medical success stories of the twentieth century [2]. Although several classes of antimicrobial compounds are presently available, microorganism's resistance to these drugs constantly emerges [3]. Resistance to sulfonamide was discovered in 1939 [4], penicillin in 1941 [5], and streptomycin in 1946 [6]. In the search for new drugs against resistant infectious diseases, the modification of existing drugs or organic molecules by coordination to a metal center has attracted considerable attention [7–9]. Substituted thioureas are interesting as reagents for the separation of metal ions [10], as antibacterial [11, 12], antiviral [13], or antifungal agents [14, 15]. In this study, we present the synthesis,

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.510558

characterization, and antibacterial screening of Zn(II), Co(II), Cu(II), and Fe(III) complexes of phenylthiourea.

2. Experimental

2.1. *Materials and instrumentation*

Solvents of analytical grade were used as obtained. Elemental analyses were performed at the Microanalytical Laboratory, School of Chemistry, The University of Manchester. FT-IR spectra were obtained as KBr discs on a Perkin-Elmer Paragon 1000 FT-IR spectrophotometer from 4000 to 250 cm^{-1}. UV-Vis spectra were obtained on a Perkin-Elmer Lambda 20 spectrophotometer equipped with an integration sphere for diffuse reflectance spectra. Magnetic susceptibility measurements were carried out using a Sherwood Scientific Magnetic susceptibility balance and $Hg[Co(SCN)_4]$ as the calibrant. Diamagnetic corrections were made using Pascal's constants [16].

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2.2. *Preparation of the metal(II) complexes*

Various complexes were prepared by the addition of 2 mmol of $CoCl_2 \cdot 6H_2O$ (0.4759 g), $Co(CH_3COO)_2 \cdot 4H_2O$ (0.4981 g), $CuCl_2 \cdot 2H_2O$ (0.3409 g), or $Zn(CH_3COO)_2 \cdot 2H_2O$ (0.4389 g) dissolved in 20 mL of absolute ethanol to a stirring solution of 4 mmol of phenylthiourea (0.6089 g) in 40 mL absolute ethanol. The mixture was refluxed for 6 h, and filtered, the solvent was removed *in vacuo* and the product was washed with ethanol and diethyl ether.

2.3. *Synthesis of $[FeCl_3(SC(NH_2)NHC_6H_5)_3]$*

$FeCl_3 \cdot 6H_2O$ (0.5406 g, 2 mmol) was dissolved in 20 mL ethanol, with phenylthiourea (0.9133 g, 6 mmol) dissolved in 40 mL ethanol, and refluxed for 6 h. The solvent was removed *in vacuo* and the product was washed with ethanol and diethyl ether.

2.4. *X-ray crystallography*

Single crystals suitable for X-ray analysis for $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$ were obtained after a few days by slow evaporation of ethanolic solution of the complex. The data sets for the single crystal X-ray studies were collected with Mo-Kα radiation at 100 K on a Bruker SMART APEX CCD diffractometer equipped with an Oxford Cryosystems low-temperature device. A semi-empirical absorption correction was applied using SADABS [17] with maximum and minimum transmissions of 0.8450 and 0.7502, respectively. The structure was solved by direct methods and refined employing full-matrix least-squares with the program SHELXL-97 refining on F^2 [18]. All non-H atoms were refined anisotropically. Hydrogens bonded to C and O were included in the calculated positions while those bonded to N were found by difference Fourier techniques and refined isotropically.

2.5. *Qualitative antimicrobial assay*

Six pathogenic microbials were used to test the biological potentials of the compounds: *Escherichia coli* (ATCC 8739), *Pseudomonas aeruginosa* (ATCC 7700), *Klebsiella pneumoniae* (ATCC 4352), *Basicullus cereus* (ATCC 10702), *Staphylococcus aureus* (ATCC 6538), and *Bacillus pumilus* (ATCC 14884) cultures as obtained from the American Type Culture Collection (ATCC). The antibacterial activity of the complexes was qualitatively determined by a modified disc diffusion method [19]. A lawn of microorganisms was prepared by evenly spreading inocula onto nutrient agar set in Petri dishes. Whatman no. 1 filter paper discs of 6-mm diameter were impregnated with stock solution of the complexes and dried under sterile conditions. The dried discs were then placed on previously inoculated agar surface. The plates were incubated overnight at 37°C. Antibacterial activity was indicated by the presence of clear inhibition zones around the discs. Commercially available ampicillin was used for antibacterial control.

