



Synthesis and Characterization of a New Bidentate Ligand 5-Substituted-(2-methyl-5-nitro-1-imidazomethyl)-1,3,4-oxadiazole-2-thione and its Metal Complexes of Ag(I), Cu(II) and Zn(II)

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Abstract: A new ligand (2-methyl-5-nitro-1-imidazomethyl)-1,3,4-oxadiazole-2-thione (L) and its Ag(I), Cu(II) and Zn(II) complexes were synthesized. The authenticity of the ligand and its transition metal complexes were established by elemental analyses, conductance and magnetic susceptibility measurements, as well as spectroscopic (IR, ^1H NMR, electronic, mass and ESR) and thermal studies. The IR spectral studies revealed the existence thiol-thione tautomerism in the ligand molecule. The magnetic and electronic spectral studies suggest an octahedral geometry for Cu(II) and Zn(II) complexes. The ligand acts as a bidentate coordinating through the N-3 nitrogen and the exocyclic sulfur atoms of oxadiazole rings. Antimicrobial screening of the ligand and its metal complexes were determined against the bacteria *Escherichia coli* and *Salmonella paratyphi* A.

Keywords: Oxadiazoles, Transition metal complexes, Bidentate ligand, Synthesis, Metal Complex, Biological activity

Introduction

1,3,4-Oxadiazoles are of considerable pharmaceutical and material interest¹⁻³. They have been shown to possess muscle relaxant, anti mitotic, analgesic, anti-inflammatory, anticonvulsive, diuretic and anti-emetic properties¹⁻³. They also possess tranquilizing, antitubercular, hypoglycemic, herbicidal, antiviral, amoebicidal, insecticidal, hypnotic and

sedative activities. Some material applications of 1,3,4-oxadiazole derivatives lie in the field of liquid crystals⁵. Oxadiazole derivatives, which belong to an important group of heterocyclic compounds, have been the subject of extensive study in the recent past. Numerous reports have highlighted their chemistry and use¹⁻³. Diverse biological activities, such as anti-tuberculostatic, anti-inflammatory, analgesic, antipyretic and anticonvulsant⁴, have been found to be associated with oxadiazole derivatives⁵. For this reason our aim was to synthesize various 1,3,4-oxadiazole-2-thione derivatives to make notable contributions to this class of heterocyclic compounds. We report the synthesis and characterization of some 5-substituted-1,3,4-oxadiazole-2-thiones using the synthetic procedure based on the ring closure reactions of appropriate acid hydrazides with carbon disulphide. The heterocyclic thiones represent an important type of compound in the field of coordination chemistry because of their potential multifunctional donor sites, *viz* either exocyclic sulfur or endocyclic nitrogen⁶⁻⁷. There are a few reports on the metal complexes of 5-substituted-1,3,4-oxadiazole-2-thione⁴. To the best of my knowledge I am reporting for the first time metal complexes based on 1,3,4-oxadiazole-2-thione containing 2-methyl-5-nitroimidazole moiety (Figure 1).

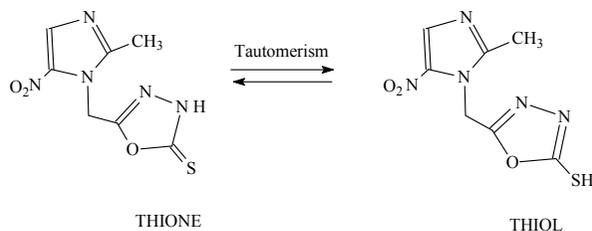


Figure 1

Influenced by these various properties of 1,3,4-oxadiazoles and their complexes, a programme to design and study the title ligand (Figure 1), which has an appropriate architecture to interact directly with metal centre was commenced. In order to reveal the conformational changes of the newly synthesized ligand upon coordination with transition metals, a study on the synthesis, characterization and spectroscopic evidence for their structural elucidation was undertaken.

Experimental

Commercial reagents were used without further purification and all experiments were carried out in open atmosphere. 2-Methyl-5-nitroimidazole (1) was purchased from Himedia and used as received. All the solvents were purchased from Merck Chemicals, India and used after purification. 2-Methyl-5-nitro-1-imidazo-acetylhydrazide (3) was prepared by refluxing 2-methyl-5-nitroimidazo-ethylacetate (2) and hydrazine hydrate².

