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Complexes of 1,3-Diisobutyl Thiourea with Copper(I), Zinc(II) and Mercury(II): Their Antioxidant and Antibacterial Evaluation

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Abstract: The reaction of 1,3-Diisobutyl thiourea (Tu) with metal salts, {[CuX (X = Cl, I)], [ZnCl₂] and [HgI₂] in an appropriate stoichiometric ratio afforded the corresponding metal complexes [Tu₂CuCl] (1), [Tu₃Cu] (2), [Tu₂ZnCl₂] (3) and [Tu₂HgI₂] (4) in good yields. The FT-IR data show typically broad signals (3278–3288 cm⁻¹) attributed to the involvement of NH bonds in extensive hydrogen bonding. The structures of complexes were proposed based on a spectroscopic data set. Compounds **1** and **2** were additionally characterized by single-crystal X-ray analysis. Complexes **1–4** were tested for their free radical scavenging efficiency using 2,2-diphenyl-1-picrylhydrazyl free radical (hereafter abbreviated as DPPH). The free radical scavenging activity was a function of decrease in the resultant absorption of DPPH solution after the mixing of an appropriate concentration of the respective complex. The activity of complexes was determined to be dose dependent and increased concentration of the complex resulted in improved antioxidant activity. Compound **1** was found to be the most efficient, with 79.9% free radical scavenging activity. Complexes were also tested for their efficiency against selected strains of bacteria (*E. coli*, *S. flexneri*, *S. typhi*, and *P. aeruginosa*) and the activities were compared to commercially available standard drug *cephradine*. Compound **1** was more active against *P. aeruginosa* (ZI 13.25), while compound **4** was found to be more active against *E. coli* (ZI 11.0), *S. flexneri* (ZI 11.2), and *S. typhi* (ZI 10.5).

Keywords: antioxidant activity; antibacterial efficiency; diisobutylthiourea; metal complexes

1. Introduction

Thiourea derivatives make a versatile group of compounds, with applications in organic, coordination, and material chemistry [1,2]. These compounds act as organocatalysts in a variety of reactions which lead to outstanding products [3–6]. There are two potential functional groups in thiourea derivatives, the C=S and NH groups. These sites provide interesting coordination modes and make thiourea derivatives very attractive candidates for several applications. The NH function is mainly responsible for the establishment of H-bonding and is able to make these compounds usable as sensors [7,8]. The C=S function has also been effectively used for sensor applications of metal ions (cations) [9,10] and has a very rich coordination chemistry with late transition metals [11,12]. Since the discovery

of cisplatin, coordination compounds have been in use against various ailments. Thus, the design and synthesis of coordination compounds has continued to remain a hot topic. The two main segments in the designing of a coordination compound for biological function are the ligand and the metal ion. The selection of the ligand is made on its coordination ability to afford stable synthons, the least toxicity and easy accessibility. Metal ions should be biologically acceptable, and their complex is supposed to tolerate physiological conditions for better efficiency. Since thiourea is the active part of bioorganic chemistry for a handsome number of applications, its selection as a ligand raises no question [13–16]. Complexes with late transition metals, such as Zn and Hg, possess photoluminescence properties and applications in nonlinear optics [17–19]. Complexes with Cu and Zn have been synthesized and tested in the field of bioinorganic chemistry [20–23]. The wide range of biological activities of thiourea complexes such as antimicrobial, pesticidal, herbicidal, rodenticidal, and anticancer exponentially increases the importance of these compounds. The modification of properties in a desired direction such as hydrophobicity, biocompatibility, and the potency of compounds can be varied by changing the nature and size of certain substituents.

Recently, we reported Cu complexes stabilized by monodentate non-thiourea ligands bearing coordination numbers (CN) four [24,25] and six [26,27], where steric bulk and/or M-X fragment (X = halogen, AcO) played a vital role in coordination around the metal ion. These complexes with thiourea ligands [28,29] showed better biological activities. Thus, we extended our studies and treated the thiourea ligand with Cu(I) metal salts, where halogen function was found responsible for defining the CN of the metal ion. Under identical conditions, Zn and Hg afforded the proposed complexes. Besides structural studies, these complexes were evaluated for their antioxidant and antibacterial efficiency.