2.6. *Quantitative antimicrobial assay*

Substances showing positive antibacterial activity *via* the disc diffusion assay were subjected to the broth diffusion method for quantitative measurement of microbiostatic (inhibitory) activity as described by Hufford and Clark [20]. The lowest concentration that completely inhibited visible microbial growth was recorded as the minimum inhibitory concentration (MIC). Ampicillin was used as positive control for bacteria.

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3. Results and discussion

3.1. *Syntheses*

Zn(II), Cu(II), Co(II), and Fe(III) complexes of phenylthiourea have been synthesized by reaction between the metal salt and phenylthiourea in ethanol. The complexes are air-stable and formulated as $[M(OOCCH_3)_2(ptu)_2]$, $[MCl_2(ptu)_2]$, and $[FeCl_3(ptu)_3]$, where M = Zn, Co, or Cu and ptu = phenylthiourea. Analytical and spectroscopic data are consistent with the proposed formulation. The analytical data of the compounds are presented in table 1; proposed structures for the complexes are shown in figures 1 and 2.

3.2. *Crystal structure of* $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2]\cdot C_2H_5OH$

Single X-ray studies of the zinc compound were undertaken to determine the coordination sphere around Zn(II). The molecular structure of the complex with atom numbering scheme is shown in figure 3. The crystal data and structure refinement parameters are presented in table 2 and selected bond lengths and angles are given in table 3. The structure of the complex consists of orthorhombic *Pca*2(1) space group. The zinc is tetrahedrally coordinated in ZnO_2S_2 form. The distorted tetrahedral coordination around zinc consists of two terminal, monodentate, S-donating phenylthiourea ligands and one oxygen from each monodentate acetate, with an enlargement of S(1)–Zn(1)–S(1) [115.82(2) Å] and slight enlargement of O(3)–Zn(1)–O(1) [110.24(7) Å] and O(3)–Zn(1)–S(1) [112.53(5) Å] while there is a large compression of

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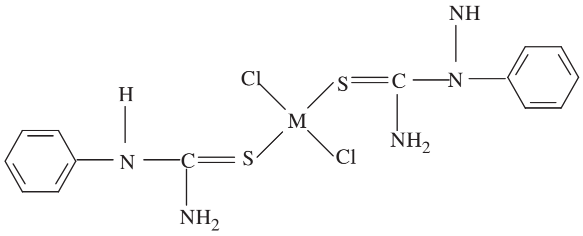
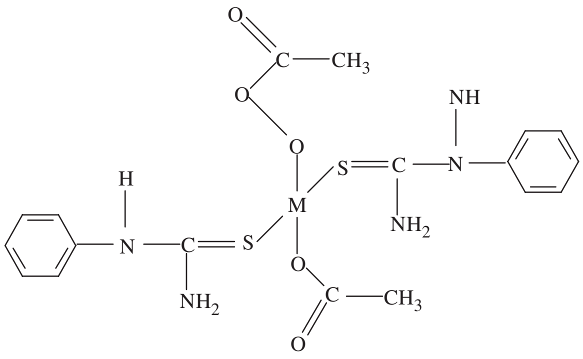
Table 1. Analytical data for the compounds.

Compounds	Empirical formula	Formula weight	Elemental analyses (Calcd) C	H	N	S
$[CoCl_2(ptu)_2]$	$CoCl_2C_{14}H_{16}N_4S_2$	434.27	39.10 (38.72)	4.14 (3.71)	12.62 (12.90)	14.34 (14.77)
$[Co(CH_3COO)_2(ptu)_2]$	$CoC_{18}H_{22}N_4S_2O_4$	486.46	44.67 (44.90)	4.12 (4.61)	11.32 (11.64)	13.19 (13.32)
$[CuCl_2(ptu)_2]$	$CuCl_2C_{14}H_{16}N_4S_2$	438.88	38.02 (38.31)	3.28 (3.67)	12.43 (12.77)	14.18 (14.61)
$[Zn(CH_3COO)_2(ptu)_2]$	$ZnC_{18}H_{22}N_4S_2O_4$	487.91	43.98 (44.31)	4.19 (4.54)	11.01 (11.48)	12.89 (13.14)
$[FeCl_3(ptu)_3]$	$FeCl_3C_{21}H_{24}N_6S_3$	618.86	40.38 (40.76)	4.10 (3.91)	13.24 (13.58)	15.19 (15.54)



M=Co, Cu



M=Co, Zn

Figure 1. Proposed structure for metal(II) complexes.

