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Research Article

Copper(II) Complexes of 2-(Methylthiomethyl)anilines: Spectral and Structural Properties and *In Vitro* Antimicrobial Activity

Temitope E. Olalekan,[1] Denzil R. Beukes,[2] Bernardus Van Brecht,[3] and Gareth M. Watkins[1]

[1] *Department of Chemistry, Rhodes University, P.O. Box 90, Grahamstown 6140, South Africa*
[2] *Faculty of Pharmacy, Rhodes University, P.O. Box 90, Grahamstown 6140, South Africa*
[3] *Department of Chemistry, Nelson Mandela Metropolitan University, Port Elizabeth 6001, South Africa*

Correspondence should be addressed to Temitope E. Olalekan; topeolalekan11@yahoo.com

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Copper(II) complexes of 2-(methylthiomethyl)anilines (**1a**–**1f**) have been obtained and characterized by elemental analyses, IR, electronic spectra, conductivity, and X-ray crystallography. The complexes (**2a**–**2f**) have the structural formula $[CuCl_2L]$ with the bidentate ligand coordinating through sulfur and nitrogen. The single crystal X-ray diffraction data reveal that the copper complex (**2f**) has a tetragonally distorted octahedral structure with long Cu–Cl equatorial bonds. Magnetic susceptibility measurements indicate the availability of one unpaired electron in the complexes and the conductivity measurements in DMF show their behaviour as nonelectrolytes. The solid reflectance spectra and the electronic spectra of the complexes in DMSO were determined. The ligands and their copper complexes were screened for *in vitro* antimicrobial activity against *S. aureus*, *B. subtilis*, *E. coli*, and *C. albicans*. The methoxysubstituted complex (**2c**) showed more promising antibacterial activity against *S. aureus* and *B. subtilis* than other compounds at the concentration tested.

1. Introduction

The alkylthioalkylated anilines have found application as intermediates in production of many organic compounds [1–3] including dyes, rubber, and herbicides [4]. They act as coordinating ligands due to the presence of the aniline nitrogen and the thioether sulfur in their moiety. The hard-borderline and soft nature of the nitrogen and sulfur, respectively, in alkylthioalkylated anilines permits the formation of stable complexes between them and metal ions under mild nonextreme reacting conditions. Donor groups commonly found in many known biologically active compounds and ligands used in pharmaceutical synthesis include the nitrogen, oxygen, sulfur, and chlorine atoms. Such biopotent organic compounds with their metal complexes are being explored for their activity against a wide range of microorganisms. Sulfur-containing ligands and complexes have been explored for biological activity and practical application [5–7]. Some metal complexes of SN ligands were investigated and reported. Copper(II) complexes $CuX_2(N–SMe)$ (X = Cl, Br) obtained from alcohol solution at 0°C were not very stable [8]. Ni(II) complexes of 2-methylthiomethylaniline [8] and 8-methylthioquinoline [9] have the composition $NiX_2(N–SMe)_2$ (X = Cl, Br [8]; X = Cl, Br, I, NCS [9]). The Pd(II) and Pt(II) complexes of these ligands, on being heated in dimethylformamide were S-demethylated to yield the thiolo-bridged complexes $M_2Cl_2(N–S)_2$. Complexes $MX_2(N–SMe)$ and $[M(N–SMe)_2](ClO_4)_2$ (M = Pd, Pt, Cu, Hg) were derived with 2-(2-methylthioethyl)pyridine [10] and 2-methylthiomethylpyridine [11]. The structural, spectroscopic, and biological studies of alkylthioalkylated anilines and their copper complexes are less investigated in comparison to their sulfonamide analogues. Copper ions are biologically relevant in living systems as Cu(I)/Cu(II) cuproproteins which transport molecular oxygen and act as good catalysts in related oxidation-reduction processes. Here, the spectral, structural, and antimicrobial properties of copper(II) complexes of 2-(methylthiomethyl)anilines are reported with the spectral property and antimicrobial activity of the complexes compared to their corresponding ligands.

