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Spectral, thermal stability and antibacterial studies of copper, nickel and cobalt complexes of *N*-methyl-*N*-phenyl dithiocarbamate

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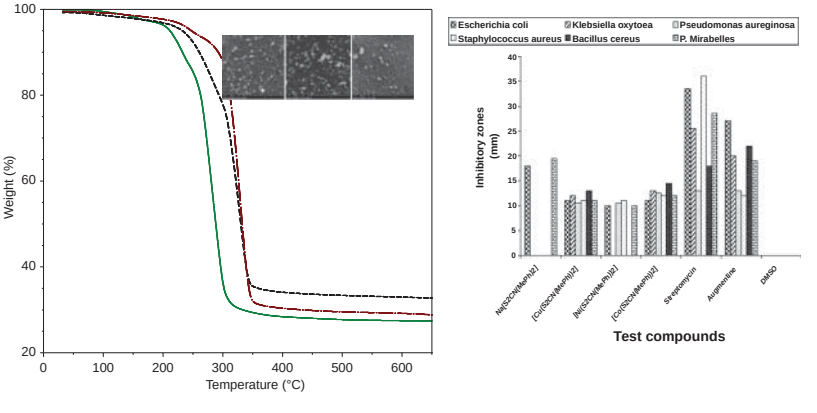
Copper(II), cobalt(II) and nickel(II) bis(*N*-methyl-*N*-phenyl dithiocarbamate) complexes having the general formula [M{S_2CN(MePh)}$_2$] (where M = Cu, Co and Ni) have been prepared and characterized by spectral and thermal analysis. The IR spectra suggest that coordination of dithiocarbamate (DTC) occurred through the two sulfur atoms in a symmetrical bidentate fashion. The electronic spectra, conductance measurement and magnetic moment analysis support the proposed geometry for the electronically dilute complexes. The results of the thermal analysis showed that after dehydration, a one-step decomposition pattern leading to the formation of respective metal sulfide as the end-product occurred. The results are consistent with the proposed composition of the complexes. The *in vitro* antibacterial activity of the complexes was investigated against strains of gram-negative *Escherichia coli*, *Klebsiella oxytoea* and *Pseudomonas aureginosa*, and gram-positive *Bacillus cereus*, *Staphylococcus aureus* and *Protues mirabilis*. The antibacterial activity of the complexes compared favorably with that of streptomycin and augmentine against *S. aureus* and *B. cereus*. The cobalt complex had the best antibacterial activity against the test compounds with inhibitory zone range of 11–14.5 mm.



Keywords: dithiocarbamate; metal complex; thermal stability; antibacterial properties

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1. Introduction

The chemistry of transition metal complexes with dithiocarbamate (DTC) has played an important role in coordination, and solid state chemistry. The high nucleophilic property of the ligand has led to a large number of compounds being isolated, including different biologically active derivatives.[1] Metal complexes of S chelating ligands have interesting physico-chemical properties, pronounced biological activities and are also useful as models for metalloenzyme active sites. Commercially, DTCs are well known for their application such as NO-trapping agents, lubricants, vulcanizers and solar control devices.[2–4] Furthermore, DTC ligands are used as reagents for the extraction of metals from different mineral acids, and their complexes are utilized as precursor materials in the synthesis of sulfide nanoparticles in modern electronics.[5–7]

DTCs are capable of stabilizing metals in a wide range of oxidation states. This property is attributed to the different resonance forms, and the delocalization of the nitrogen lone pair onto the sulfurs. Nickel(II) bis(DTC) complexes exists as a mononuclear slightly distorted square planar structure.[8,9] Similar copper(II) complexes can either be monomeric or dimeric. The monomeric structures adopt the square planar arrangement, while the dimeric complexes exist in five-coordinate geometry around the copper ions.[10] Dithiocarbamates are capable of stabilizing metals in a wide range of oxidation states, due to its different resonance forms. Consequently, cobalt can be present in $+1$, $+2$, $+3$ and $+4$ states.[11] Cobalt(II) DTCs undergoes spontaneous oxidation into the corresponding cobalt(III) compounds. Apart from the propensity of DTC ligands to stabilize relatively higher oxidation states, the larger ligand field stabilization energy in cobalt(III) complexes (a d^6 system) also play an important role.[12] For most of the cobalt(II) DTC complexes, the coordination mode is considered to be square planar. Although tetrahedral geometry has been reported for some compounds,[13,14] and the stability of Co(II) DTCs compounds is known to improve with the use of larger alkyl (R) groups.

In view of the growing interest in DTCs, the present work reports the synthesis, and characterization of DTC metal complexes of copper(II), nickel(II) and copper(II), as well as their thermal stability studies and biological activity in inhibiting the growth of some pathogenic bacteria.