2. Experimental Section

2.1. General and Spectroscopy

The handling of chemicals and other reagents was carried out under aerobic conditions. Solvents were distilled prior to use. The ligand was prepared by a literature procedure [30] and analytical-grade metal salts CuI, CuCl, ZnCl₂ and HgCl₂ were purchased from TCI, Japan, or Sigma Aldrich and were used as received. The ¹H- and ¹³C-NMR spectra (for ca. 5–10% solutions) were recorded by VARIAN INOVA 300 MHz in deuterated chloroform at room temperature. Chemical shifts are given relative to TMS (δ ¹H(CHCl₃) = 7.26 and δ ¹³C(CHCl₃) = 77.16 ppm). FT-IR spectra of complexes were recorded by the SHIMADZU model 8400s as KBr pellets, in the range 4000–400 cm⁻¹. The EIMS analyses were carried out with the help of a FOCUS DSQ (thermo) mass spectrometer and the m/z refer to isotopes ¹H and ¹²C, ¹⁴N, and ⁶³Cu. The crystal structure of complex **1** and **2** was determined by STOE IPDSII, fitted with a low-temperature unit. In both experiments/diffractometers, Mo-K α source with λ = 0.71073 Å was used. Crystal structure refinements and solutions were accomplished by software SIR97, SHELXL97, WinGX, and PLATON [31–35].

2.2. Synthesis of Compounds 1–4

For the synthesis of compound **1**, a solution of CuCl (0.0501 g, 0.51 mmol) was prepared in acetonitrile and was kept stirring for 2 h, followed by the dropwise addition of 1,3-diisobutyl thiourea (0.2802 g, 1.49 mmol, solution in acetonitrile) over a time of ca. 10 min. The color of the resultant solution turned from yellow to colorless which indicated the reaction was complete. Stirring of the reaction mixture was continued for 12 h, in order to ensure maximum product formation. The reaction mixture was filtered for the separation of unreacted salt and other insoluble material and the filtrate was kept for slow evaporation at room temperature. Colorless crystals of the desired compound **1** appeared after a few days and were separated from the mother liquor, then studied with the help of EI-MS, UV/Vis spectroscopy, FT-IR, and X-ray diffraction. Following the same procedure, compound **2** was prepared by treating CuI (0.0500 g, 0.26 mmol) and the ligand (0.148 g, 0.79 mmol) together; colorless block crystals were grown after 6 days. Compound **3** was obtained by treating ZnCl₂ (0.0602 g, 0.44 mmol) with the ligand

(0.167 g, 0.89 mmol), using MeOH as solvent. Colorless crystals appeared after 2 days, were separated and then studied. Compound **4** was prepared in the same way, with HgI₂ (0.2407 g, 0.529 mmol) and the ligand (0.2003 g, 1.06 mmol) in MeOH.

Complex 1, bis(1,3-Diisobutylthiourea)copper(I) chloride: Yield: 60%; C₁₈H₄₀N₄ClS₂Cu; Found (Cal): C 45.54 (45.45), H 8.36 (8.48), N 12.06 (11.78); EI-MS: *m/z* (%) 188 (99) Tu, 255 (85) Cu-Tu, 96 (25) Cu-Cl; FT-IR (KBr) $\nu(\text{cm}^{-1}) = 3280\text{br}, 2965\text{s}, 2878\text{s}, 1734\text{s}$.

Complex 2, tris(1,3-diisobutyl thiourea)copper(I) iodide: Yield: 65%; C₂₇H₆₀N₆IS₃Cu; Found (Cal): C 38.47 (40.93), H 7.18 (8.01), N 10.65(11.12); MS (+ESI): *m/z* 188 (99) Tu, 254 (45) Cu-Tu, 380 (20) I-Cu-Tu; FT-IR (KBr) $\nu(\text{cm}^{-1}) = 3288\text{br}, 2971\text{s}, 2882\text{s}, 1751\text{s}$.

Complex 3, bis(1,3-diisobutylthiourea)zinc(II) chloride: Yield: 76 %; C₁₈H₄₀N₄Cl₂S₂Zn; Found (Cal): C 40.61 (42.15), H 7.39 (7.86), N 10.43 (10.92); ¹H-NMR (300 MHz, CDCl₃) δ (ppm) = 0.95 (br, Me), 1.96 (br, CH), 3.36 (br, CH₂), 6.06 (br, NH); ¹³C-NMR (75.8 MHz, CDCl₃); δ (ppm) = 20.2 (Me), 28.3 (CH), 52.4 (N-CH₂), 174.8 (C=S); MS(EI): *m/z* (%): 188 (99) Tu, 253 (25) Zn-Tu; FT-IR (KBr) $\nu(\text{cm}^{-1}) = 3278\text{br}, 2956\text{s}, 2868\text{s}, 1748\text{s}$.