2. Materials and Methods

2.1. Materials and Physical Measurements. The reagents and solvents used in the experimental procedures were of analytical grade and used without further purification. The elemental analysis was carried out on Elementar Analysensysteme varioMICRO V1.6.2 GmbH. ^{1}H and ^{13}C NMR spectra of the ligands were obtained in $CDCl_3$ relative to the residual proton in the solvent on Bruker Avance 400 MHz NMR spectrometer. The midinfrared spectra (400–4000 cm^{-1}) were determined as solids on PerkinElmer Spectrum 100 ATR-FTIR spectrometer. Far-infrared spectra (30–700 cm^{-1}) were obtained in nujol mulls held between polyethene discs and recorded on Perkin Elmer Spectrum 400 FTIR/FIR spectrometer. The electronic spectra (250–1100 nm) of ligands and complexes were measured in DMF using PerkinElmer Lambda 25 UV/VIS Spectrometer. The solid reflectance spectra of the copper complexes (300–1500 nm) were obtained on Shimadzu UV-3100 UV-VIS-NIR Spectrometer. Conductivity measurements of the complexes were taken at room temperature on AZ 86555 conductivity instrument. A Gouy balance was used to determine the room temperature magnetic moments of the powdered samples employing Hg(II) tetrathiocyanatocobaltate(II) as a calibrant and diamagnetic corrections were made from Pascal's constants.

2.2. Crystallographic Measurements. Crystallography data were collected at −73°C using a Bruker KAPPA APEX II diffractometer equipped with a graphite monochromator and a molybdenum fine focus sealed X-ray tube as source of X-ray (Mo-$K\alpha$ radiation, $\lambda = 0.71073$ Å) and an Oxford Cryostream 700 system for sample temperature control. Bruker APEX II software was used for instrument control. The structures of the compounds were solved and refined using SHELXL-97 software package [13–15]. Numerical absorption corrections were done and all nonhydrogen atoms were refined anisotropically. The positions and temperature parameters of the hydrogen atoms were fixed to the adjacent atoms. Diagrams and publication materials were generated using ORTEP [16]. Crystal size (mm), 0.06 × 0.06 × 0.17; chemical formula (per unit cell), $C_8H_{10}Cl_2CuN_2O_2S$; formula weight, 332.68; sum formula per unit cell, $C_{16}H_{20}Cl_4Cu_2N_4O_4S_2$; formula weight, 665.40; monoclinic; $P2_1/c$; unit cell parameters: a (Å) 5.5999(2), b (Å) 27.2688(9), c (Å) 7.6550(2), α (°) 90.00, β (°) 97.8850(10), γ (°) 90.00; V (Å^3), 1157.89(6); Z, 4; T (K), 200(2); D_{calc} (Mg/m^3), 1.908; absorption coefficient (mm^{-1}), 2.512; absorption correction (min., max.), 0.6705, 0.8721; F (000), 668; θ range for data collection (°), 2.79–27.99; limiting indices, $-4 \le h \le 7$, $-36 \le k \le 35$, $-10 \le l \le 10$; reflections collected, 11213; unique reflections (R_{int}), 3530 (0.0232); completeness to θ, 27.99 (99.9%); refinement method, full-matrix least-squares on F^2; data/restraints/parameters, 2798/0/162; goodness-of-fit on F^2, 1.080; final R indices [$I > 2\sigma(I)$], $R_1 = 0.0262$, w$R_2 = 0.0576$; R indices (all data), $R_1 = 0.0354$, w$R_2 = 0.0601$; largest difference in peak and hole (e A^{-3}), 0.383 and −0.337.

2.3. Antimicrobial Susceptibility Procedure. The ligands (**1a**–**f**) and copper complexes (**2a**–**f**) were screened *in vitro* for their antibacterial activity against *Staphylococcus aureus* ATCC 6538, *Bacillus subtilis* (subsp. *spizizenii*) ATCC 6633, and *Escherichia coli* ATCC 8739 and for antifungal activity against *Candida albicans* ATCC 2091. Ampicillin (AMP) and ketoconazole (KTZ) were, respectively, used as positive controls for the antibacterial and antifungal tests. All the growth media (Mueller Hinton agar (MHA), agar bacteriological, potato dextrose agar (PDA), and nutrient broth) were prepared in double-distilled water according to standard procedure. Sterile saline was prepared by dissolving 0.85 g saline in double-distilled water and making up to 100 mL. McFarland solution (0.5 turbidity standard) was prepared by adding 0.5 mL of 1% barium chloride to 99.5 mL of 1% sulphuric acid [17]. Agar disc diffusion method was employed to determine the susceptibility of the microorganisms to the test compounds [18, 19]. The preparation of the agar plates, culturing of the microbial strains, and the inoculation of the plates followed described procedure [20, 21]. Each microbial inoculum was standardized by reference to 0.5 McFarland turbidity standard [17]. Stock solutions (100 mg/mL) of ampicillin and ketoconazole were also prepared and diluted to lower concentrations [21].