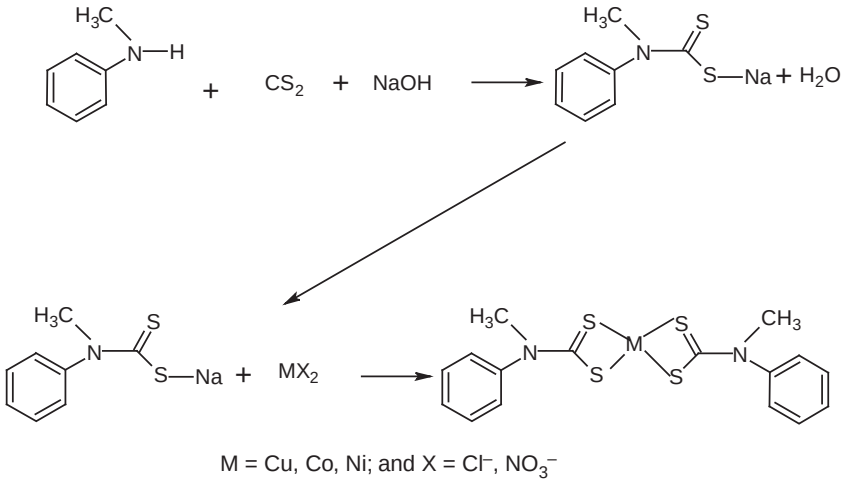
2. Results and discussion

2.1. *Synthesis*

The complexes were prepared according to the synthetic procedure in Scheme 1 and obtained in good yield. Similar experimental procedures were adopted for the synthesis of all the complexes; except for the cobalt complexes where an inert atmosphere was a slight precautionary measure that was adopted to avoid the oxidation of cobalt(II) to cobalt(III). The data obtained from their elemental analysis indicate that the complexes are of good purity. All the complexes show good stability at ambient conditions, and are soluble in acetone and DMSO.

2.2. *Magnetic moment and conductivity measurement*

The magnetic moment of nickel compounds in a cubic field falls between 2.8 and 4.2 B.M. Deviation from spin only moment of 2.83 B.M is attributed to orbital contribution to the magnetic moment, and it depends very much on stereochemistry. Octahedral complexes should have magnetic moments between 2.9 and 3.3 B.M. Generally, square planar complexes are diamagnetic, while tetrahedral complexes have moments in the range 3.2–4.1 B.M. However, situations exist whereby there is equilibrium between two 4-coordinate geometries. In this case, the value of the



Scheme 1. Schematic representation for the complex formation.

magnetic moment falls below the prescribed range of 2.83 B.M.[15] The [Ni{S_2CN(MePh)}$_2$] complex in our study has a magnetic moment of 2.46 BM. The value shows that the Nickel complex exists in an equilibrium between the tetrahedral and square planar 4-coordinate geometry. (tetrahedral ↔ square planar geometry.) Consequently, a magnetic moment value in the range of 1.9–2.2 B.M is usually observed for mononuclear copper(II) complexes regardless of stereochemistry. This is usually higher than the spin only value of 1.73 B.M, due to orbital contribution and spin-orbit coupling.[16] The [Cu{S_2CN(MePh)}$_2$] complex has a magnetic moment of 1.90 BM, confirming it is mononuclear nature. Tetrahedral cobalt complexes are expected to have magnetic moments in the range 4.20–4.60 B.M. Values slightly below this is ascribed to anti-ferromagnetisim.[17] The [Co{S_2CN(MePh)}$_2$] complex has a moment of 4.31 BM which is expected for 4-coordinate tetrahedral geometry. The molar conductances of the metal complexes were done in nitromethane and were in the range 10.2–28.7 Λ^{-1} cm^3 mol^{-1} indicating their covalent nature.

2.3. *FT-IR and electronic spectra*

The analysis of the FT-IR spectra of the ligand and the complexes provided information on the coordination mode between the ligands and the metal ion. In the IR spectra of the ligand, the ν(C=N) and the ν(C_2–N) peaks were observed at 1454 and 1262 cm^{-1}, respectively.[18] In the IR spectra of the complexes, the ν(C=N) peak appeared between 1463 and 1492 cm^{-1} and the ν(C_2–N) peak appeared between 1279 and 1284 cm^{-1}. The shift to higher frequency on complexation showed the involvement of thiureide nitrogen [19] in the coordination. The value of the ν(C=N) peak increased in the order cobalt $<$ nickel $<$ copper. The highest peak observed in the copper complex may be due to the fact that the value of coordination bond length of copper complexes is shorter than the corresponding value of the nickel and cobalt complexes. This has been attributed to the increase in the strength of the electrostatic field of copper ion as a result of its small ionic radius and its many d-electrons. Thus, the copper ion would have a greater tendency for complex formation than the other metal ions involved.[20] The ν(C=S) frequency appeared at 903 cm^{-1} in the cobalt complex and at 901 cm^{-1} in both the copper and nickel complex. The appearance of only one peak in this region indicates a symmetrical bonding of the metal ion to the DTC ligand in a bidentate fashion through the sulfur atoms.[21] All the complexes showed