O(1)–Zn(1)–S(1) [103.68(5)] and O(1)–Zn(1)–S(2) [104.44(5) Å] angles with respect to ideal tetrahedral. The distorted tetrahedral geometry around zinc can be attributed to the slight difference between the electronegativities of O and S or steric hindrance of the phenylthiourea ligands and intramolecular hydrogen bonding interactions (N–H ··· O) between phenylthiourea and the acetate ligands (table 4). A highly crowded environment around zinc and the formation of intramolecular hydrogen bonds preclude bidentate binding of the acetate to zinc [21]. Distorted tetrahedral coordination with monodentate carboxylates is normal for complexes of the type $[Zn(thiourea)_2(CH_3COO)_2]$ [21–25]. The zinc is too small to allow a chelating mode

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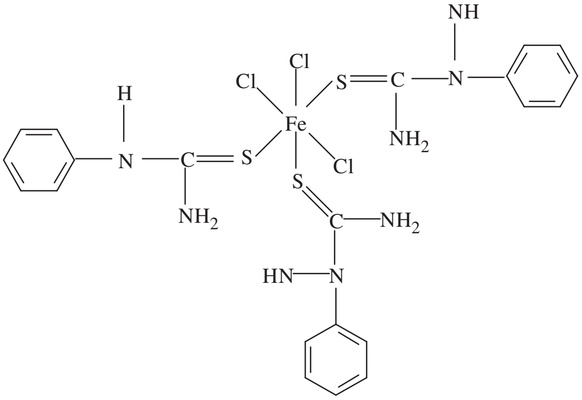

Figure 2. Proposed structure for [$FeCl_3(ptu)_3$].

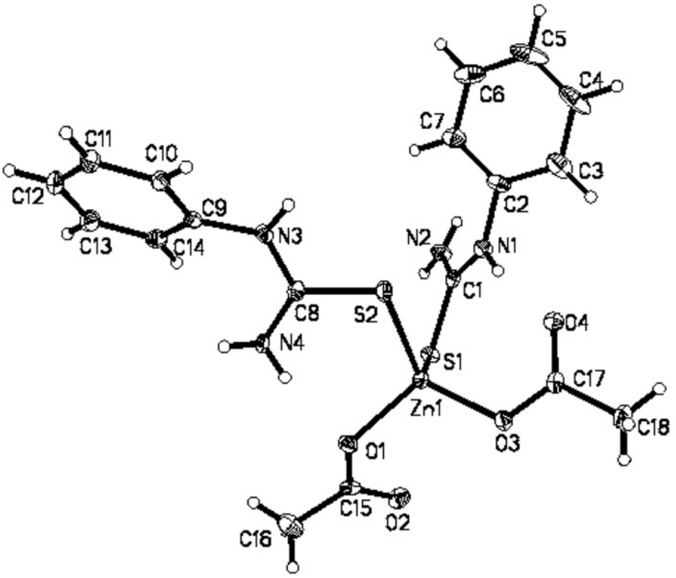

Figure 3. X-ray crystal structure of [$Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2$].

of coordination by carboxylate or any other means of increasing the coordination number from four.

In the coordinated acetate ligand, the longer carboxylate bonds O(1)–C(15) [1.294 Å] and O(4)–C(17) [1.240 Å] with greater single bond character involve the oxygen which coordinates to zinc. The lengths of the N–C bond in phenylthiourea in the complex are N(4)–C(8) = 1.316(3) Å, N(2)–C(1) = 1.324(3) Å, N(1)–C(1) = 1.327(3) Å, and C(8)–N(3) = 1.335(3) Å. These C–N bond lengths with an average of about 1.32 Å are considerably shorter than expected for a typical single C–N bond (1.47 Å) and closer to that of C–N double bond (1.28 Å) [26]. The C–N distance in the compound,

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Table 2. Summary of crystal data and structure refinement parameters.