2.3.1. Agar Disc Diffusion Method. The sterile assay disks were kept in sealed containers at 5°C and allowed to equilibrate to room temperature before use. The test compounds, namely, ligands (**1a**–**2f**) and complexes (**2a**–**2f**) were dissolved in DMF. Known concentrations of test solutions were delivered on to sterile assay disks of 6 mm diameter each using a micropipette; the quantity taken was 250 μg per disc. 125 μg of Ampicillin and ketoconazole was measured on separate disks and allowed to dry under the laminar flow. Six disks were placed on each inoculated agar plate containing the appropriate growth medium and incubated for 24 h (bacteria) and 60 h (fungus) at 37°C. The diameter of zone of inhibition of the microbial growth by each compound was thereafter measured. The tests were carried out in triplicate and the mean values are recorded in Table 5.

2.4. Synthesis of Ligands and Complexes. The ligands, 4-R-2-(methylthiomethyl)anilines (**1a**–**1f**), were prepared according to reported procedure [2]. Appropriate aniline (10.7 mmol) and dimethyl sulfide (15.00 mmol) in dichloromethane were vigorously stirred at room temperature. *N*-chlorosuccinimide (15.0 mmol) was added in small portions. The mixture was stirred for 10 min; triethylamine (15.0 mmol) was added and the mixture was heated at reflux for 12 h. The organic layer was extracted with 10% NaOH (25 mL) and dried over anhydrous magnesium sulfate. Solvent was removed *in vacuo* to give the crude which was purified by column chromatography on silica gel 60 (0.040–0.063 mm) using hexane: ether (4 : 1 vol/vol) as the eluent. Fractions were collected in test tubes in 30 mL portions and R_f value of each fraction was determined on TLC plate (silica gel 60 F_{254}). Fractions with similar R_f values were combined and dried *in vacuo* to remove the solvent and the NMR spectra obtained to identify the desired product (Scheme 1).

The copper(II) complexes (**2a**–**2f**) were prepared by adding equimolar amounts of cupric chloride dihydrate

Table 1: Analytical and physical data for ligands (**1a–1f**) and complexes (**2a–2f**).

Complexes	Molecular formula	Colour	M. pt. (°C)	% found (calculated)				Yield	μ_{eff}[a]	Molar conductance[b]	
				C	H	N	S	%	(B.M.)	DMF	DMSO
2MT **1a**	$C_8H_{11}NS$	—	oil	62.87 (62.70)	7.08 (7.23)	9.27 (9.14)	19.61 (20.92)	80			
4Me-2MT **1b**	$C_9H_{13}NS$	Pale brown	65-66	63.12 (64.62)	7.87 (7.83)	8.09 (8.37)	18.11 (19.17)	69			
4MeO-2MT **1c**	$C_9H_{13}NOS$	—	oil	57.97 (58.98)	7.92 (7.15)	7.51 (7.64)	17.32 (17.50)	26			
4Cl-2MT **1d**	$C_8H_{10}NSCl$	Pale brown	69-70	51.84 (51.19)	5.51 (5.37)	7.38 (7.46)	16.49 (17.08)	78			
4Br-2MT **1e**	$C_8H_{10}NSBr$	Pale brown	68-69	41.25 (41.39)	4.22 (4.34)	5.89 (6.03)	13.42 (13.81)	62			
4-NO_2-2MT **1f**	$C_8H_{10}N_2O_2S$	Yellow	70–73	47.58 (47.39)	5.30 (5.22)	13.74 (13.82)	16.01 (15.82)	33			
$CuCl_2$(2MT)] **2a**[c]	$[Cu(C_8H_{11}NS)Cl_2]$	Green	153–155	33.30 (33.40)	3.97 (3.85)	4.86 (4.87)	10.93 (11.15)	91	2.30	27.9	29.4
[$CuCl_2$(4Me-2MT)] **2b**	$[Cu(C_9H_{13}NS)Cl_2]$	Brown	158–160	36.19 (35.83)	4.09 (4.34)	4.56 (4.64)	10.45 (10.63)	89	1.95	32.2	28.6
[$CuCl_2$(4MeO-2MT)] **2c**	$[Cu(C_9H_{13}NOS)Cl_2]$	Brown	147–149	34.09 (34.02)	4.19 (4.12)	4.30 (4.41)	9.58 (10.09)	89	1.76	38.3	29.6
[$CuCl_2$(4Cl-2MT]) **2d**[c]	$[Cu(C_8H_{10}ClNS)Cl_2]$	Green	158–160	30.10 (29.83)	2.86 (3.13)	4.31 (4.35)	9.90 (9.95)	75	2.12	29.5	28.5
[$CuCl_2$(4Br-2MT)] **2e**	$[Cu(C_8H_{10}NSBr)Cl_2]$	Green	170–172	26.35 (26.21)	2.41 (2.75)	3.86 (3.82)	8.38 (8.75)	79	2.21	28.5	32.9
[$CuCl_2$(4NO_2-2MT)] **2f**	$[Cu(C_8H_{10}N_2O_2S)Cl_2]$	Green	146–148	29.68 (28.88)	2.91 (3.03)	8.50 (8.42)	9.73 (9.64)	73	1.87	27.2	31.5

[a]Measured at room temperature, 298 K.