aliphatic C–H stretching bands due to the methyl groups in the 2930–2980 cm^{-1} range for asymmetric stretch. The ν(M–S) peaks depend on the nature of the metal ion, and the substituents attached to the nitrogen.[22] However, these peaks usually occur in the far-IR region, 300–400 cm^{-1}, and could not be observed in the range of our spectral measurement.

The solid reflectance band for the [Cu{S_2CN(MePh)}$_2$] complex showed a single band at 14.99 kk which corresponds to a square planer geometry. For tetrahedral copper geometry, a single band is observed below 10.00 kk while octahedral copper complexes show two or three bands due to Jahn Taller distortion with one appearing below 10 kk.[23] A d^7 system for a tetrahedral geometry for copper(II) complexes gives an A ground term with an upper ^{4}T terms which give rise to transitions that are Laporte forbidden.[23,24] [Co{S_2CN(MePh)}$_2$] gave a single band at 16.13 kk which is consistent with transition bands for ^4A_2g–$^4T_1$(f) in a tetrahedral geometry.[25] [Ni{S_2CN(MePh)}$_2$] complex gave transition bands consistent with tetrahedral geometry for a $^3T_1$(f)–$^3A_2$ at 16.10 kk.[24,26]

2.4. *Antibacterial studies*

The results of the antibacterial activities of the complexes are presented in Table 1 and Figure 1. Six pathogens; *Klebsiella oxytoea, Pseudomonas aureginosa, Staphylococcus aureus, Bacillus cereus, Escherichia coli* and *Prunus mirabelles* were used in the screening. The ligand, *N*-methyl-*N*-phenyldithiocarbamate was active against two gram-negative bacteria; *E. coli* and *P. mirabelles* with inhibitory zones of 18.0 and 19.5 mm, respectively. This corresponds to 53% and 68% of Streptomycin and 66.6% and 103% of Augmentine antibacterial activity against the same bacteria. Its toxicity was resisted by *K. oxytoea, P. aureginosa, S. aureus and B. cereus.* The resistivity of the ligand by these bacteria could be due to its nonpermeation through lipid layers of the cell wall of the gram-positive bacteria (*S. aureus and B. cereus*), and the detoxification of the compound by the gram-negative *K. oxytoea* and *P. aureginosa* through the secretion of beta lactamase.

The cobalt, copper and nickel metal complexes showed increased activity against the test bacteria, compared with the ligand with inhibitory zone ranging from 10 to 14.5 mm. This is in agreement with chelation theory. Chelation increases antibacterial activity due to partial sharing of the metal ion positive charge with donor groups of the ligand, and in turn reduces its polarity and the possible π-electron delocalization over the aromatic rings of the ligands. Thus, it increases the lipophilic character of the complex, and favors its permeation through lipid layers of the bacterial membrane.[27,28] The antibacterial activity of the complexes compared favorably with that of Streptomycin and Augmetine against *P. aureginosa, S. aureus* and *B. cereus,* thus establishes their potentials as lead compounds for bactericidal research. The cobalt complex of *N*-methyl-*N*-phenyldithiocarbamate had the best antibacterial activity against the test compounds. The minimum inhibitory concentration (MIC) which was determined for compounds

Table 1. Antibacterial activity table for the ligands and metal complexes.

Test compounds	*E. coli*	*K. oxytoea*	*P. aureginosa*	*S. aureus*	*B. cereus*	*P. mirabelles*
Na[S_2CN(MePh)$_2$]	18 ± 0	R	R	R	R	19.5 ± 1.4
[Cu{S_2CN(MePh)}$_2$]	11 ± 0	12 ± 0	10.5 ± 0.7	11 ± 0	13 ± 0	11 ± 0
[Ni{S_2CN(MePh)}$_2$]	10 ± 0	R	10.5 ± 0.7	11 ± 0	R	10 ± 0
[Co{S_2CN(MePh)}$_2$]	11 ± 0	13 ± 0	12.5 ± 0.7	12 ± 0	14.5 ± 0.7	12 ± 0
Streptomycin	33.5 ± 2.1	25.5 ± 0.7	13 ± 0	36 ± 5.7	18 ± 2.8	28.5 ± 3.5
Augmentine	27 ± 1.4	20 ± 0	13 ± 4.2	12 ± 0	22 ± 0	19 ± 1.4
DMSO	R	R	R	R	R	R

Note: [S_2CN(MePh)$_2$] = bis (*N*-methyl-*N*-phenyldithiocarbamato), R = resistant.