Compound	$[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$
Empirical formula	$C_{20}H_{28}N_4O_5S_2Zn$
Formula weight	533.95
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Orthorhombic
Space group	*Pca*2(1)
Unit cell dimensions (Å)	
a	23.270(6)
b	8.282(2)
c	12.644(3)
Volume (Å^3), *Z*	2436.9(11), 4
Calculated density (Mg m^{-3})	1.4555
Absorption coefficient (mm^{-1})	1.217
F(000)	1112
Crystal size (mm^3)	0.45 × 0.36 × 0.15
θ range for data collection (°)	1.75–26.41
Limiting indices	$-29 \leq h \leq 29$; $-5 \leq k \leq 10$; $-15 \leq l \leq 15$
Reflections collected	13,355
Independent reflection	4851 [R(int) = 0.0333]
Completeness to $\theta = 26.40$ (%)	99.8
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4851/1/311
Goodness-of-fit on F^2	0.992
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0276$, $wR_2 = 0.0.0566$
R indices (all data)	$R_1 = 0.0322$, $wR_2 = 0.0580$
Largest difference peak and hole (e Å^{-3})	0.307 and −0227

Table 3. Selected bond lengths and angles for $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$.

Bond lengths (Å)		Bond angles (°)	
Zn(1)–O(3)	1.9706(16)	O(3)–Zn(1)–O(1)	110.23(7)
Zn(1)–O(1)	1.9784(17)	O(3)–Zn(1)–S(1)	112.53(5)
Zn(1)–S(1)	2.3272(8)	O(1)–Zn(1)–S(1)	103.68(5)
Zn(1)–S(2)	2.3586(8)	O(3)–Zn(1)–S(2)	109.54(5)
N(1)–C(1)	1.327(3)	O(1)–Zn(1)–S(2)	104.44(5)
N(1)–C(2)	1.422(3)	C(15)–O(1)–Zn(1)	115.82(3)
N(1)–H(1 N)	0.78(3)	C(17)–O(3)–Zn(1)	117.41(15)
N(2)–C(1)	1.324(3)	O(3)–Zn(1)–O(1)	117.11(16)
N(3)–C(8)	1.335(3)	C(3)–N(1)–C(2)	128.5(2)
N(3)–C(9)	1.415(3)	C(1)–S(1)–Zn(1)	107.69(9)
N(3)–H(3 N)	0.84(2)	C(8)–S(2)–Zn(1)	107.80(9)
N(4)–C(8)	1.316(3)	N(2)–C(1)–N(1)	121.6(2)
S(1)–C(1)	1.732(2)	N(2)–C(1)–S(1)	117.89(18)
S(2)–C(8)	1.732(2)	N(1)–C(1)–S(1)	120.53(19)
C(15)–C(16)	1.499(3)	O(2)–C(15)–O(1)	122.3(2)
C(17)–C(18)	1.501(3)	O(4)–C(17)–O(3)	123.8(2)
O(1)–C(15)	1.294	S(1)–Zn(1)–S(1)	115.82(2)
O(4)–C(17)	1.240	N(3)–C(8)–N(4)	121.0(2)

1.316–1.335 Å, indicates partial double bond nature, showing that the metal–sulfur bonds have high covalent character. These results are in agreement with the expected delocalization in the phenylthiourea molecule and confirmed by N(3)–C(8)–N(4) = 121.0(2) Å and N(2)–C(1)–N(1) = 121.6(2) Å showing sp^2 hybridization

Table 4. Hydrogen bond details for $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(1 S)–H(1O)···2(2)$^{\#1}$	0.82	2.06	2.811(3)	152.3
N(1)–H(1 N)···O(4)	0.78(3)	2.07(3)	2.848(3)	170(3)
N(2)–H(2 M)···O(1 S)$^{\#2}$	0.93(3)	1.97(3)	2.888(3)	167(2)
N(3)–H(3 N)···O(4)$^{\#3}$	0.84(2)	2.15(3)	2.954(3)	160(3)
N(2)–H(2 N)···O(3)$^{\#4}$	0.80(3)	2.16(3)	2.916(3)	156(3)
N(4)–H(4 N)···O(2)$^{\#5}$	0.76(3)	2.16(3)	2.857(3)	153(3)
N(4)–H(4 M)···O(1)	0.83(3)	1.98(3)	2.800(3)	168(3)