Carbon, hydrogen and nitrogen contents were estimated on a truspec model microanalyser. By following standard procedures⁸, the complexes were analyzed for their metal content. For metal ion determination, a solution of the complex was first prepared by decomposing a known amount of complex with a mixture of conc. nitric acid and conc. Sulfuric acid⁸. The digestion was continued with repeated addition of acid mixture to ensure complete decomposition of organic matter in the complex. The residue was extracted with distilled water and the metal contents were determined by standard methods. The copper

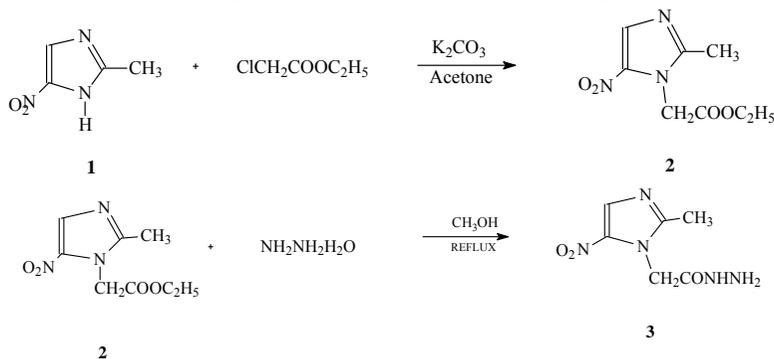
content was determined by volumetric analysis⁸ (Iodometric titrations), zinc by EDTA method⁹ and Silver content by gravimetric analysis⁸. The sulfur was estimated as BaSO₄ by gravimetric method⁸ and chloride was estimated by volumetric method⁸ using standard AgNO₃ solution.

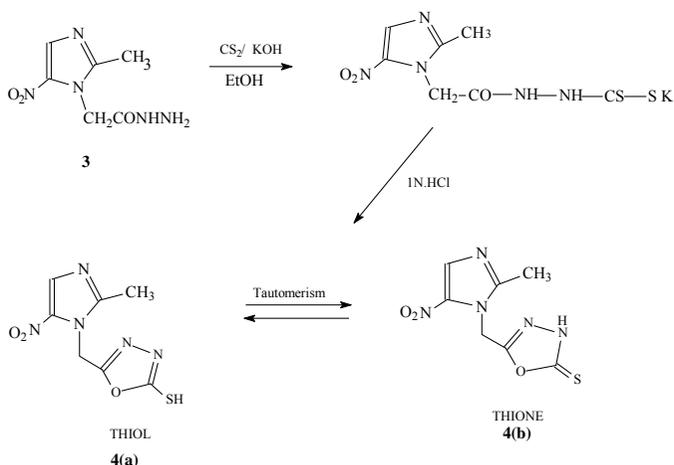
The molar conductance measurements were made in DMSO with 10⁻³ M solutions⁹ using an EI Conductivity meter, type CC-01 with a cell constant of 1.02. The molar conductance values and magnetic susceptibility data are included in Table 2.

Magnetic susceptibility measurements were performed at room temperature on a Gouy balance using Hg[Co(NCS)₄] as the calibrant⁹. Electronic spectra were recorded on a Shimadzu 1700 UV-Vis spectrophotometer using 10⁻⁵ M solution of ligand and complexes in DMSO solvent. IR spectra were recorded in the 4,000–400 cm⁻¹ region (for the ligand) IR spectrophotometer PE FTIR and in 4000–200 cm⁻¹ region (for metal complexes) on Nicolet instrument model MAGNA 550 spectrophotometer as KBr pellets. ¹H NMR spectra were recorded in DMSO-d₆ on Bruker AV III NMR spectrometer using TMS as internal reference. The EI- Mass spectrum was recorded on JEOL GC -MATE GC--MS Spectrometer using 70 eV with a source temperature of 150 °C. The ESR spectra were recorded on a Varian E-112 ESR spectrometer, x-band microwave frequency (9.5 GHz) with sensitivity of 5x10¹⁰ Δ H spins. The thermal studies of the complexes were performed on a NETZSCH TGA/DTA/DSC Thermal analyzer under a nitrogen atmosphere at a heating rate of 10 °K/min in the temperature range of 50 to 1400 °C.