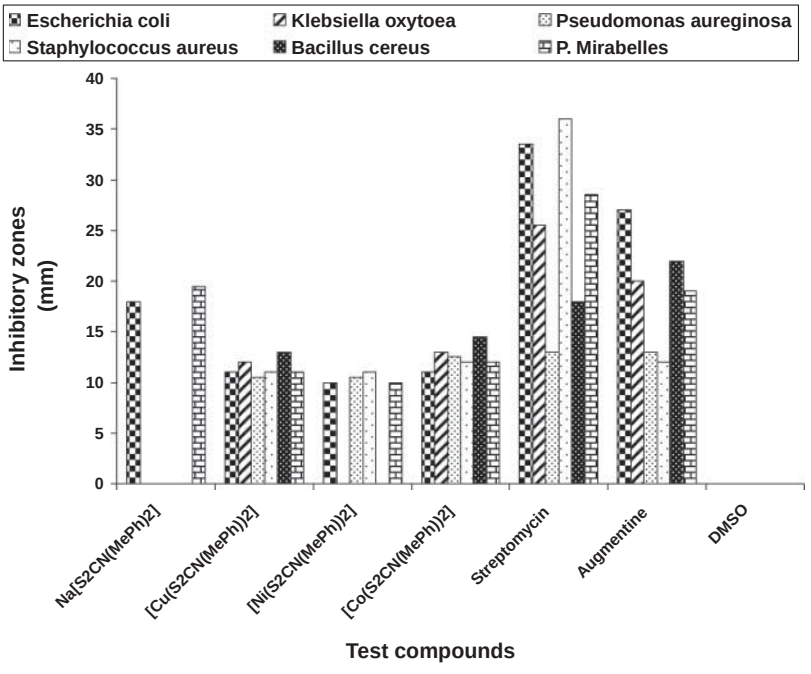


Figure 1. A histogram representation of the antibacterial activity of the ligand and the metal complexes.

Table 2. Minimum inhibitory concentration.

Compounds	Mg/mL	Bacteria
$Na[S_2CN(MePh)_2]$	4	*E. coli*
$Na[S_2CN(MePh)_2]$	4	*P. mirabelles*
$[Cu\{S_2CN(MePh)\}_2]$	8	*K. oxytoea*
$[Cu\{S_2CN(MePh)\}_2]$	8	*B. cereus*
$[Ni\{S_2CN(MePh)\}_2]$	6	*P. aureginosa*
$[Ni\{S_2CN(MePh)\}_2]$	5	*S. aureus*
$[Co\{S_2CN(MePh)\}_2]$	2	*B. cereus*
$[Co\{S_2CN(MePh)\}_2]$	3	*K. oxytoea*
$[Co\{S_2CN(MePh)\}_2]$	6	*P. mirabelles*
$[Co\{S_2CN(MePh)\}_2]$	6	*S. aureus*
$[Co\{S_2CN(MePh)\}_2]$	6	*P. aureginosa*

with inhibitory zones above 11 mm against the selected organisms were between 2 and 8 mg/mL, and presented in Table 2. The MIC's appear to vary with organisms for a particular compound. The cobalt complex with MIC's of 2 and 3 mg/mL appears to be the most toxic against *B. cereus* and *K. Oxytoea*, respectively, among the tested compounds. The copper complex with the highest MIC is the least toxic of the test compounds.

2.5. *Thermal studies*

DTC complexes either volatize leaving negligible amounts of residue or decompose to yield respective metal sulfide.[29] According to the curves, the complexes decompose in a two-step mechanism. Thermal studies of DTCs suggest that decomposition of these complexes proceeds through the formation of metal thiocyanate intermediates,[30] except in a cyclic DTCs or closed