Symmetry transformations used to generate equivalent atoms: $^{\#1}-x+3/2, y-1, z+1/2$; $^{\#2}-x+3/2, y, z-1/2$; $^{\#3}-1+1, -y+2, z+1/2$; $^{\#4}x, y-1, z$; and $^{\#5}-x+3/2, y, z+1/2$.

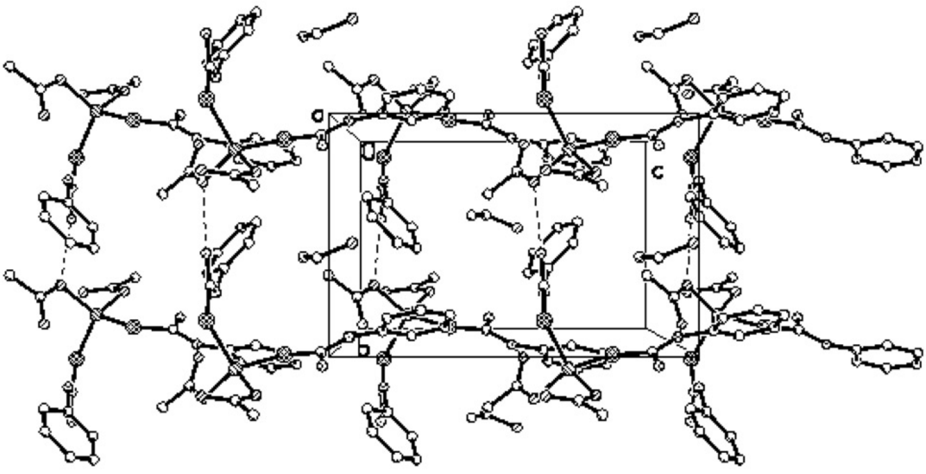

Figure 4. Crystal packing for $[Zn(SC(NH_2)NHC_6H_5)_2(OOCCH_3)_2] \cdot C_2H_5OH$.

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on C(8) and C(1). The two C–N bonds, N(3)–C(9) = 1.415(3) Å and N(1)–C(2) = 1.423(7) Å have typical C–N single bond lengths. The Zn–S distances [average 2.3429(8) Å] and Zn–O distances [average 1.9745(16) Å] indicate a fairly strong covalent interaction. The average C–S and C–N distances of 1.732(2) and 1.3565(3) Å, respectively, of the phenylthiourea molecules agree well with the values 1.725(19) and 1.3565(16) Å for terminally coordinated thiourea [27]. The crystal structure consists of discrete $[Zn(SC(NH_2)NHC_6H_5)_2(OOCH_3)_2] \cdot C_2H_5OH$ molecules linked to four other molecules by hydrogen bonds (table 4). Packing of the complex (figure 4) shows that the intermolecular hydrogen bonding interactions lead to sheets of molecules lying parallel to each other with ethanol found between the sheets and involved in intermolecular hydrogen bonds. There are three intramolecular hydrogen bonds within the asymmetric unit and several intermolecular H-bonds. Thus, each molecule of phenylthiourea acts as an H-bond donor as well as an acceptor.