Synthesis of the ligand (L) (2-Methyl-5-nitro-1-imidazomethyl)-1,3,4-oxadiazole-2-thione(MNIMOT). 4a,4b

The reactions involved in the synthesis of the ligand are shown in Scheme 1. The 2-methyl-5-nitro-1-imidazo-ethylacetate (2) and 2-methyl-5-nitro-1-imidazo-acetylhydrazide(3) were prepared by the reported procedures^{2,11}. To a solution of potassium hydroxide (4.2 g, 0.075 mole) in methanol (50 mL), 2-methyl-5-nitro-1-imidazo-acetylhydrazide(3) (10 g, 0.05 mole) was added. Carbon disulfide (6 mL, 0.075 mole) was added to the reaction mixture which led to the formation of a pale yellow precipitate. The reaction mixture was heated under reflux for 12 h during which time the mixture became clear. The solution was concentrated by distillation and the concentrate was diluted with water. The solution was acidified with 1 N HCl⁹⁻¹¹. The separated solid was collected by filtration, dried and recrystallized with a mixture of methanol and DMF. Yield= 7.5 g (63%) mp = 238-240 °C. Mol. Wt= 241. The mass spectrum of the ligand exhibits a molecular ion peak [M+1] at *m/z* 241 and a base peak at *m/z* 128.





Preparation of metal complexes of MNIMOT

To a refluxing solution of ligand (L) MNIMOT (4 mmole, 0.97 g) in 18 mL methanol and 2 mL DMF a hot solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (2mmole, 0.34 g) in 15 mL methanol was added with constant stirring. A light green color precipitate was separated. The reaction mixture was further refluxed for 30 minutes. It was cooled, filtered, washed with hot water, warm methanol and finally with ether. The complex was dried at 120°C and was cooled in a desiccators. The complexes of AgNO_3 and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ were prepared by following the similar procedure⁹.

Results and Discussion

Examination of elemental analyses data, given in Table.1 for the complexes $[\text{CuL}_2\text{Cl} \cdot \text{H}_2\text{O}] \cdot \text{Cl} \cdot \text{H}_2\text{O}$ and $[\text{ZnL}_2(\text{CH}_3\text{COO})_2] \cdot 3\text{H}_2\text{O}$ indicate their 1:2 (metal:ligand) stoichiometry. Whereas for the complex AgLNO_3 it is 1:1. They are insoluble in chloroform, carbon tetrachloride, methanol and ethanol but soluble in DMF and DMSO. The molar conductivity data obtained in DMSO suggest that the complex is $[\text{CuL}_2\text{Cl} \cdot \text{H}_2\text{O}] \cdot \text{Cl} \cdot \text{H}_2\text{O}$ 1:1 electrolyte and other two complexes are non-electrolytes in nature.

Table 1. Analytical data of MNIMOT(L) and its metal complexes

Compounds (color)	Mol. wt	Found (Calculated)%					
		M	C	H	N	S	Cl
$\text{C}_7\text{H}_7\text{N}_5\text{O}_3\text{S}$ Ligand (Brown)	241	-	33.5 (35.5)	3.22 (3.0)	27.7 (28.8)	13.27 (13.29)	
$[\text{Cu}(\text{C}_7\text{H}_7\text{N}_5\text{O}_3\text{S})_2\text{Cl} \cdot \text{H}_2\text{O}] \cdot \text{Cl} \cdot \text{H}_2\text{O}$ (Light Green) (A)	652	9.55 (9.66)	26.3 (25.8)	2.66 (2.76)	20.5 (21.4)	9.7 (9.81)	10.60 (10.88)
$[\text{Zn}(\text{C}_7\text{H}_7\text{N}_5\text{O}_3\text{S})_2(\text{CH}_3\text{COO})_2] \cdot 3\text{H}_2\text{O}$ (Brown). (B)	717	8.9 (9.04)	28.2 (30.0)	3.33 (3.6)	21.7 (20.0)	8.6 (8.90)	-
$[\text{Ag}(\text{C}_7\text{H}_7\text{N}_5\text{O}_3\text{S}) \cdot \text{NO}_3]$ (Grey) (C)	410	25.86 (26.0)	23.2 (22.0)	2.10 (18.0)	19.3 (20.0)	8.0 (7.8)	-

Table 2. Molar conductance and Magnetic properties of metal complexes

Compounds (colour)	mp °C	Molar Cond. Scm ² mol ⁻¹	Magnetic moment. $\mu_{\text{eff}}\mu_B$
C ₇ H ₇ N ₅ O ₃ S Ligand (Brown)	238-240		
[Cu(C ₇ H ₇ N ₅ O ₃ S) ₂ Cl.H ₂ O].Cl.H ₂ O (Light Green) (A)	286-290	41.5	1.75
[Zn(C ₇ H ₇ N ₅ O ₃ S) ₂ (CH ₃ COO) ₂].3H ₂ O (Brown). (B)	>360	13.6	dia
[Ag(C ₇ H ₇ N ₅ O ₃ S).NO ₃] (Grey) (C)	320-325	18.6	dia