Complex 4, bis(1,3-diisobutylthiourea)mercury(II) iodide: Yield: 79 %; C₁₈H₄₀N₄I₂S₂Hg; Found (Cal): C 26.24 (26.01), H 5.6 (4.85), N 7.57 (6.74); ¹H-NMR (300 MHz, CDCl₃) δ (ppm) = 0.97 (d, 24H, Me, $J(^1\text{H}, ^1\text{H}) = 6.63$ Hz), 2.01 (Sep, 4H, CH, $J(^1\text{H}, ^1\text{H}) = 6.67$), 3.21 (br, 8H, CH₂), 5.80 (br, 4H, NH); ¹³C-NMR (75.8 MHz, CDCl₃); δ (ppm) = 20.5 (Me), 27.9 (CH), 51.9 (N-CH₂), 176.9 (C=S); MS(EI): *m/z* (%) 188 (99) Tu, 328 (7) HgI, 456 (35) HgI₂; FT-IR (KBr) $\nu(\text{cm}^{-1}) = 3281\text{br}, 2961\text{s}, 2872\text{s}, 1741\text{s}$.

2.3. Determination of Antioxidant Potentials

DPPH is a stable free radical and is capable of utilizing its unpaired electron in a chemical interaction with any other species. The involvement of this unpaired radical with foreign species is a function of free radical scavenging of that species/compound. Compounds **1–4** were tested for their antioxidant activities against DPPH. A solution containing 0.039 g/100 mL of DPPH was prepared and used as a standard/control. Absorbance of this solution was measured at 517 nm under normal conditions of temperature. After mixing the solution of the respective compound with DPPH solution, a change in the resultant absorbance was observed. The decrease in maximum absorbance of the solution was taken as a function of the compound. Prior to the determination of absorbance, all solutions were incubated in the dark for 30 min at room temperature (23 ± 1 °C). The percent inhibition capacity of each complex (I)%, was calculated as below [36].

$$\text{Percent Inhibition I\%} = \frac{A_{\text{DPPH}} - A_{\text{sample}}}{A_{\text{DPPH}}} \times 100$$

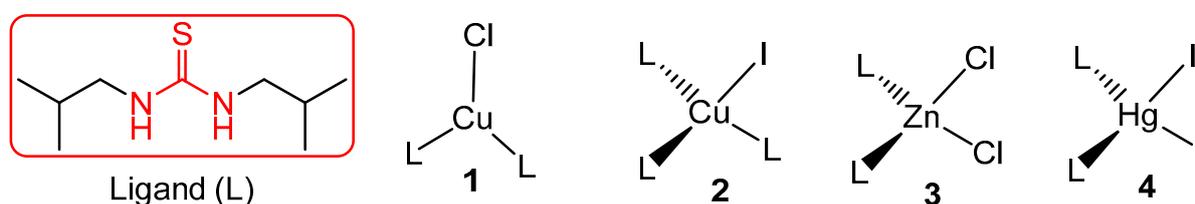
2.4. Antibacterial Screenings of Selected Compounds

The agar well diffusion assay was used to evaluate antimicrobial potentials of complexes **1–4** [37,38]. Sterile, nutrient agar was prepared and poured in Petri dishes. Bacterial cultures were evenly applied on the surface of the agar Petri dishes by sterile swab sticks. Wells of 6 mm diameter were bored (five per plate) with a sterile borer. An amount of 6.25 mg/mL of each compound was applied to each well. The commercially available antibiotic *cephradine* was used for comparing the efficiency of each complex. For the sake of accuracy, the same concentration of each complex and the standard was applied. The agar plates were covered with lids and were incubated at 37 ± 1 °C for 24 h in an oven. Growth inhibition was observed in each bore and the respective zones were measured manually. The diameter of the zones of inhibition is a measure of antimicrobial activity of the corresponding complex. The data presented for antibacterial activity are the average diameter of the zones of inhibition in mm.

3. Results and Discussion

3.1. General Chemistry and Spectroscopy

The proposed structures of compounds and the corresponding ligand (inserted) are shown in Scheme 1. The treatment of ligand (1,3-diisobutylthiourea) with copper(I) chloride in molar ratio 3:1, respectively, afforded Complex 1. The reaction of CuCl with a two-fold excess of the ligand was carried out under identical conditions and the same products were obtained. By changing the reaction medium from acetonitrile to MeOH, all attempts were unsuccessful in obtaining exclusively tetrahedral complex of geometry $[\text{CuL}_3\text{Cl}]$, $[\text{CuL}_2\text{Cl}_2]$, or $[\text{CuL}_4]\text{Cl}$, where L = thiourea ligand [39–41]. The ligand reacted with CuI in a molar ratio 3:1 and the proposed compound 2 was thus obtained. These observations reveal that the presence of halogen function can affect the coordination sphere around the metal ion. The reaction of the ligand with Zn and Hg metal ions was straightforward, as was reported for structurally analogous species [42].