3.3. *Infrared spectra of the complexes*

Infrared (IR) spectra of the free ligand and the metal complexes were studied and bands were assigned based on careful comparison. In the region 3000–3488 cm^{-1}, the asymmetric and symmetric N–H stretching bands of the free ligand observed at 3488 sh, 3423, 3278 sh, and 3181 cm^{-1} were shifted to higher wavenumbers on formation of the complexes. The observed shift is due to formation of S → M bonds in all the complexes, which lead to an increase in the double bond character for the C–N bond and an increase in the carbon-to-sulfur bond [28–30]. These could also be attributed to the overlap of ν(N–H) from different ligands or inter- and intra-molecular hydrogen bonding. This indicates that NH of phenylthiourea is not involved in coordination. The single crystal X-ray structure for the Zn(II) complex confirmed the existence of hydrogen bonding interactions. The strong band observed at 1610 cm^{-1} in the spectrum of ligand shifted to 1610–1589 cm^{-1} in the complexes. The band at 1447 cm^{-1} in the ligand assigned to the N–C–N stretching vibration shifted in all the complexes to about 1455 cm^{-1}. In the metal complexes, the shift could be attributed to greater double bond character of the C–N bond. The NH rocking vibration, N–C–N and C=S stretching vibrations as multiple bands in the region 1273–1294 cm^{-1} in the ligand occur as a single broad band in all the complexes. The characteristic absorptions in spectra of all the complexes are similar, which indicate that the complexes have similar coordination. IR spectra of the complexes confirm that phenylthiourea is coordinated to metal *via* the sulfur with a reduction in π-electron density of the C=S bond. The ν(C=S) bond of the free ligand, which appears at 797 cm^{-1}, is red-shifted to 727 cm^{-1} in the complexes.

3.4. *Electronic spectra and magnetic properties of the complexes*

Co(II) occurs in a great variety of structural environments and thus gives varied spectra and magnetic properties [31]. For high spin d^7 systems, the ground term is ^4F with a low-lying ^4P excited term. Six-coordinate octahedral or pseudo-octahedral species will exhibit three transitions [32, 33], $^4T_{1g}(F) \rightarrow {}^4T_{2g}$, $^4A_{2g} \rightarrow {}^4T_{1g}$, and $^4T_{1g}\,(F) \rightarrow {}^4T_{1g}(P)$. The second transition is very weak and rarely observed. A wide variety of tetrahedral and pseudo-tetrahedral Co^{2+} complexes exist mostly with intense blue or green color, though other color derivatives are known. The $^4A_2(F) \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ transitions appear as multiple absorption in the near and visible regions, respectively. The intensities of these bands are generally of the order 10–10^2 for $^4A_2(F) \rightarrow {}^4T_1(F)$ and $10^2 - 2 \times 10^3\ L\,mol^{-1}\,cm^{-1}$ for $^4A_2 \rightarrow {}^4T_1(P)$. There are also bands occurring as shoulder on the high-frequency side assigned to $^4T_{1g} \rightarrow {}^4T_{1g}(F)$. The electronic spectra of $[CoCl_2(ptu)_2]$ and $[Co(OOCCH_3)_2(ptu)_2]$ showed two bands at 580 and 670 nm typical of tetrahedral cobalt(II). There is no ambiguity about assignments in tetrahedral complexes because only two bands are expected. Tetrahedral Co(II) complexes are expected to have room temperature magnetic moments in the range 4.20–4.60 B.M. while octahedral complexes should have moments between 4.70 and 5.20 B.M. A magnetic moment of 4.32 B.M. for $[CoCl_2(ptu)_2]$ and 4.39 B.M. for $[Co(OOCCH_3)_2(ptu)_2]$ confirmed the proposed tetrahedral formulation for the complexes.

A survey of copper(II) electronic spectroscopy presents difficulty because of the lack of definitive statements which could relate spectra to structure. Since the ground state in an octahedral field is the Jahn–Teller unstable ^2E_g, very few regular octahedral copper(II) complexes exist. In octahedral Cu(II) complexes, a single absorption band in the visible region corresponding to $^2E_g \rightarrow {}^2T_{2g}$ transition is expected. Due to strong

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Jahn–Teller distortion, octahedral Cu(II) complexes often give broad bands resulting from several overlapping bands or, where the bands are resolved, up to three close bands [34, 35]. For approximately regular tetrahedral geometry, a single broad band of about 10^2 molar absorptivity located near the IR region, is usually observed with the spectra being blank in certain region. The spectra of Cu(II) complexes in square planar geometry normally show two bands in the visible region. The spectrum of $[CuCl_2(ptu)_2]$ shows two bands of low-to-medium intensity at 470 and 625 nm that are assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow E_g$ transitions, respectively, in the four-coordinate square planar geometry [36–39]. A magnetic moment of 1.93 B.M. confirms the suggested square planar arrangement proposed for the complex. Iron(III) is a moderately oxidizing ion and many of its complexes exhibit ligand-to-metal charge transfer transitions. In general, both $L \rightarrow {}^2T_{2g}$ and $L \rightarrow {}^2E_g$ transitions may be expected [33]. In most cases, the d–d absorption in octahedral complexes is rarely observed because the ligand-to-metal charge transfer absorptions obscure such weak bands. Furthermore, the high-spin iron(III) complexes are not stabilized by crystal field. The electronic spectrum of $[FeCl_3(ptu)_3]$ showed absorption at about 320 nm which could be attributed to $L \rightarrow MCT$. Iron(III) complexes with high-spin electronic configuration have magnetic moments at room temperature close to 5.9 B.M. and many exceed 2.0 B.M. due to orbital contribution if they are low spin. Magnetic moments of 5.4 B.M. for the complex indicates that it is a high-spin octahedral Fe(III) complex [33].