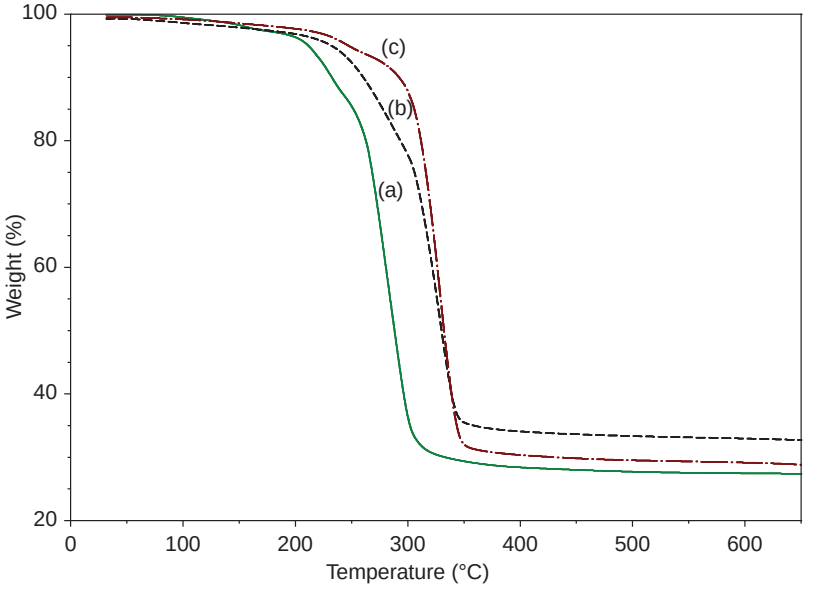


Figure 2. TGA curves of the compounds (a) [Cu{S_2CN(MePh)}$_2$], (b) [Co{S_2CN(MePh)}$_2$] and (c) [Ni{S_2CN(MePh)}$_2$] obtained in nitrogen atmosphere (75 mL/min), heating rate 10°C/min.

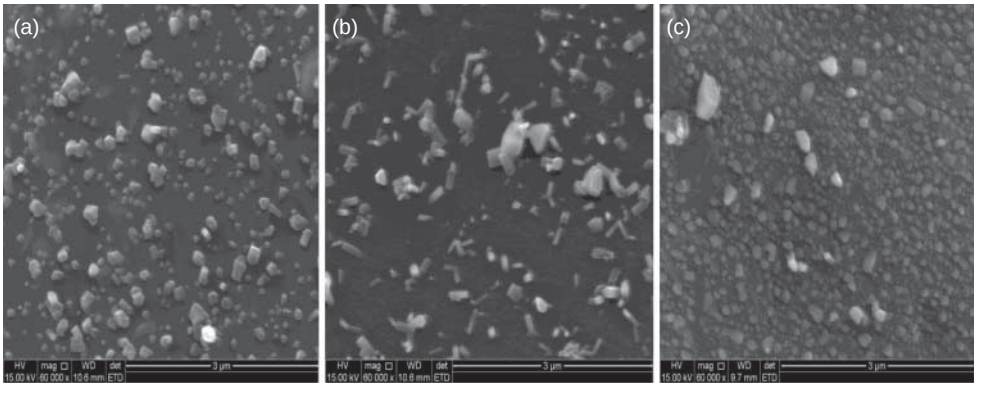


Figure 3. SEM micrographs of thermal residues of (a) [Cu{S_2CN(MePh)}$_2$], (b) [Co{S_2CN(MePh)}$_2$] and (c) [Ni{S_2CN(MePh)}$_2$] obtained in nitrogen atmosphere (75 mL/min), heating rate 10°C/min.

rings.[31,32] Similarly, in the present study (Figure 2), the weight loss of about 15–20% could be ascribed to the breakdown of the DTC moiety and the formation of the thiocyanate intermediates. The final products, from stoichiometric calculation, indicate the formation of the respective metal sulfides. The thermal stability order is nickel > cobalt > copper. Thus, it is evident that nickel(II), with its smaller ionic radius, gives the most thermally stable complexes. The DTC complexes studied earlier under the same conditions followed similar behavior.[33] To study the dependence of the surface morphology of the metal sulfide particles on the decomposition profile, SEM analysis was conducted for the residues obtained from thermogravimatric analyses. The SEM images in Figure 3 and show a marked influence of metal ions on the thermal behavior of the compounds studied. The residues have different shapes of non-uniform sizes. Changes in the decomposition profiles of the different complexes can be attributed to the differences in the breaking of the bond between the central metallic ion and the volatile ligand which is evolved as fragments.

3. Conclusion

We have reported the synthesis, thermal and antibacterial studies of copper(II), nickel(II) and cobalt(II) complexes of *N*-methyl-*N*-phenyl DTC. The complexes were characterized by elemental analysis, electronic, FTIR and NMR spectroscopy. The spectral data obtained are consistent with the proposed composition, with the DTCs coordinating in a symmetrical bidentate fashion. The antibacterial screening of the complexes against some strains of gram-positive and gram-negative bacteria showed varied activities against the test bacteria, but increased activity compared with the ligand. The cobalt complex had the best antibacterial activity of the test compounds.