[b]Molar conductance of 10^{-3} M solution at 298 K, Λ_m values given in Ω^{-1} cm^2 mol^{-1}.

[c]Reference [12].

Table 2: ^{1}H and ^{13}C chemical shifts (δ, ppm) of the ligands.

Ligands	(C)1	(C)2	H (C)3	H (C)4	H (C)5	H (C)6	H (C)7	H (C)8	H9	H (C)10
2MT	(144.96)	(121.19)	7.05 *d* (130.49)	6.76 *t* (117.96)	7.14 *t* (128.21)	6.71 *d* (116.15)	3.71 *s* (35.14)	2.01 *s* (14.32)	4.06 *s*	—
4Me-2MT	(142.62)	(121.61)	6.85 *s* (131.23)	— (127.44)	6.93 *d* (128.98)	6.62 *d* (116.52)	3.67 *s* (35.48)	2.02 *s* (14.63)	3.95 *s*	2.25 *s* (35.60)
4MeO-2MT	(138.64)	(123.71)	6.70 *d* (116.46)	— (152.21)	6.64 *s* (113.45)	6.64 *d* (117.41)	3.64 *s* (35.48)	1.99 *s* (14.57)	3.81 *s*	3.73 *s* (55.56)
4Cl-2MT	(143.85)	(122.84)	6.98 *s* (130.18)	— (123.14)	7.04 *d* (128.23)	6.58 *d* (117.53)	3.59 *s* (35.20)	1.97 *s* (14.66)	4.07 *s*	—
4Br-2MT	(144.24)	(109.72)	7.13 *s* (132.83)	— (123.47)	7.18 *d* (130.99)	6.60 *d* (117.82)	3.60 *s* (35.00)	1.98 *s* (14.57)	4.08 *s*	—
4NO_2-2MT	(151.60)	(119.95)	7.96 *s* (126.68)	— (138.42)	8.02 *d* (125.08)	6.67 *d* (114.76)	3.70 *s* (34.94)	2.00 *s* (14.57)	4.76 *s*	—

s: singlet; *d*: doublet; *t*: triplet.

Table 3: Selected IR bands and the electronic spectra of the ligands and complexes.

Compound	$\nu_{(N-H)}$	δ_{NH2}	$\nu_{(C-N)}$	$\nu_{(Cu-L)}$ (cm^{-1})	Electronic spectra [a] λ_{max}, nm (ε, mol^{-1} dm^3 cm^{-1})
L–H (**1a**)	3424, 3352	1618	1272		259, 300
2a	3294, 3217	1609	1251	430, 398, 364, 327, 295, 274	259, 298, 322, 430, 925
				Solid	353, 400, 706
L–CH_3 (**1b**)	3420, 3346	1625	1275		259, 306
2b	3276, 3221	1599	1259	446, 405, 335, 321, 294, 268	259, 303, 330, 430, 916
				Solid	354, 450, 754
L–OCH_3 (**1c**)	3409, 3341	1626	1293		259, 319, 360
2c	3256, 3202	1617	1272	430, 364, 338, 303, 271	259, 286, 336, 447, 595, 885
				Solid	352, 403, 479, 786
L–Cl (**1d**)	3399, 3307	1625	1275		275, 316
2d	3261, 3221	1609	1244	439, 398, 322, 297, 272	261, 309, 335, 430, 936
				Solid	364, 405, 782
L–Br (**1e**)	3398, 3317	1624	1275		272, 312
2e	3259, 3219	1607	1244	437, 393, 341, 322, 293, 281	262, 308, 333, 430, 920
				Solid	348, 425, 795
L–NO_2 (**1f**)	3450, 3347	1639	1278		258, 295, 392
2f	3267, 3222	1620	1250	425, 380, 365, 323, 294, 271	263, 301, 381, 399, 428, 925
				Solid	367, 450, 765

[a]In DMSO.
[b]CT: charge transfer.

Table 4: Selected bond lengths [Å] and angles [°] for [$CuCl_2$($4NO_2$-2MT)] (**2f**).