Dia=diamagnetic

Infrared spectra

The IR spectra of the ligand (L) and complexes have been recorded and the probable assignments are given in the Table 3. The IR spectra of the ligand shows two bands at 2753 cm⁻¹ (SH group) and 1159 cm⁻¹ (C=S group) respectively which confirms the existence of thiol-thione tautomerism in the ligand molecule. The IR band appearing at 2753 cm⁻¹ (SH) in the ligand molecule has disappeared in the complexes indicating the presence of ligand molecule only in thione form in the complexes. The IR spectra of complexes indicate that the ligand behaves as a bidentate and co-ordinate to the metal via C-NH and C=S groups. In the ligand, band appearing at 3434 cm⁻¹ due to NH stretching either decreased or increased in the complexes. In the complexes of Cu(II) and Zn(II) of it has increased to 3458 cm⁻¹ and 3444 cm⁻¹ respectively. Whereas in complexes of Ag(I) it has decreased to 3429 cm⁻¹. This shows the involvement of N-atom at position 3 in the bond formation with the metal ions. The shifting of C=S stretching vibration to the lower wave number *i.e.* 1153,1152 and 1136 cm⁻¹ respectively compared to the free ligand *i.e.* 1159 cm⁻¹ is indicative of participation of thio carbonyl group(C=S) in coordination. The new bands appearing in the complexes are shown in Table 4. The bands at 535 cm⁻¹, 420 cm⁻¹, 360 cm⁻¹ and 345 cm⁻¹ are assigned for M-N, M-O and M-Cl and M-S stretching frequencies respectively which is indicative of metal-ligand bond formation.

Table 3. Major IR bands of ligand(MNIMOT) and its metal complexes

Compound	C-NH	C-H ¹	C-H ²	S-H	C=C	C-O-C	NO ₂	C=S	N-N
MNIMOT.(L)	3434	3136	2920	2753	1504	1398	1336	1159	946
[Cu(II)L ₂ Cl.H ₂ O].Cl.H ₂ O (A)	3458	3137	2924	---	1504	1398	1336	1153	944
[Zn(II)L ₂ (OAc) ₂].3H ₂ O (B)	3444	3140	2931	---	1504	1392	1335	1136	997
[Ag(I)LNO ₃] (C)	3429	3142	2929	---	1506	1399	1336	1152	945

1=Aromatic, *2*=Alkyl

Table 4. IR bands of metal complexes.

Compound	M-N	M-O	M-Cl	M-S
MNIMOT.(L)	---	---	---	---
[Cu(II)L ₂ Cl.H ₂ O].Cl.H ₂ O (A)	535	420	360	345
[Zn(II)L ₂ (OAc) ₂].3H ₂ O (B)	535	415	--	345
[Ag(I)LNO ₃] (C)	---	420	--	340

¹H NMR spectra

The proposed structure of the ligand molecule is shown in (Figure 1). The ¹H NMR signals have been tabulated in Table 5. The CH₃ proton shows signal at δ 2.39-2.51 and N-CH₂ proton at δ 5.52. The singlet observed at δ 8.4 ppm is due to the imidazole proton. A peak expected for SH proton of 1,3,4-oxadiazole-thiol (4a) is either shifted to the higher region or has disappeared because of proton exchange occurring in the thiol-thione tautomerism. The formation of the ligand is further confirmed by the mass spectra which have a molecular ion peak at *m/z* 241; which is equivalent to its molecular weight. Signals observed in the complexes at region of δ 8.39-8.42 due to the imidazole proton either remained unaffected or shifted slightly downfield with reference to those of the parent ligand and the position of signal due to N-CH₂ protons almost remained unaffected in the complexes. In the metal complexes of Cu(II) and Zn(II) additional peaks have made their appearance. In the complex(A) the peak at 2.5 δppm is due to the protons of coordinated H₂O molecule. Similarly a new peak appearing at 2.5δ ppm in the complex (B) is due to the methyl protons of coordinated CH₃COO⁻ ions. These observations support for assigning structure to the complexes.