4. Experimental

4.1. *Materials and physical methods*

Nickel(II) chloride hexahydrate, cobalt(II) chloride and copper(II) nitrate trihydrate (Merck), carbon disulfide, and N-methyl aniline (Aldrich) were used as received. Methanol and diethyl ether (Ace chemicals) were used directly. The percentages of C, H and N were determined by an Elementar, Vario EL Cube, setup for CHNS analysis. UV–Vis spectra were obtained on a Perkin Elmer Lambda 40 UV–Vis spectrometer by solid reflectance. FT-IR spectra were recorded in the range of 4000–500 cm^{-1} on a Bruker alpha-P FT-IR spectrometer. Magnetic susceptibilities were measured on a Johnson Matthey magnetic susceptibility balance and diamagnetic corrections were calculated using Pascal's constant.[34] Conductivity measurements were conducted using a MC-1, Mark V conductivity meter with a cell constant of 1.0. TGA was performed with a SDTQ 600 thermal instrument under a nitrogen atmosphere using an alumina pan as reference. Scanning electron microscopy images were obtained on a Quanta FEG 250 Environmental Scanning electron microscope. The weight of the sample was between 10 and 12 mg and the heating rate was maintained at 10°C/min.

4.2. *Preparation of the ligand Na[$S_2CN(MePh)_2$]*

Sodium *N*-methyl-*N*-phenyl DTC was prepared according to the published procedure.[35] A solution of sodium hydroxide (8 g, 0.2 mol) in 10 mL of distilled water was prepared in a two necked flask with a thermometer. This was added to the cold carbon disulfide (12.00 mL, 0.2 mol), and was followed with the addition of 21.80 mL of N-methyl aniline (density 0.985). The mixture was stirred for about 2 h at a low temperature range of 2–4°C. The yellowish-white solid product which separated out was filtered, washed with small portions of ether, and recrystallized in acetone

4.3. *Preparation of the complexes*

4.3.1. *[Ni{$S_2CN(MePh)$}$_2$]*

Nickel(II) chloride hexahydrate (0.59 g, 2.5 mmol) was added to a methanol solution of [Na{$S_2CN(MePh)$}$_2$] and stirred for 1 h producing a dark green precipitate. The solid was obtained by filtration and washed with methanol and water. Recrystallization of the sample was carried out by layering an acetone solution with methanol. Yield (0.76 g, 72%).

Selected IR, υ (cm^{-1}): 1477 (C=N), 12,684(C_2-N), 901 (C=S). Electronic spectra (λ_{max} in Kk): 16.10 Kk. Anal. Calc. for $C_{16}H_{16}N_2S_4Ni$ (423.26): C, 45.40; H, 3.81; N, 6.62; S, 30.30. Found: C, 44.88; H, 3.84; N, 6.92; S, 30.49.

4.3.2. *[Cu{S_2CN(MePh)}$_2$]*

Copper nitrate trihydrate (0.60 g, 2.5 mmol) was added to a methanol solution of [Na{S_2CN(MePh)}$_2$] and stirred for 1 h to produce a dark brown precipitate. The solid was obtained by filtration and washed with methanol and water. It was recrystallized from layering an acetone solution with methanol. Yield (0.77 g, 72%).

Selected IR, υ (cm^{-1}): 1492 (C=N), 1282 (C_2–N), 901 (C=S). Electronic spectra (λ_{max} in Kk):14.99 Kk. Anal. Calc. for $[C_{16}H_{16}N_2S_4Cu]\cdot H_2O$ (446.13): C, 43.07; H, 4.07; N, 6.28; S, 28.75. Found: C, 43.50; H, 4.60; N, 6.30; S, 28.70%.

4.3.3. *[Co{S_2CN(MePh)}$_2$]*

Cobalt chloride (0.32 g, 2.5 mmol) was injected into a methanol solution of [Na{S_2CN(MePh)}$_2$] in a current of nitrogen, and left to stir for 1 h producing a green precipitate. The slurry was filtered through a fine porosity glass frit and washed successively with water and acetone–water mixture (1:3). The compound was reprecipitated from acetone (under nitrogen atmosphere), dried and stored in vacuo. Yield (0.53 g, 50%).

Selected IR, υ (cm^{-1}): 1463 (C=N), 1279 (C_2–N), 903 (C=S). Electronic spectra (λ_{max} in Kk): 16.13 kk. Anal. Calc. for $C_{16}H_{16}N_2S_4Co$ (423.50): C, 45.37; H, 3.80; N, 6.61; S, 30.28. Found: C, 45.22; H, 3.25; N, 6.20; S, 29.85%.