Cu1–N1	2.0750(18)	Cu1–S1	2.3214(6)
Cu1–Cl1	2.2554(6)	Cu1–Cl2*	2.3184(5)
Cu1–Cl2**	2.6902(5)	Cl2–Cu1***	2.9321(5)
S1–C8	1.798(2)	S1–C7	1.817(2)
N1–C1	1.434(3)	C4–N2	1.464(3)
N2–O2	1.203(3)	N2–O1	1.212(3)
N1–Cu1–Cl1	176.82(5)	Cl2–Cu1–S1	163.90(2)
S1–Cu1–Cl2	105.455(19)	N1–Cu1–Cl2	85.39(6)
N1–Cu1–Cl2	88.60(5)	Cl1–Cu1–Cl2	93.19(2)
Cl1–Cu1–Cl2	94.27(2)	Cl2–Cu1–Cl2	90.625(17)
N1–Cu1–S1	91.93(5)	Cl1–Cu1–S1	85.69(2)
Cu1–Cl2–Cu1	89.376(17)	C8–S1–C7	102.40(11)
C8–S1–Cu1	105.25(9)	C7–S1–Cu1	104.90(7)
C1–N1–Cu1	118.59(13)	O2–N2–O1	122.3(2)
O2–N2–C4	118.5(2)	O1–N2–C4	119.2(2)

*x, y, z; **$1 - x, -y, 1 - z$; ***$-x, -y, 1 - z$.

(0.65 mmol) in ethanol (2 mL) to a stirred solution of the ligand (0.65 mmol) in ethanol or a mixture of ethanol/dichloromethane (2 mL). The mixture was further stirred for 1 h and the resulting solid precipitates were filtered off, washed with cold ethanol, and dried under vacuum (Scheme 1).

3. Results and Discussion

The synthesis route for the copper complexes is shown in Scheme 1. The complexes are stable solids in air, with varying shades of green colouration, and their structures were established from their elemental analyses, infrared and electronic spectra and X-ray crystallography. The results of the elemental analysis are in good agreement with the calculated values of 1 : 1 metal to ligand combination for the copper complexes. The complexes are completely soluble in DMF and DMSO, partially soluble in other polar solvents such as water, acetonitrile, and methanol but are completely insoluble in nonpolar organic solvents. Low molar conductance values between 27.2 and 38.3 Ω^{-1} cm^2 mol^{-1} obtained for the complexes in DMF indicate they are nonelectrolytes [22] and the nature of chlorine to metal bonds can be described as coordinative. The summary of the analytical data and other physical properties of the complexes are recorded in Table 1.

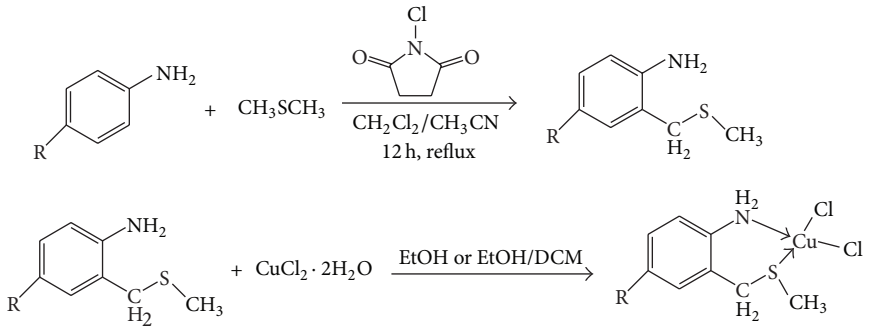
3.1. NMR Spectra. The NMR shifts for the protons and carbon atoms of the respective ligands are shown in (Scheme 2, Table 2). The proton NMR spectra of the ligands can be classified into three distinct classes; the thiomethyl (–CH_3) and methylene (–CH_2) protons appear as singlet peaks and resonate in the ranges 1.97–2.02 δ and 3.59–3.70 δ, respectively. The broad singlet peaks found between 3.81 and 4.76 δ are due to amine (–NH_2) protons and the peaks downfield in the region 6.58–7.96 δ which appear as multiplets are due to the aromatic protons. The ligands with the methyl or methoxy group show additional singlet peak due to methyl (–CH_3) protons at 2.25 δ or methoxy (–OCH_3) protons at 3.73 δ.

3.2. Infrared Spectra. Selected infrared bands of the ligands and copper complexes are recorded in Table 2. The vibrational frequencies in the 2MT ligands (**1a**–**1f**) were

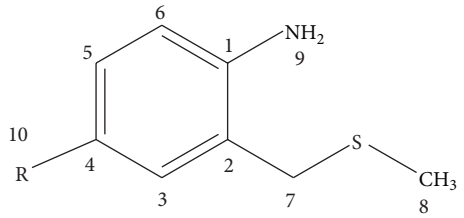
Table 5: Agar disk diffusion test of compounds against microbial strains.

