



Synthesis, Characterization Antibacterial and Antifungal Activity of Some Mixed Ligand Complexes of Zinc (II) Formed with 1-Methoxycarbonyl-1-Cyanoethylene-2, 2- Dithiolate and Various Nitrogen Donors

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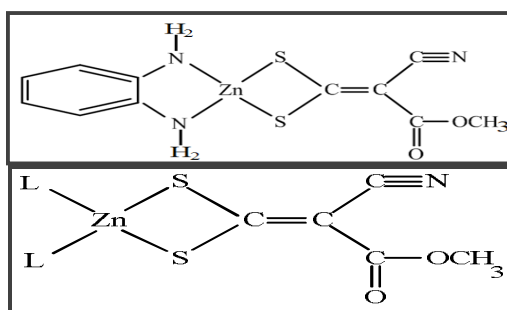
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ABSTRACT

This chapter describes introduction of mixed ligand dithiolate complexes of zinc, synthesis of mixed ligand complexes of Zn(II) with dithiolate (1-methoxy carbonyl-1-cyano ethylene -2,2- dithiolate) and nitrogen donors like pyridine, α -picoline, β -picoline, γ -picoline, orthophenylenediammine and characterization by elemental analysis, molar conductance, IR, NMR spectroscopy and thermogravimetric analysis (TGA). These complexes are of non electrolyte nature as expected. Thermogram of $[Zn(S_2C=C(CN)COOMe)(OPD)].3H_2O$ suggest that water present in the complex is not coordinated to metal. The antibacterial and antifungal properties of these complexes have been screened against bacteria *E.coli*, *B.subtilis* and fungi *Aspergillus niger* and *Aspergillus fumigates*.

Graphical Abstract



The structure of mixed ligand complexes of dithiolate of zinc(II).

$C_6H_4N_2$ = O-Phenylene diammine, L= Pyridine, α -Picoline, β -Picoline, γ -Picoline

Keywords: Zn(II), Dithiolate, Mixed Ligand, Nitrogen donor.

INTRODUCTION

Zinc is an important metal that exists in divalent state in its complexes. Its complexes are diamagnetic and have low thermodynamic stability. This metal has well disposed tendency for tetracoordination. Square planar zinc dithiolates tend to dimerise and metal increases its coordination number [1]. The

hexacoordinate zinc complexes are also well known. Zinc is important biological metal [2-5]. It plays important role in digestive metabolism, nervous reproduction and function in immune system. It is a part of several enzymes and proteins which are found in mammals. The dithiolates of zinc found various applications as semiconductors [6], vulcanization accelerators [7], antioxidants [8-10], metal sulfide nanoparticles thin films [11], catalysts [12] and nonlinear optical particles [13].

The mixed ligand complexes of zinc formed with various sulfur and nitrogen donors have been reported in literature [14-29]. We herein report synthesis, characterization of some mixed ligand complexes of zinc formed with the dithiolate ligand $\text{Na}_2\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOM}.5\text{H}_2\text{O}$ (1-methoxy carbonyl-1-cyanoethylene-2, 2- dithiolate) with various nitrogen donors ligand (orthophenylene diamine, pyridine, α -picoline, β -picoline, γ -picoline).

MATERIALS AND METHODS

Zinc was determined gravimetrically after decomposing organic part of the ligands by aquaregia. Sulfur was estimated as BaSO_4 . Melting points were taken in an open capillary and are uncorrected. The molar conductance of the millimolar solutions of the complexes in DMSO was measured using Systronics conductivity meter 304 with dip type cell. IR spectra were recorded $500\text{-}4000\text{ cm}^{-1}$ in KBr pellets on Perkin Elmer. ^1H NMR spectra were recorded DMSO solution on av 300 spectrometer. Thermogram was recorded on Perkin Elmer thermal analysis instrument.

Synthesis of the ligand: Ligand has synthesized as reported [31]. Finely crushed NaOH (4 g, 0.2 mol) was poured in 12 mL methanol and solution of methylcyanoacetate (5.5 mL, 0.1 mol) and CS_2 (5 mL, 0.1 mol). Methanol (10 mL) was added with constant stirring and cooling by maintaining the temperature in range of $15\text{-}20^\circ\text{C}$. The yellow product obtained was filtered and dried over CaCl_2 .

Synthesis of Complexes $[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})\text{L}]$ L= Py, α -picoline(pic), β -picoline, γ -picoline and OPD(o-phenylenediamine).