Scheme 1. Structures of ligand (left inserted) and its corresponding complexes with Cu, Zn and Hg ions.

Complexes 1–4 were obtained as crystalline material from their respective reaction mixtures and structures of complexes were deduced from a consistent set of spectroscopic data. The FT-IR spectra of all compounds contain typically broad signals ($3278\text{--}3288\text{ cm}^{-1}$) that correspond to the involvement of NH bonds in extensive hydrogen bonding. NMR spectroscopy is a reliable technique in the structural elucidation of compounds and is of particular importance in coordination chemistry, where the coordination behavior of thiourea ligands can easily be determined to be an N or S donor. The $^1\text{H-NMR}$ of complex 3 and 4 show distinct typically broad signals at 4.01 and 3.47 ppm, respectively, which can be assigned unambiguously to NH group. These signals show considerable shift with respect to the free ligand (5.89 ppm, given in supporting information). The $^{13}\text{C-NMR}$ process is quite useful in this regard: the C=S signal appeared at 181.7 ppm in the free thiourea ligand and was found to be considerably shifted in complex 3 and 4 to 174.8 and 176.9 ppm, respectively. These data indicate the bond formation through the S atom, thus affording the proposed coordination behavior of the TU ligand [43]. The mass fragmentation pattern of compounds 1–3 was also studied using the EI-MS technique. The information retrieved from these data were not too informative because of the high-energy ionization technique. All the complexes gave a base peak at m/z 188, which corresponds to the ion of the thiourea ligand. A molecular ion peak for these complexes was not observed.

3.2. Structural Description of Complex 1

Ethyl fragments in the structure of compound 1 (shown in Figure 1) suffer from some sort of disorder which makes it very difficult to precisely solve and refine the structure. The diffraction data provide enough information which is sufficient for the establishment of connectivity. The reaction of the ligand with CuCl in molar ratio 3:1 exclusively afforded compound 1. The molecule is monoclinic, bearing space group Cc (further details pertaining to refinements and crystal structure solution are summarized in Table 1). The geometry around the metal ion is trigonal planar. Two thiourea ligands are attached to the metal ion through the S atom, which is normal behavior of thiourea derivatives [28]. Bond angles around the metal ion are $115.76(13)^\circ$, (S1-Cu1-S2), $120.94(11)^\circ$, and $123.30(12)^\circ$ (S1-Cu1-C1 and S2-Cu1-Cl , respectively). The sum of all three angles around metal ion is 360° , which clearly supports the trigonal environment. The Cu-S bond lengths with

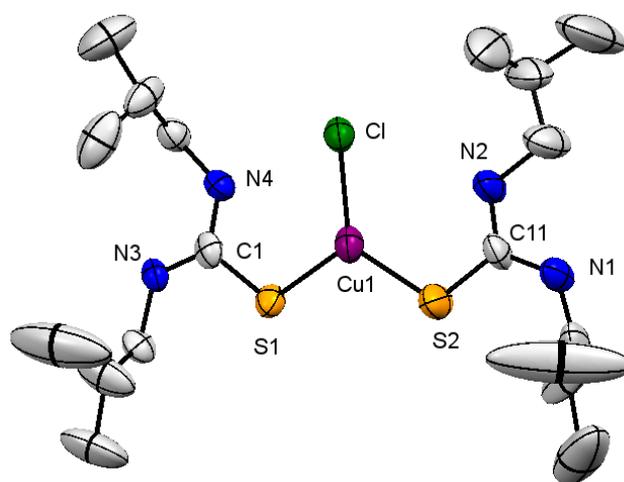
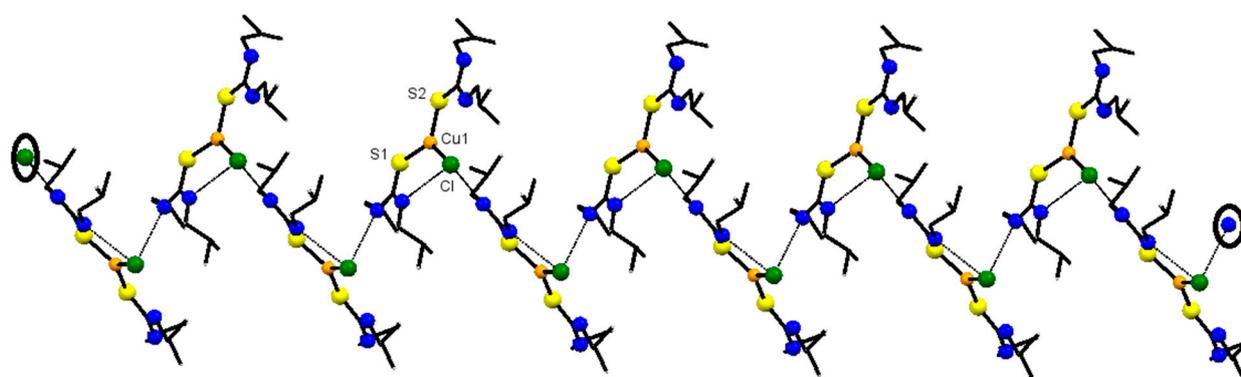
negligible difference, 2.213(4) and 2.216(3) Å, are shorter than the Cu-Cl bond (2.272(3) Å) and are within the expected limit [44] (Table 2). Coordination with the metal ion through S reduces the bond order between C and S; therefore, it results in C=S bond elongation as compared to the uncoordinated thiourea derivative and are comparable to structurally analogous compounds [28,30,45,46]. A close view of molecules of complex **1** in solid state reveals that chloro function is actively involved in intra- as well as intermolecular secondary interactions. The intramolecular separation distance between N4 ··· Cl is 3.268 Å, and the (intermolecular) Cl ··· N3 distance is 3.268 Å (Figure 2). The difference in bond lengths, C1-N3 1.306(14) and C1-N4 1.349(14) Å, can possibly be explained on the basis of intramolecular interactions wherein N atoms of one coordinated thiourea ligand are involved (Figure 2). Each molecule offers an N3 of a coordinated ligand to participate in secondary interactions, which is the probable reason for slightly different C-N bond lengths.