Table 5. ¹H NMR Spectra of ligand (MNIMOT) and its metal complexes

Compound	(3H, -CH ₃)	(2H, -NCH ₂)	(1H, Imidazole)	(2H of H ₂ O)	(6H of OAc)
MNIMOT(4a,4b)	2.39	5.52	8.40	---	---
Cu(II)-MNIMOT (A)	2.37	5.52	8.39	2.5	---
Zn(II)-MNIMOT (B)	2.36	5.45	8.42	---	2.5
Ag(I)-MNIMOT (C)	2.49	5.55	8.38	---	---

Mass spectrum of ligand [L]

The mass spectrum of the ligand exhibits a molecular ion peak [M+1] at *m/z* 241 which is equivalent to its molecular weight. The fragmentation peaks, at *m/z* 167, 142 and 128 are ascribed due to the cleavage of C₆H₆N₄O₂, C₅H₆N₃O₂ and C₄H₄N₃O₂ fragments respectively.

Mass spectrum of Cu(II) complex

The mass spectrum of the complex [CuL₂Cl.H₂O].Cl.H₂O shows a molecular ion peak at *m/z* 652 which is equivalent to molecular mass of the complex. This complex shows a fragment ion peak with loss of hydrated water molecule at *m/z* 634; this fragment on further losing chlorine atom gives fragment ion peak at *m/z* 599. This fragment on losing coordinated water molecule and chlorine atom gives fragment ion peak at *m/z* 546 and this on demetallation gave another fragment ion peak for [L₂]⁺ at *m/z* 483.

Electronic spectra and magnetic properties

The electronic spectra of the ligand and complexes were recorded in 10⁻⁵ M solution in DMSO. The probable assignments are included in Table 6. The Electronic spectra of Cu(II) complex display two prominent bands¹². A low intensity broad band around 12987 cm⁻¹ and 16393 cm⁻¹ is assignable to ²T_{2g} → ²E_g transition¹². Another high intensity band at 25562 cm⁻¹ is due to ligand - metal charge transfer. On the basis of electronic spectra distorted octahedral geometry around Cu(II) ion is suggested. The Cu(II) complex showed magnetic moment 1.75 B M, is slightly higher than the spin-only value 1.73 B M expected for one unpaired electron, which offers possibility of an octahedral geometry¹³.

Table 6. UV-Vis Spectra of free ligand and its metal complexes in 10^{-5} M solution in DMSO solvent

Compounds	λ_{max} nm	ABS	Wave Number, cm^{-1}	ϵ , $\text{L.mol}^{-1}.\text{cm}^{-1}$	Transitions
MNIMMOT (LIGAND)	274	0.663	36496	15809	$n \rightarrow \pi^*$
	320	0.435	31250	10372	$n \rightarrow \pi^*$
	262	0.350	38167	22820	(L-M,C.T)
	308	0.288	32467	18777	(L-M,C.T)
Cu(II)-MNIMMOT (A)	390	0.035	25641	2282	$2T_{2(D)} \rightarrow {}^2E_{(D)}$
	460	0.025	21739	1630	${}^5E_{(D)} \rightarrow {}^5T_{2(D)}$
	610	0.026	16393	1695	d-d
	770	0.026	12987	1695	d-d
Zn(II)-MNIMMOT (B)	276	0.556	36231	39865	(L-M,C.T)
	315	0.410	31746	29397	(L-M,C.T)
	390	0.031	25641	2222	(L-M,C.T)
	252	0.328	39682	13448	(L-M,C.T)
Ag(I)-MNIMMOT (C)	272	0.333	36764	13653	(L-M,C.T)
	320	0.270	31250	11070	(L-M,C.T)
	390	0.035	25641	1435	(L-M,C.T)

ESR spectra

The ESR spectrum of copper(II) complex $[\text{Cu(II)}\text{L}_2\text{Cl.H}_2\text{O}]\text{Cl.H}_2\text{O}$. At RT exhibits three different g -values indicating magnetic anisotropy in the complex. The distorted structure of the complex is supported by its ESR spectrum recorded in solid state both RT and LNT, which shows anisotropic effects with g -tensor as g_1 , g_2 and g_3 respectively at 2.2222, 2.1345 and 2.0341 in consistent with earlier report¹⁴. The trend $g_1(2.30) > g_2(2.27) > g_3(2.05)$, for the complex suggest a rhombic octahedral geometry for the complex.