$[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})(\text{OPD})]$: To 20 mL of an aqueous solution of zinc acetate (1.09 g, 5 mM), 20 mL of methanol solution of OPD (0.54 g, 5 mM) was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(\text{NaS})_2\text{C}=\text{C}(\text{CN})\text{COOMe}.5\text{H}_2\text{O}$) (1.5 gm, 5 mM) was added drop wise followed by addition of 20 mL distilled water. Cream white colored product was washed with water, alcohol and ether, dried over CaCl_2 .

$[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})(\text{py})_2].3\text{H}_2\text{O}$: To 20 mL of an aqueous solution of zinc acetate (1.09 g, 5 mM), 25 mL of pyridine in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(\text{NaS})_2\text{C}=\text{C}(\text{CN})\text{COOMe}.5\text{H}_2\text{O}$) (1.5 g, 5 mM) was added drop wise followed by addition of 20 mL distilled water. Cream yellow colored product was washed with water, alcohol and ether, dried over CaCl_2 .

$[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})(\alpha\text{-pic})_2]$: To 20 mL of an aqueous solution of zinc acetate (1.09 g, 5 mM), 3 mL of α -picoline in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(\text{NaS})_2\text{C}=\text{C}(\text{CN})\text{COOMe}.5\text{H}_2\text{O}$) (1.5g, 5 mM) was added drop wise followed by addition of 20 mL distilled water. Cream orange colored product was washed with water, alcohol and ether, dried over CaCl_2 .

$[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})(\beta\text{-pic})_2]$: To 20 mL of an aqueous solution of zinc acetate (1.09 g, 5 mM), 3 mL of β -picoline in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ($(\text{NaS})_2\text{C}=\text{C}(\text{CN})\text{COOMe}.5\text{H}_2\text{O}$) (1.5 g, 5 mM) was added drop wise followed by addition of 20 mL distilled water. Cream orange colored product was washed with water, alcohol and ether, dried over CaCl_2 .

[Zn(S₂C=C(CN)COOMe)(γ -pic)₂]: To 20 mL of an aqueous solution of zinc acetate (1.09 g, 5 mM), 3 mL of γ -picoline in ethanol was added. The solution was thoroughly mixed and an aqueous solution of the ligand ((NaS)₂C=C(CN)COOMe .5H₂O) (1.5 g, 5 mM) was added drop wise followed by addition of 20 mL distilled water. Cream orange colored product was washed with water, alcohol and ether, dried over CaCl₂.

RESULTS AND DISCUSSION

Molar Conductance: Molar conductance of the complexes, [Zn(OPD)(S₂C=C(CN)COOMe)], [Zn(py)₂(S₂C=C(CN)COOMe)].3H₂O, [Zn(α -pic)₂(S₂C=C(CN)COOMe)], [Zn(β -pic)₂(S₂C=C(CN)COOMe)] and [Zn(γ -pic)₂(S₂C=C(CN)COOMe)], in 10⁻³ M solution in dimethylsulfoxide have been found in range 7.1-13.2 μ S cm⁻¹. The conductance value of all complexes indicates their non-electrolyte behavior (Table 1).

Table 1. Colour, molar conductance and analytical data of the complexes

S.No.	Complex	Colour	Mol. Wt.	M.P. (°C)	Found (Cal.%)		Molar Conductance in 10 ⁻³ M DMSO (μ S cm ⁻¹)
					M	S	
1	[Zn(OPD)(S ₂ C=C(CN)COOMe)] (C ₁₁ H ₁₁ N ₃ O ₂ S ₂ Zn)	Cream White	346.39	85	17.9 (18.8)	17.5 (18.4)	12.5
2	[Zn(py) ₂ (S ₂ C=C(CN)COOMe)].3H ₂ O (C ₁₅ H ₁₉ N ₃ O ₅ S ₂ Zn)	Light Yellow	450.39	125-130	13.5 (14.5)	12.8 (14.2)	7.1
3	[Zn(α -pic) ₂ (S ₂ C=C(CN)COOMe)] (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	Light Orange	424.39	120	14.01 (15.4)	14.5 (15.08)	9.7
4	[Zn(β -pic) ₂ (S ₂ C=C(CN)COOMe)] (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	Light Orange	424.39	160	14.5 (15.4)	13.9 (15.08)	13.2
5	[Zn(γ -pic) ₂ (S ₂ C=C(CN)COOMe)] (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	Light Yellow	424.39	95-100	14.0 (15.4)	14.5 (15.08)	8.5

IR Spectra: IR spectral bands of the complexes have been shown in table 2. IR spectra of these complexes show strong band of ν (C-S) vibrations in the region (1000-1090 cm⁻¹). These bands are similar to ν (C-S) vibration found in metal dithiolate complexes. ν (C=CS₂) band in these complexes have been found in the region (1400-1425 cm⁻¹) [31, 34]. ν (C \equiv N) has been observed in the range (2180-2260 cm⁻¹)^{32,33}. Splitting of ν (C \equiv N) in these complex suggest their lower symmetry. In the ligand ν (C-S), ν (C=CS₂), ν (C \equiv N) and ν (C=O) frequencies have been found at 1053 cm⁻¹, 1366 cm⁻¹, 2178 cm⁻¹ and 1628 cm⁻¹ respectively (Fig. 2). ν (C=O) has been observed at 1560-1690 cm⁻¹ in all the complexes.