Table 1. Crystal structure solution and refinement parameters of complexes **1** and **2**.

Compound	1	2
Empirical formula	C ₃₆ H ₈₀ Cl ₂ Cu ₂ N ₈ S ₄	C ₂₇ H ₆₀ N ₆ CuIS ₃
Formula weight	951.30	755.43
Temperature (K)	296	133
Crystal system	Monoclinic	Trigonal
Space group	Cc	P-3
a, Å	19.675(5)	13.592(7)
b, Å	12.226(5)	13.592(7)
c, Å	10.772(8)	11.254(5)
B, deg	95.04(5)	90
Volume Å ³	2581.2(13)	1800.5(2)
Z/Z'	2/0.5	2/0.5
μ (mm ⁻¹)	1.12	1.66
F (000)	1016	788
Wavelength (Å)	0.71069	0.71069
Diffractometer	STOE-IPDSII	STOE-IPDSII
θ _{min} -θ _{max} , deg	1.963–26.240	1.730–26.174
Range of indices	−24 ≤ h ≤ 24 −15 ≤ k ≤ 15 −13 ≤ l ≤ 13	−16 ≤ h ≤ 16 −16 ≤ k ≤ 16 −13 ≤ l ≤ 13
Total number of reflections	17780	25350
R _{int}	0.123	0.048
Completeness of data to θ _{max} , %	99.4	99.7
T _{max} /T _{min}	None	0.813/0.915
Number of observed reflections (I > 2σ(I))	2450	2238
Number of refined parameters	243	127
Goodness of Fit	0.844	1.088
Crystal size	0.26 × 0.19 × 0.14	0.28 × 0.27 × 0.13
R ((I > 2σ(I)))	R ₁ = 0.0586 wR ₂ = 0.1176	R ₁ = 0.0279 wR ₂ = 0.0683
R for all reflections	R ₁ = 0.1411 wR ₂ = 0.1418	R ₁ = 0.0301 wR ₂ = 0.0713
Residual electron density (max/min), (e/Å ³)	0.46/−0.39	0.80/−0.59

Table 2. Selected bond lengths (Å) and angles (°) of structures 1 and 2.

Compound	Atoms	Bond Length	Atoms	Angles
1	Cu1-S2	2.213(4)	S2-Cu1-S1	115.76(13)
	Cu1-S1	2.216(3)	S2-Cu1-Cl	123.30(12)
	Cu1-Cl	2.272(3)	S1-Cu1-Cl	120.94(11)
	S1-C1	1.736(12)	N3-C1-N4	121.4(10)
	N3-C1	1.306(14)	N3-C1-S1	120.5(9)
	N4-C1	1.349(14)	N4-C1-S1	118.0(8)
	N2-C11	1.342(15)	N1-C11-N2	117.6(10)
	N1-C11	1.337(14)	N1-C11-S2	122.1(10)
2	I1-Cu1	2.610(5)	S1-Cu1-S1	100.32(2)
	Cu1-S1	2.336(6)	S1-Cu1-I1	117.55(16)
	S1-C1	1.713(2)	C1-S1-Cu1	112.72(7)
	N1-C1	1.329(3)	N1-C1-N2	118.08(19)
	N1-C2	1.456(3)	N1-C1-S1	120.88(19)
	N2-C1	1.335(3)	N2-C1-S1	120.03(16)
	N2-C6	1.456(3)		