3.5. *Antibacterial activity*

The *in vitro* antibacterial properties of the complexes were evaluated against Gram-positive and Gram-negative bacteria. The obtained results are given in table 5. The complexes showed varied bacterial activities but some of the complexes are more active than ampicillin. A significant inhibitory activity higher than that of the ligand is displayed by all the metal complexes against all bacterial isolates with the exception of *P. aeruginosa* in which the ligand is more active than all the corresponding metal complexes and also against *B. cereus* in which the Cu(II) and Fe(III) complexes are less active than the ligand. The Zn(II) and Co(II) complexes showed the highest activities against all bacterial isolates. The MICs were determined for all the complexes and presented in table 6. The values were between 0.625 and 5 mg mL^{-1}. The ligand and zinc complexes with MIC value of 0.625 mg mL^{-1} appear to be the most toxic, while the Cu and Co complexes with the highest MIC value of 5 mg mL^{-1} appear to be the

Table 5. Zones of inhibition in mm of the compounds against various bacteria.

	Zones of inhibition for active compounds					
Organisms	Ligand	$[Zn(CH_3COO)_2(ptu)_2]$	$[CuCl_2(ptu)_2]$	$[FeCl_3(ptu)_3]$	$[CoCl_2(ptu)_2]$	Ampicillin
E. coli	10.5	12.5	–	12	12.5	11.5
P. aeruginosa	13	12	10	–	12	11.5
K. pneumoniae	10.5	12	13	11	12	12
B. cereus	11.5	14	10.5	10.5	14	12.5
S. aureus	12	13.5	13	15	13.5	12
B. pumilus	12.5	15	15	13	15	12.5

Table 6. MIC in $mg\,mL^{-1}$.

Organisms	Ligand	$[Zn(CH_3COO)_2(ptu)_2]$	$[CuCl_2(ptu)_2]$	$[FeCl_3(ptu)_3]$	$[CoCl_2(ptu)_2]$
E. coli	0.625	0.625	2.5	1.25	2.5
P. aeruginosa	2.5	1.25	1.25	5	1.25
K. pneumoniae	2.5	2.5	2.5	2.5	2.5
B. cereus	2.5	2.5	5	2.5	5
S. aureus	2.5	2.5	5	2.5	2.5
B. pumilus	2.5	2.5	2.5	2.5	2.5

least toxic. It can thus be concluded that toxicity does not appear to contribute to the activity of the most active complexes. Even though all the complexes showed enhanced activity against *B. pumilus*, their toxicity is intermediate.

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4. Conclusions

We report the synthesis, characterization, and antibacterial studies of Co(II), Cu(II), Zn(II), and Fe(III) complexes of phenylthiourea. The complexes were formulated as either four coordinate for the metal(II) or six coordinate for Fe(III). The single crystal X-ray structure of the Zn(II) complex showed that the metal ion is coordinated to two phenylthioureas through sulfur and two acetates to complete the four-coordinate geometry around Zn. The antibacterial screening of the complexes showed selective activity for the complexes against *S. aureus* and *B. pumilus*, while the ligand is more active than the complexes against *P. aeruginosa*.

Supplementary material

CCDC no. 680336 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif or from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgments

The authors thank the University of Zululand for microanalyses and GMRDC: University of Fort Hare and NRF for the financial support. They also thank Paul O'Brien and M. Helliwell (University of Manchester), A.O. Oyedeji (University of Zululand) for their contributions.

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