Table 2. Important IR bands (cm⁻¹) of the complexes

S.No.	Complexes	ν (C \equiv N)	ν (C=O)	ν (C-O)	ν (C=CS ₂)	ν (C-S)	Coordination of nitrogen donor ring	Substituted ring(o,m,p)
1	[Zn(OPD)(S ₂ C=C(CN)COOMe)] (C ₁₁ H ₁₁ N ₃ O ₂ S ₂ Zn)	2180	1560	1110	1420	1090	630	730
2	[Zn(py) ₂ (S ₂ C=C(CN)COOMe)].3H ₂ O (C ₁₅ H ₁₉ N ₃ O ₅ S ₂ Zn)	2230	1625	1105	1400	1000	630	-
3	[Zn(α -pic) ₂ (S ₂ C=C(CN)COOMe)] (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	2260	1638	1110	1425	1010	630	680
4	[Zn(β -pic) ₂ (S ₂ C=C(CN)COOMe)] (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	2260	1690	1150	1430	1090	620	670
5	[Zn(γ -pic) ₂ (S ₂ C=C(CN)COOMe)] (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	2190	1620	1100	1420	1040	620	790

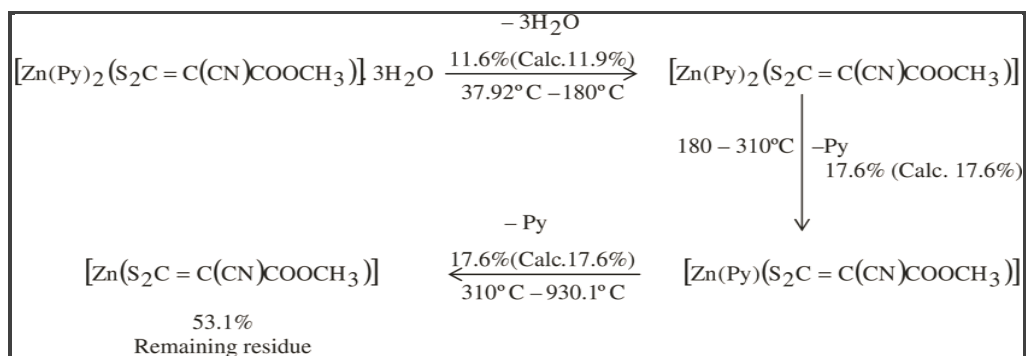
Coordinated pyridine ring vibration [32, 33] has been found at around 620-630 cm^{-1} . For mono substituted rings, bands at 690-780 cm^{-1} has been found. C-H deformation for o-substituted ring (OPD) [30] has been found at 730 cm^{-1} . $\nu(\text{C-H})$ stretching vibrations for aliphatic and aromatic types have been observed in the region 2973-2933 cm^{-1} and respectively. A broad band at 3412-3448 cm^{-1} was found in all the complexes shows presence of water molecule. Thermogram of $[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})\text{(OPD)}].3\text{H}_2\text{O}$ suggest that water present in the complex is not coordinated to metal.

^1H NMR Spectra: ^1H NMR spectra of some of the complexes have been recorded for obtaining structural information. In the complex $\text{Zn}(\text{OPD})(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})$, two sets of signal in the region 6 to 7 ppm has been found from two kinds of ring protons. $-\text{NH}_2$ protons appeared at 4.40 ppm. $-\text{OCH}_3$ proton of the ester in this complex has been observed at 3.58 ppm (Table 3).