**Figure 1.** Molecular structure of Complex 1, ball and stick representation with partial numbering scheme. All hydrogen atoms are omitted for clarity, summarized bond lengths (Å) and angles (°) are shown in Table 2. Two of the ethyl groups show disorder, which is the reason for relatively large displacement parameters and unusual bond distances (C21A-C51 1.08(3), C21A-C32 1.68(4) and C14-C35 1.29(3) Å).**Figure 2.** 1D representation of Complex 1, the infinite pseudo-polymeric zigzag chain stabilized by intermolecular NH...Cl interactions. Hydrogen atoms are omitted for clarity and hanging contacts at both ends of the chain are circled to make them prominent. Intramolecular NH...Cl interactions are also indicated.

3.3. Structural Description of Complex 2

The structure of complex **2** is depicted in Figure 3, together with selected bond lengths and angles. The structure solution and refinements were carried out as per details given in Table 1. The crystal structure is trigonal with space group P-3. The Cu⁺ ion is surrounded by three thiourea ligands and a halogen (iodide), making the tetrahedral geometry with expected deviation owing to hetero-ligands [47,48]. The ligand is attached through the S atom, as normally expected for this class of compounds. The angles S1-Cu1-S1 and S1-Cu1-I1 are 100.32(2) and 117.55(16), respectively, with the sum of all six angles amounting to 653.6°, which supports distorted tetrahedral geometry around the metal ion [49]. These features are within the expected limit and are very close to structurally analogous complexes [50,51]. The M-S bond distance of 2.336(6) Å for complex **2** is within the expected limit for analogous thiourea complexes [41]. The C=S bond slightly elongates (1.713(2) Å) with respect to the uncoordinated ligand (1.698 Å) because of electronic flow towards the metal ion. The abovementioned behavior of the ligand causes an electron delocalization over the S-C-N fragment [1,52]. There are a number of secondary short-range interactions within the molecules of the complex, which can be useful for further studies and in predicting certain applications of the complex. The hydrogen of C2H and N2H of each ligand are involved in interactions with S atoms of neighboring molecules. Each S atom of the ligand is pseudo-four-coordinated, and the supramolecular structure of complex **2** extends in a 3D fashion.

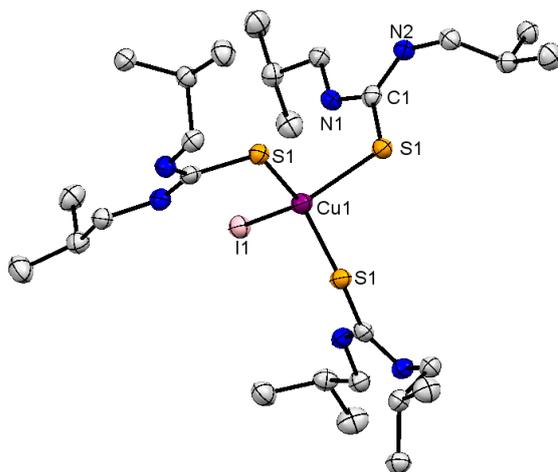


Figure 3. Molecular structure of compound **2** with partial numbering scheme. Thermal ellipsoid drawn at 50% probability level, hydrogens are omitted for simplicity, summarized bond lengths (Å) and angles (°) are given in Table 2.

3.4. Free Radical Scavenging Activities of Complexes 1–4

The inhibitory effects of thiourea complexes **1–4** were studied using DPPH as the free radical. For these complexes, which include S-coordinated 1,3-diisobutyl thiourea molecules, high antioxidant activity was discovered. The absorption intensity of DPPH was reduced by the addition of complexes **1–4**, in a dose-dependent manner ranging from 00–100 ppm. The decrease in absorbance of the resultant solution was quite regular, as expected for an antioxidant reagent. The percent RSA (radical scavenging activity) of compounds was at its lowest at a lower concentration and was at its maximum at a 100 ppm concentration of each complex, in a dose-dependent manner. A comparison of the activity of **1–4** at 100 ppm (maximum concentration) was found to be 79.9%, 19.5%, 29.3%, and 19.2%, respectively, which indicates that compound **1** is more potent as compared to **2–4**. Data pertaining to the free radical scavenging efficiency of complexes are summarized in Table 3 and the same are graphically described in Figure 4. The complex reveals a reasonable R² value of 0.9453, shown in Figure 5 (see Figures S1–S6 for complexes **2**, **3** and **4**) (see Supplementary Materials). Among these four complexes, **1** is a far better antioxidant

and the activity can be observed by the naked eye due to the change in the color of the solution after mixing the appropriate concentration with DPPH (Figure 6). The activity of compounds 2–4 were the least, and color change was difficult to be observed with the naked eye. The activity of compound 1 was better than the Cu complex stabilized by phosphine ligands, as has been reported recently [25].