Preparation of antibacterial assay. The antibacterial assay was carried out on the ligand and its metal complexes. The bacteria used were identified clinical strains of gram-negative *E. coli*, *K. oxytoea* and *P. aureginosa*, and gram-positive *B. cereus*, *S. aureus* and *Protues mirabilis.* The antibacterial susceptibility test was carried out using the agar well diffusion technique [36] with DMSO as the delivery medium. The surface of the agar plate (Muller Hinton) was uniformly inoculated with 0.3 mL of 18 h old test bacteria culture. Using a sterile cork borer, 9 mm wells were bored into the agar. Then 0.06 mL of 10 mg/mL concentration of each metal complex in DMSO was introduced into the wells and the plates were allowed to stand for 30 min before incubation at 37°C for 24 h, after which inhibitory zones (in mm) were taken as a measure of its antibacterial activity. The experiments were conducted in duplicates with streptomycin and augmentine as the reference drugs. The MIC was carried out for the biological active complexes.

References

[1] Ileiv V, Yordanov ND, Shopov D. Studies on the intermolecular interaction of metal chelates complexes IX. On the interaction of copper(II) dithiocarbamate with some Lewis acids. Polyhedron. 1984;3:297–301.
[2] Siddiqia KS, Khan S, Nami SAA, El-ajaily MM. Polynuclear transition metal complexes with thiocarbohydrazide and dithiocarbamates. Spectrochim Acta Part A. 2007;67:995–1002.
[3] Law NA, Dietzsch W, Duffy NV. A multinuclear (^{1}H, ^{13}C, ^{15}N) NMR study of *cis*-halonitrosylbis(dithiocarbamato) iron(II) complexes: effect of replacement of S by Se. Polyhedron. 2003;22:3423–3432.
[4] Barone G, Chaplin T, Hibbert TG, Kana AT, Mahon MF, Molly KC, Worsley ID, Parkin IP, Louise SP. Synthesis and thermal decomposition studies of homo- and heteroleptic tin(IV) thiolates and dithiocarbamates: molecular precursors for tin sulfides. J Chem Soc Dalton Trans. 2002;1085–1092.
[5] Lo JM, Lee JD. Dithiocarbamate extraction and Au(III) back extraction for determination of mercury in water and biological samples by anodic stripping voltammetry. Anal Chem. 1994;66:1242–1248.
[6] Revaprasadu N, Mlondo SN. Use of metal complexes to synthesize semiconductor nanoparticles. Pure Appl Chem. 2006;78:1691–1702.