Thermogravimetric analysis

The heating rates were suitably controlled at $10\text{ }^\circ\text{C min}^{-1}$ under nitrogen atmosphere and the weight loss was measured from the ambient temperature up to $1400\text{ }^\circ\text{C}$. The thermo gravimetric studies reveal that no water molecules associated with the ligand. The decomposition of organic matter starts around $220\text{ }^\circ\text{C}$. The thermogram of ligand showed first mass loss of 14% (cal. 13.6%) at $219.3\text{ }^\circ\text{C}$ which is due to loss S-atom of ligand molecule. The second mass loss of 21% occurred at $264.4\text{ }^\circ\text{C}$ is due to the loss of NO_2 -group. After this TGA curve of ligand molecule showed maximum mass loss of 60% and is almost removed as a volatile components at about $750\text{ }^\circ\text{C}$. The TGA curves of the complexes showed that the initial mass loss occurring within $100\text{-}120\text{ }^\circ\text{C}$ range is interpreted as loss of moisture and hydrated water molecules during the chelate drying process and the second weight loss at around $200\text{ }^\circ\text{C}$ range is due to loss of coordinated water molecules.

The TGA curve of $[\text{Cu(II)}\text{L}_2\text{Cl.H}_2\text{O}]\text{Cl.H}_2\text{O}$ complex showed first mass loss of 2.7% at $76.7\text{ }^\circ\text{C}$ due to the loss hydrated water molecule, the second mass loss of 23% at $252.8\text{ }^\circ\text{C}$ is due to the loss of 2-methyl-5-nitroimidazole and chlorine atom. The third mass loss of 5.4% occurring at $343.4\text{ }^\circ\text{C}$ is due to the loss of coordinated chlorine atom. The fourth stage mass loss occurring at about $700\text{ }^\circ\text{C}$ attributed to the removal organic components from the complex. After this the thermogram is almost horizontal due the formation of metal oxide. Similarly the TGA curves of $[\text{Zn(II)}\text{L}_2(\text{CH}_3\text{COO})_2]\cdot 3\text{H}_2\text{O}$ complex showed first mass loss of

7.9% (cal=7.5%) at 89.9 °C due to the loss of three hydrated water molecules. The second mass loss of 36% occurring at 315 °C is due to the decomposition of two (2-methyl-5-nitroimidazole) moieties. The third mass loss of 8.8% is due to the loss of one coordinated acetate ion. The final mass loss of 13% at 798 °C is due to the conversion Zn metal ion into ZnO.

Biological activities

The antimicrobial activity of the ligand and the complexes were determined by the disc diffusion technique¹⁵⁻¹⁷. The compounds were screened in vitro against *Escherichia coli* and *Salmonella paratyphi* A. A 1 mg/mL solution in DMSO was used. The standard used was gentamycin sulphate. Media Used: Peptone-10 g, NaCl-10 g and Yeast extract 5 g, Agar 20 g in 1000 mL of distilled water.

Initially, the stock cultures of bacteria were revived by inoculating in broth media and grown at 37 °C for 18 h. The agar plates of the above media were prepared and wells were made in the plate. Each plate was inoculated with 18 h old cultures (100 µL, 10⁴ cfu) and spread evenly on the plate. After 20 min, the wells were filled with of compound at different concentrations. The control wells with Gentamycin were also prepared. All the plates were incubated at 37 °C for 24 h and the diameter of inhibition zone were noted. The Table 7 contains diameter of inhibition zones (in cm).