Table 3. Percent free radical scavenging activities of compound 1–4.

Concentration (ppm)	1	2	3	4
20	63.6	5.2	9.4	6.5
40	66.7	13.7	16.8	12.5
60	74.9	18.2	18.2	15.6
80	78.2	19.2	27.9	16.0
100	79.9	19.5	29.3	19.2

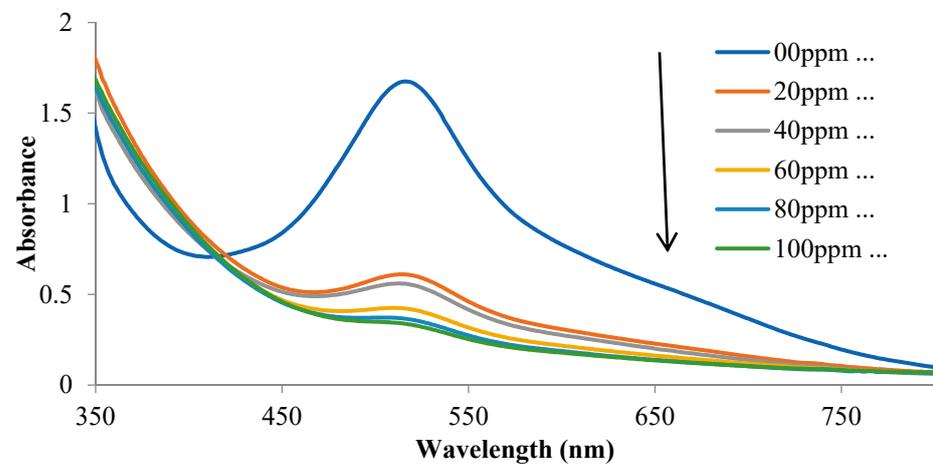


Figure 4. Absorption spectra of DPPH in the absence (top spectra) and presence of the compound 1 (20, 40, 60, 80, and 100 ppm). There is abrupt drop in the absorbance of the solution by addition of the antioxidant agent (compound 1).

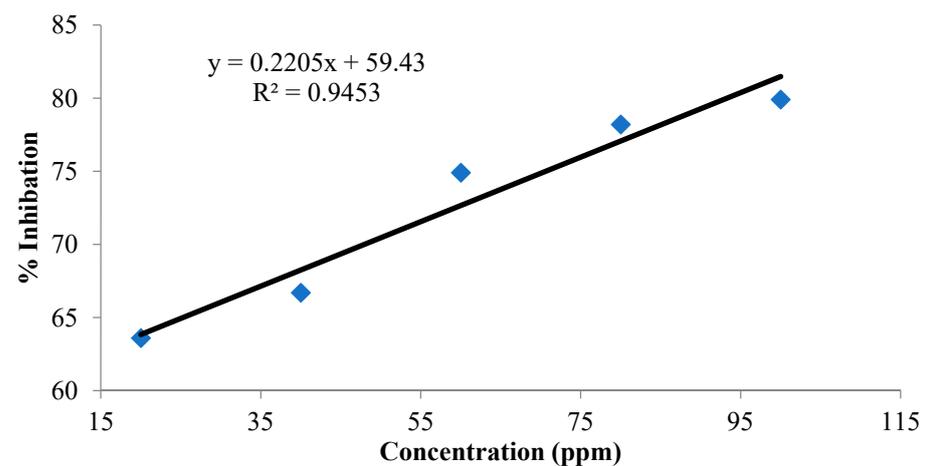


Figure 5. Graphical representation of percent inhibition versus concentration of compound 1 for radical scavenging activity.



Figure 6. Naked eye detection of DPPH radical scavenging activity of compound 1. Sample flask to the right-hand side contains free DPPH, and concentration of compound 1 increases in the preceding flasks from right to left.

3.5. Antibacterial Activity

The agar well diffusion method was used to assess the antimicrobial activity of complexes 1–4. *Escherichia coli*, *Shigella flexneri*, *Pseudomonas aeruginosa*, and *Salmonella typhi* were selected for this study and complexes 1–4 were studied against these strains. The antibacterial evaluation of these complexes reveal that they exhibit moderate activity in comparison to *cephradine*. The overall inhibition range of 6.2–13.25 mm (Table 4) was observed for these complexes. Compound 1 shows comparatively better activity against *E. coli* and *P. aeruginosa*, comparable with standard drugs, and compound 4 is most active against three strains: *E. coli*, *S. typhi* and *S. flexneri*. Compounds 2 and 3 were found to be poor antibacterial agents among these four complexes. The activity of all complexes and the standard is graphically represented in Figure 7.