Compound	Diameter of zones[a] of inhibition (mm)			
	B. subtilis	*S. aureus*	*E. coli*	*C. albicans*
1a	7	8	NI[b]	NI
2a	14	10	7	9
1b	8	8	7	NI
2b	13	10	8	9
1c	12	13	7	NI
2c	18	20	7	13
1d	8	8	7	NI
2d	9	8	7	10
1e	9	8	7	NI
2e	9	9	7	11
1f	9	7	7	NI
2f	10	8	7	NI
AMP 125 μg/disk	40	38	23	—
KTZ 125 μg/disk	—	—	—	23
$CuCl_2{\cdot}2H_2O$	8	8	7	8
DMF	6	6	6	6

[a]250 μg disc^{-1} sample concentration, disc diameter 6 mm.
[b]NI: No inhibition.



Scheme 1: Synthesis of ligands (**1a**–**1f**) and copper complexes (**2a**–**2f**).



Scheme 2: Labelling arrangement of ^{1}H and ^{13}C chemical shifts (δ) of ligands (**1a**–**1f**) in ppm.

characterized by those observed in primary amines [23]. The N–H symmetric and asymmetric stretches were found between 3320 and 3400 cm^{-1}, respectively; NH_2 scissor was in the range 1590–1600 cm^{-1} and C–N stretching frequency was seen around 1280 cm^{-1}. The band expected from the thioether group due to C–S–C bend (around 1100 cm^{-1}) and that due to C–S stretch between 650 and 780 cm^{-1} was not observed as they are weak bands and were masked by vibrations associated with the benzene ring [24]. There was no deprotonation of the amine hydrogen atoms upon complexation as two N–H stretches were observed, shifted to lower energies by 100–200 cm^{-1}. The N–H bends were similarly shifted to lower frequencies (cm^{-1}) in the complexes. The shift to lower frequency of these vibrational modes after chelation is a result of the electron density of the nitrogen being directed to the metal ion, leaving the amino protons less tightly bound to the nitrogen [25]. Copper to ligand vibrations were seen in the far infrared region; νCu–N was observed in the range 425–450 cm^{-1} [26] and the vibrations due to Cu–Cl stretches consist of a mixture of medium and intense bands in the complexes between 268 and 365 cm^{-1} [27, 28]. In the crystal structure of complex (**2f**) below, the arrangement of the ligand atoms around the Cu^{2+} center includes two chloride ions, one of them terminally

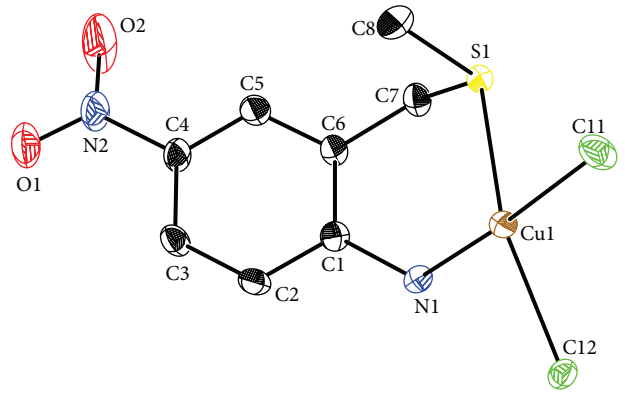


FIGURE 1: Monomer unit of $[CuCl_2(4NO_2\text{-}2MT)]$ **2f**. Ellipsoids drawn at 50% probability and hydrogen atoms are omitted for clarity.

bonded, while the other is linked to two other adjacent copper centres in a bridging mode. Frequencies between 268 and 303 cm^{-1} are assigned as νCu–Cl for equatorial bonds [29]. Bands close to 320 cm^{-1} were assigned to Cu–S stretches [30].