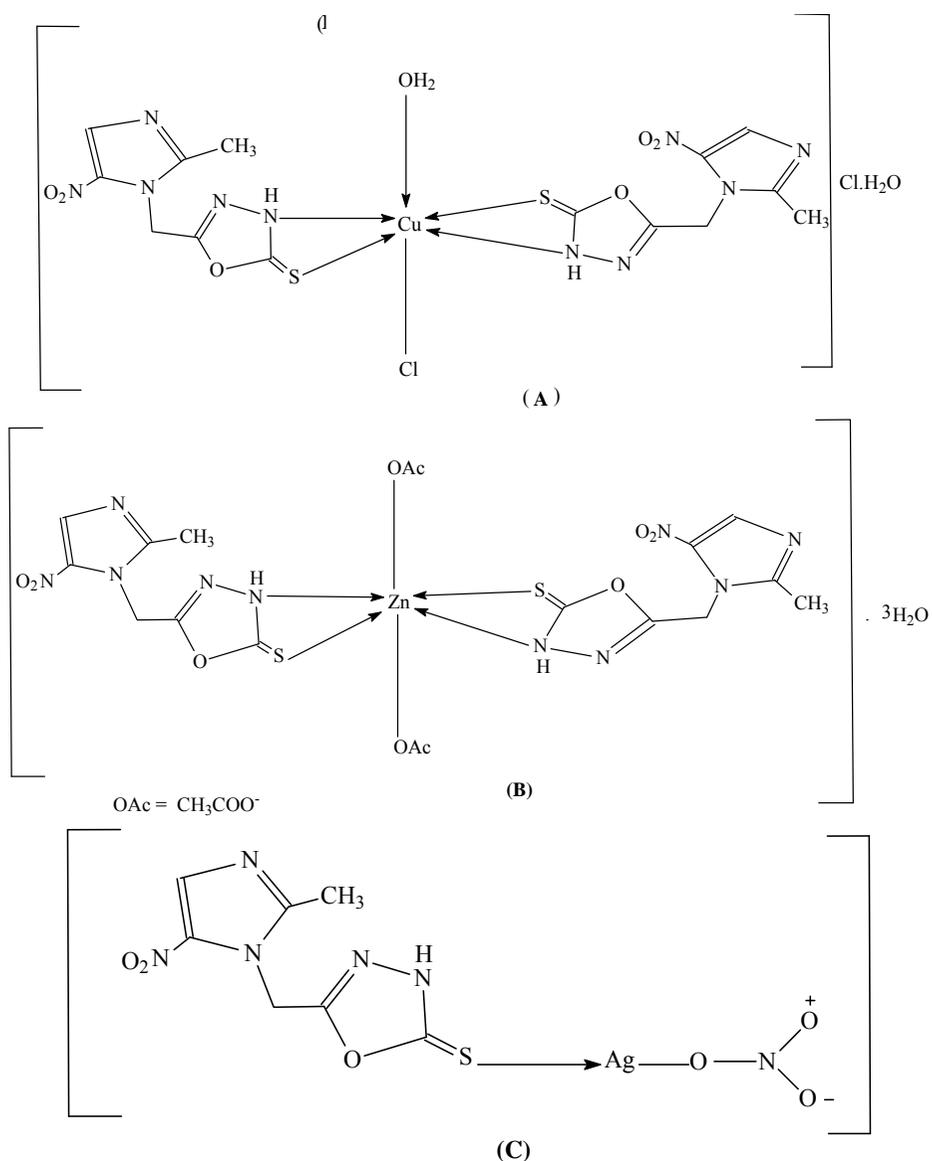
Table 7. Results of Antibacterial activities of ligand (MNIMOT) and its metal complexes *Escherichia coli*

Compound	100 µg	200 µg	500 µg	MIC µg			
MN IMOT	0.6	0.8	0.9	>500			
Cu (II)MNIMOT	0.1	0.3	0.6	>500			
Zn(II) MNIMOT	0.	0.2	0.3	>500			
Ag(I)MNIMOT	0.2	0.5	0.3	500			
	25 µg	50 µg	100 µg	200 µg	400 µg	800 µg	MIC µg
Gentamycin	1.8	2.1	2.7	2.9	3.2	3.4	25

<i>Salmonella paratyphi</i> A							
Compound	100 µg	200 µg	500 µg	MIC µg			
MN IMOT	0.3	0.8	1	100			
Cu (II)MNIMOT	0.1	0.2	0.5	200			
Zn(II) MNIMOT	0.1	0.2	0.3	>500			
Ag(II)MN IMOT	0.1	0.3	0.6	200			
	25 µg	50 µg	100 µg	200 µg	400 µg	800 µg	MIC µg
Gentamycin	0.2	1.3	1.6	2.1	2.5	2.7	25

Conclusion

The ligand molecule acts as a bidentate ligand. The spectroscopic results show the involvement of C=N(at position 3) and C=S(at position 2) groups in coordination to the central metal ion. On the basis of various techniques such as IR, ¹H-NMR, Mass, ESR, UV-Vis, Molar conductance and thermal studies used for the characterization of metal-complexes a rhombic octahedral geometry for Cu(II) complex and octahedral geometry for Zn(II) complex is proposed. In view of the foregoing discussions, the high melting points and insolubility in common organic solvents, we have assigned following probable structure of the complexes (Figure 2).


Figure 2

Acknowledgment

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