Table 4. Antimicrobial activities of compounds 1–4, ZI were measured in mm.

Bacterial Strain	1	2	3	4	<i>Cephadrine</i>
<i>E. coli</i>	10.0	8.0	9.2	11.0	12.01
<i>S. typhi</i>	7.5	6.2	8.0	10.5	13.02
<i>S. flexneri</i>	9.0	7.5	8.7	11.2	14.50
<i>P. aeruginosa</i>	13.25	10.5	6.25	8.0	15

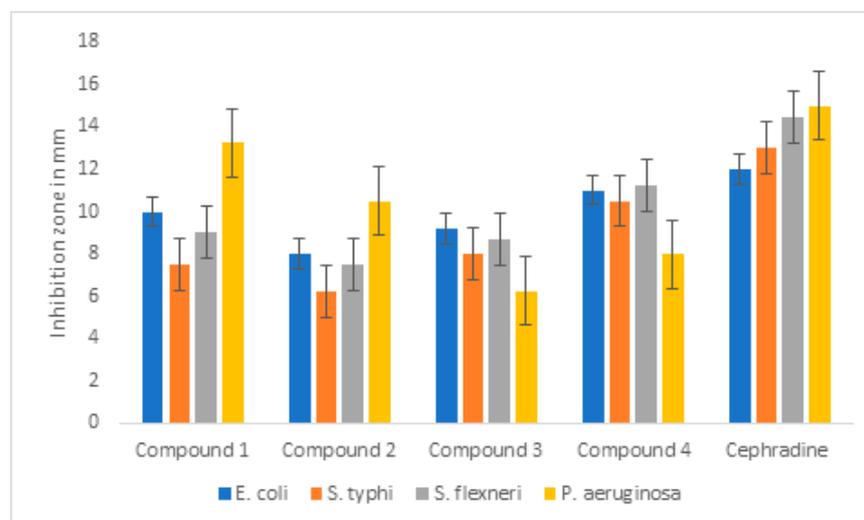


Figure 7. Graphical representation of antimicrobial activities of compounds 1–4.

4. Conclusions

Four new heteroleptic transition metal complexes (1–4) were successfully obtained by reacting 1,3-diisobutyl thiourea with CuCl, CuI, ZnCl₂, and HgI₂, respectively. Despite the same reaction conditions, reaction with CuCl and CuI afforded bis-ligated and tris-ligated copper halide complexes, respectively. Compounds 1 and 2 were also characterized by single-crystal X-ray analysis. The Zn and Hg metals were included in the study with the intent to explore the coordination behavior of the ligand, and the proposed geometries were obtained. All complexes were tested for their free radical scavenging ability and antimicrobial potentials; the data reveal that compound 1 is an excellent antioxidant and the activity could be observed with the naked eye. All compounds showed antioxidant potentials in a dose-dependent manner. In comparison to the standard, compound 1 was active against *E. coli* and *P. aeruginosa*, while compound 4 was a potent antibacterial agent against *E. coli*, *S. typhi* and *S. flexneri*. Future work regarding functionalization can explore potentials of thiourea complexes as antioxidant and antibacterial reagents.

Supplementary Materials: CCDC No 1,994,970 (1) and 1,979,130 (2) contain the supplementary crystallographic data for complex 1 and 2. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> accessed on 17 August 2021, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Figures S1–S6 are available online at <https://www.mdpi.com/article/10.3390/cryst11080989/s1>, Figure S1. Absorption spectra of DPPH in the absence of compound 2 (Top spectra) and presence of increasing concentration of the compound (20, 40, 60, 80 & 100 ppm). Arrow shows the change in absorption as a function of activity with respect to increasing concentration of compound 2. Figure S2. Plot of % Inhibition versus concentration of compound 2 for radical scavenging activity. Figure S3. Absorption spectra of pure DPPH, the absorbance decreased when compounds 3 was added, in a dose dependent manner. Figure S4. Percent inhibition versus concentration of compound 3 for radical scavenging activity. Figure S5. Absorption spectra of free radical (DPPH) in the absence (Top spectra) and presence of increased concentration of the compound 4 (20, 40, 60, 80 & 100 ppm). Arrow show the change in spectra on increasing concentration of compound. Figure S6. Plot of % Inhibition versus concentration of compound 4 for radical scavenging activity.

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