*3.3. The Crystallographic Structure of [Cu(4NO$_2$-2MT)] (**2f**).* A single crystal of (**2f**) was grown by the slow evaporation of a mixture of DMSO/EtOH solution (2 : 1 vol/vol). The atom numbering scheme and the selected bond distances and angles are listed in Table 3. The four corners of the square plane of (**2f**) are occupied by the aniline nitrogen (N1), thioether sulfur (S1), and two chloride ions (Cl1, Cl2) which have *cis* arrangement to each other. One chlorido ligand (Cl1) is terminally bonded, while the other (Cl2) is bonded to two other copper ions in adjacent molecules as a bridging ligand giving rise to an octahedral arrangement around each copper center. Hence the complex has a monomer formula of $CuLCl_2$ (where L is the ligand) and the ORTEP drawing is shown in Figure 1. The presence of chloride bridges between the adjacent molecules results in a "ladder-like" polymeric structure seen in Figure 2. The bond distances for Cu1–N1 and Cu1–S1 which are 2.075(18) and 2.321(6) Å, respectively, fall within the expected ranges [31, 32] and the Cu1–S1 distance is typical of equatorially bound thioether sulfur [33–40]. Cu–Cl lengths are observed at 2.255(6) Å (Cu1–Cl1 terminal bond), 2.318(5) Å (Cu1–Cl2 in the basal bond), 2.690(5) Å (Cu1–Cl2 bridging bond), and 2.932(5) Å (Cu1–Cl2 bridging bond). The longer distances observed for Cu1–Cl2 bonds are within the acceptable range for Cu–Cl distances for axial bonds in previously reported copper(II) octahedral compounds [32, 41–43]. The Cu–Cu distance of 3.532 Å is normal for distorted octahedral structures [25]. The bond angles for the basal ligands *trans* to each other are 176.82° and 163.90° for N1–Cu1–Cl1 and S1–Cu1–Cl2, respectively. L(basal)–Cu–L(apical) angles which are ideally 90° range from 85.39° to 105.45°, the greater deviation being from S1–Cu1–Cl2 bond angle.

3.4. Magnetic Moment and Electronic Spectra. The magnetic moments of copper(II) complexes (**2a–2f**) are recorded in Table 1. The magnetic moments between 1.76 and 2.30 B. M. obtained for the complexes suggest the presence of one electron in the d^9 copper(II) configuration. The increase from the spin-only value of 1.73 B. M could be due to spin orbit coupling or orbital contribution from the unpaired electron in the ground state [44]. The electronic spectra of the ligands and copper(II) complexes in DMSO are recorded in Table 2. The spectra of the ligands (**1a–1f**) consist of two high energy bands found in the range 250–320 nm arising from $\pi \rightarrow \pi^*$ transitions of the phenyl ring; the ligands (**1c**) and (**1f**) show an additional band close to 360 and 390 nm, respectively, due to intraligand charge transitions of their methoxy and nitro groups. The electronic spectra of the copper(II) complexes in DMSO similarly show the $\pi \rightarrow \pi^*$ transitions which are slightly shifted to shorter wavelengths as a result of decrease in conjugation of the system after complexation. Ligand to metal charge transfer transitions are observed; the band in the region 320–390 nm is assigned as N → Cu, while that between 400 and 450 nm is associated with S(σ) → Cu [25]. In the solid reflectance spectra of the complexes in Figure 3(a), two high energy bands due to charge transfer transitions are found near 350 and 400 nm, while the broad band in the range 700–800 nm is assigned to d → d transition [25]. The description of the d → d band of the complexes changes in DMSO (Figure 3(b)) and a broad low-energy band is observed in the near-infrared between 880 and 920 nm. The shift to lower energies, by approximately 100 nm, is indicative of geometry change in the complexes as a result of probable coordination of DMSO to copper(II). From the crystal structure, the Cu–Cl distance in the bridging bonds is long and could imply a possible replacement of the axial binding site through the bridging chlorido ligand by the high coordinating DMSO molecule. Previous studies on electronic spectra of similar copper(II) complexes in DMF suggested the coordination of the solvent molecule to the metal ion resulting in distorted octahedral or tetragonal structures [19]. The large bandwidth in the electronic spectra can be attributed to Jahn-Teller distortion which is commonly observed in octahedral Cu(II) complexes.

3.5. Antimicrobial Susceptibility Testing. The results for the disc diffusion susceptibility tests recorded in Table 4 shows the inhibitory activity of each ligand was improved upon chelation to copper ion. The higher activity of the complexes could be due to the increased lipophilicity conferred on the complex by the copper ion. It was also observed that the pure metal salt solution has an inhibitory effect on the microbial growth and it shows a measure of biological activity. In this study, the gram-positive bacteria were more susceptible to the test compounds than the gram-negative *E. coli* and the fungus *C. albicans*. Among the ligands and complexes screened, those with electron donating groups are seen to inhibit the microbial growth better than the electron withdrawing groups. The compounds with the methoxy moiety (**1c**) and (**2c**) demonstrate more inhibitory activity than other compounds (**2b**) with a methyl group showing a similar though less pronounced activity.