[7] Regulacio MD, Tomson N, Stoll SL. Dithiocarbamate precursors for rare-earth sulfides. Chem Mat. 2005;17:3114–3121.
[8] Pastorek R, KamenÍČek J, PavlÍČek M, HusÁrek J, ŠindelÁŘ Z, ŽÁk Z. Dithiocarbamate complexes of Nickel(II) with 1,1′-Bis(Diphenylphosphino) Ferrocene. J Coord Chem. 2002;55:1301–1308.
[9] Pan S, Wang Y. Crystal structure and spectroscopic studies of Bis (morpholine dithiocarbamate) Nickel(II) complex, $Ni(C_4H_8ONCS_2)_2$. Chin J Chem. 2001;19:856–859.
[10] Pal S. Copper(II) complexes with aroylhydrazones. Proc Indian Acad Sci (Chem Sci.). 2002;114:417–430.
[11] Hogarth G. Transition metal dithiocarbamates: 1978–2003. Prog Inorg Chem. 2005;53:71–561.
[12] Manhas BS, Verma BC, Kalia SB. Spectral and magnetic studies on normal cobalt (II) planar and cobalt (III) octahedral, spin-crossover cobalt(III) octahedral and planar-tetrahedral cobalt(II) carbodithioates. Polyhedron. 1995;14:3549–3556.
[13] Siddiqi KS, Nishat N. Synthesis and characterization of succinimide and phthalevhde dithiocarbamates and their complexes with some transition metal ions. Synth React Inorg Met-Org Nano-Met Chem. 2000;30:1505–1518.
[14] Mohammad A, Varshneya C, Nami SAA. Synthesis, characterization and antifungal activities of 3d-transition metal complexes of 1-acetylpiperazinyldithiocarbamate, $M(acpdtc)_2$. Spectrochim Acta A. 2009;73:20–24.
[15] Chohan ZH. Synthesis, characterization and biological properties of bivalent transition metal complexes of Co(II), Cu(II), Ni(II) and Zn(II) with some acylhydrazine derived from furanyl and thienyl ONO and SNO donor Schiff base ligands. Synth React Inorg Met-Org Chem. 2001;31:1–16.
[16] Singh KN, Singh DK, Singh SB. Synthesis, characterization and biological studies on Co(II), Ni(II), Cu(II) and Zn(II) complexes with N-picolinoyl-Nthiobenzoyl hydrazine. Synth React Inorg Met-Org Chem. 2001;32:703–720.
[17] Soenmez M, Levent A, Sekerci M. Synthesis, characterization, and thermal investigation of some metal complexes containing polydentate ONOdonor heterocyclic Schiff base Ligand. Russ J Coord Chem. 2004;30:655–660.
[18] Onwudiwe DC, Ajibade PA. Synthesis, characterization and thermal studies of Zn(II), Cd(II) and Hg(II) complexes of *N*-Methyl-*N*-Phenyldithiocarbamate: the single crystal structure of $[(C_6H_5)(CH_3)NCS_2]_4Hg_2$. Int J Mol Sci. 2011;12:1964–1978.
[19] Coucouvanis D. The chemistry of the dithioacid and 1, 1-dithiolate complexes, 1968–1977. Prog Inorg Chem. 1979;26:301–469.
[20] Sekkina MMA, EL-Helbawy SM. Infrared Absorption spectra of some 8-Amino quinoline solid complexes in correlation with coordination bond length. Proc Indian Natl Sci Acad. 1985;51A:946–953.
[21] Bonati F, Ugo R. Organotin(IV) N,N-disubstituted dithiocarbamates. J Org Met Chem. 1967;10:257–268.
[22] Bensebaa F, Zhou Y, Brolo AG, Irish DE, Deslandes Y, Kruus E, Ellis TH. Raman characterization of metal-alkanethiolates. Spectrochim Acta. 1999;55A:1229–1236.
[23] Singh KN, Singh DK, Singh SB. synthesis, characterization, and biological studies on cobalt (II), nickel(II), copper(II), and zinc(II) complexes with n-picol InoyL-N′-Thiobenzoyl hydrazine Sythn. React Inorg Met-Org Chem. 2002;32:703–720.
[24] Soenmez M, Haciyusufoglu ME. Synthesis and Characterization of Cu(II), Co(II), Ni(II) and Zn(II) Schiff Base complexes derived from acetylacetone with 1-Amino-5-benzoyl-4-phenyl-1H pyrimidine-2-one. Asian J Chem. 2006;18:2032–2036.
[25] Soenmez M, Levent A, Sekerci M. Synthesis, characterization, and thermal investigation of some metal complexes containing polydentate ONO-donor heterocyclic Schiff Base Ligand Russ. J Coord Chem. 2004;30:655–660.
[26] Abd El-Wahab ZH. Complexation of 4-amino-1,3 dimethyl-2,6 pyrimidine-dione derivatives with cobalt(II) and nickel(II) ions: synthesis, spectral, thermal and antimicrobial studies. J Coord Chem. 2008;61:1696–1709.
[27] Osowole AA, Kolawole GA, Kempe R, Fagade OE. Spectroscopic, magnetic and biological studies on some metal(II) complexes of 3-(4,6-Dimethyl-2Pyrimidinylamino)-1-Phenyl-2-Butenone and the mixed complexes with 2,2′-Bipyridine and 1,10-Phenanthroline. Sythn. React Inorg Met-Org Chem. 2009;39:165–174.
[28] Osowole AA, Daramola AO. Synthesis, physicochemical and biological activities of some metal(II) complexes of (methylsulfanyl)-2,4-benzenediol Schiff base. Elixir Appl Chem. 2011;39:4876–4879.
[29] Bajpai A, Tiwari S. Application of thermogravimetric analysis for characterisation of bisdithiocarbamate of urea and its copper (II) complex. Thermochim Acta. 2004;411:139–148.
[30] Ondrušová D, Jóna E, Šimon P. Thermal properties of N-ethyl-N-phenyl-dithiocarbamates and their influence on the kinetics of cure. J Therm Anal Calorim. 2002;67:147–152.
[31] Cavalheiro ETG, Ionasshiro M, Marino G, Breviglieri ST, Chierice GO. The effect of the aminic substituent on the thermal decomposition of cyclic dithiocarbamates. J Braz Chem Soc. 1999;10:65–75.
[32] Benedini VD, Antunes PA, Cavalheiro ÉTG, ChiericeI GO. Thermoanalytical and solution stability studies of hexamethylenedithiocarbamates. J Braz Chem Soc. 2006;17:680–688.
[33] Breviglieri ST, Cavalheiro ETG, Chierice GO. Correlation between ionic radius and thermal decomposition of Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) diethanoldithiocarbamates. Thermochim Acta. 2000;356:79–84.
[34] Earnshew A. The introduction to magnetochemistry. London: Academic Press; 1980, 968.
[35] Onwudiwe DC, Ajibade PA. Synthesis and Crystal Structure of Bis(*N*-alkyl-*N*-phenyl dithiocarbamato)mercury(II). J Chem Crystallogr. 2011;41:980–985.
[36] Rao NS, Reddy MG. Studies on the synthesis, characterisation and antimicrobial activity of new Co(II), Ni(II) and Zn(II) complexes of Schiff base derived from ninhydrin and glycine. Biometal. 1990;3:19–23.