4. Conclusion

The copper(II) complexes (**2a–2f**) formed in a 1 : 1 ligand to metal reaction stoichiometry and were characterized by the

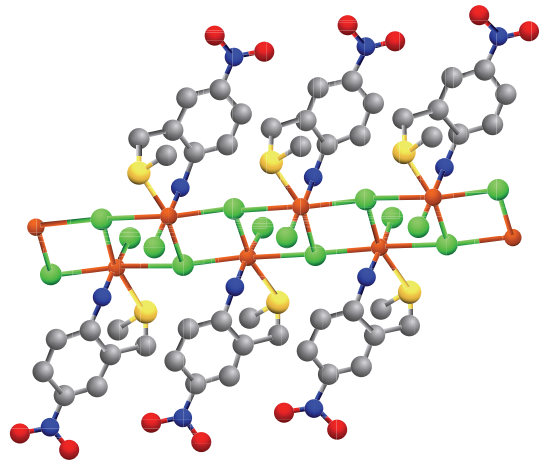


Figure 2: Ladder-like polymeric octahedral structure of $[CuCl_2(4NO_2\text{-}2MT)]$ **2f**. C, grey; Cl, green; Cu, wine; N, blue; O, red; S, yellow.

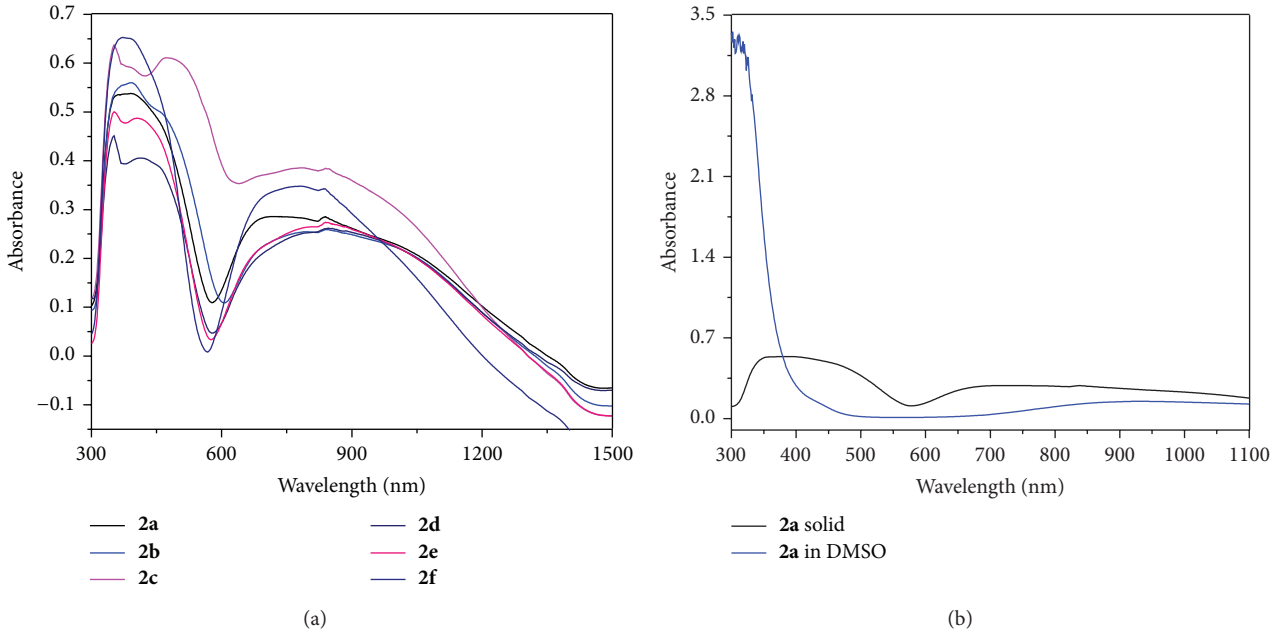


Figure 3: Solid reflectance spectra of **2a**–**2f** (a), complex **2a** compared with its solution spectrum in DMSO (b).

elemental analysis, IR and X-ray crystallography. A change in the structure of the complexes in the solid state is suspected as a result of the coordination of DMSO to the copper(II). Screening of the ligands and their copper complexes for *in vitro* antimicrobial activity against *S. aureus*, *B. subtilis*, *E. coli*, and *C. albicans* was carried out using agar disk diffusion as well as microbroth dilution techniques. The methoxy complex (**2c**) showed promising antibacterial activityagainst *S. aureus* and *B. subtilis*, while *E. coli* was not susceptible to any of the compounds at the concentration tested.

5. Extra Material

CCDC 888074 contains the supplementary crystallographic data for compound $[CuCl_2(4NO_2\text{-}2MT)]$ (**2f**) (see Supplementary Material available online at http://dx.doi.org/10.1155/2014/769573). Copies of these data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif/.

Conflict of Interests

The authors declare that there is no conflict of interests.

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