Table 3. ^1H NMR spectral data of complexes

S.No.	Complex	Aliphatic(ppm)		Aromatic(ppm)	
		OCH_3	Aromatic Proton (ppm)	NH_2	CH_3
1.	$[\text{Zn}(\text{OPD})(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ ($\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2\text{Zn}$)	3.58	6 – 7	4.40	–
2.	$[\text{Zn}(\text{py})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})].3\text{H}_2\text{O}$ ($\text{C}_{15}\text{H}_{19}\text{N}_3\text{O}_5\text{S}_2\text{Zn}$)	3.59	7.37 – 8.56	–	–
3.	$[\text{Zn}(\alpha\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ ($\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}_2\text{Zn}$)	3.69	7.08 – 8.34	–	1.63
4.	$[\text{Zn}(\beta\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ ($\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}_2\text{Zn}$)	3.50	7.27 – 8.41	–	2.29
5.	$[\text{Zn}(\gamma\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ ($\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_2\text{S}_2\text{Zn}$)	3.43	7.11 – 8.33	–	1.61

For the complex $[\text{Zn}(\text{Py})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})].3\text{H}_2\text{O}$ containing pyridine ring, three signals in the range (7.37-8.56) ppm have been noticed. In this complex, $-\text{OCH}_3$ resonance has been observed at $\delta=3.59$ ppm. In the complex $[\text{Zn}(\alpha\text{-Pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ containing $\alpha\text{-pic}$, signals for aromatic protons have been found in the region $\delta=7.08\text{-}8.34$ ppm, $-\text{OCH}_3$ resonance and CH_3 proton resonance has been noticed at 3.69 ppm and 1.63 ppm. Signals found at positions $\delta=7.27\text{-}8.41$, 3.50 and 2.29 ppm in the NMR spectra of the complex $[\text{Zn}(\beta\text{-ic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ are attributable to aromatic protons, OCH_3 of dithiolate ligand and $-\text{CH}_3$ of β -picoline. Signals of aromatic protons, OCH_3 proton and CH_3 of γ -picoline have been found at 7.11-8.33, 3.43 and 1.61 ppm for the complex $[\text{Zn}(\gamma\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$.



Scheme 1. The TGA of $[\text{Zn}(\text{OPD})(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})].3\text{H}_2\text{O}$ suggest that water present in the complex is not coordinated to metal.

Thermogravimetric Analysis: Thermal behavior of the complex, $\text{Zn}(\text{py})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOCH}_3)$ has been observed in the temperature range 37.92-930.1 $^\circ\text{C}$. Thermogram of Zn complex indicated the

total weight loss of 46.9% upto 930.1°C and decomposition seems to be incomplete. In the first step decomposition, three water molecules are eliminated accounting weight loss (11.6% (cal. 11.9%)) in the temperature range 37.92°C-180°C. In the second step decomposition, weight loss (17.6% (cal.17.6%)) shows one pyridine molecule is lost in temperature range 180°C-310°C. Subsequent step shows loss of other pyridine molecule (17.6% (cal.17.6%)) from the complex in the temperature range 310°C-930.1°C. At the final temperature (930.1°C), 53.1% of mass of the complex remained. The end product seems to be $[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOCH}_3)]$ (Table 4).

Table 4. Temperature and Weight loss data for complex $[\text{Zn}(\text{Py})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOCH}_3)] \cdot 3\text{H}_2\text{O}$

Steps	Temp. Range °C	Wight loss%		Lost fragments	Remaining residue
		Found	Calculated		
I	37.92 – 180	11.6	11.9	3H ₂ O	$[\text{Zn}(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOCH}_3)]$ (53.1%)
II	180 – 310	17.6	17.6	Py	
III	310 – 930.1	17.6	17.6	Py	
		46.8	47.1		

APPLICATIONS

Antibacterial and Antifungal activity: The $[\text{Zn}(\text{OPD})(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$, $[\text{Zn}(\alpha\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$, $[\text{Zn}(\beta\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ and $[\text{Zn}(\gamma\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ were tested against two bacteria *E. coli* and *B. subtilis* and also tested anti fungal activity against two fungi *Aspergillus niger* and *Aspergillus fumigates* at different concentrations 2000 ppm and 1000 ppm with respect to drugs gentamycin and ketoconazole respectively. The observed of antibacterial and anti fungal activity values of these complexes are given in table 5.

Table 5. Data of antibacterial and antifungal activity

Complex	Zone of Inhibition(mm)							
	Bacteria				Fungi			
	<i>E. coli</i>		<i>B. Subtilis</i>		<i>A. Niger</i>		<i>A. Fumigatus</i>	
	2000 ppm	1000 ppm	2000 ppm	1000 ppm	2000 ppm	1000 ppm	2000 ppm	1000 ppm
$[\text{Zn}(\text{OPD})(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ (C ₁₁ H ₁₁ N ₃ O ₂ S ₂ Zn)	00	9	00	9	17.6	00	00	00
$[\text{Zn}(\alpha\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	16	3	17	12.6	8.6	5	5.6	6
$[\text{Zn}(\beta\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	16.3	2.3	23.3	10	7	5.6	9.6	5
$[\text{Zn}(\gamma\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ (C ₁₇ H ₁₇ N ₃ O ₂ S ₂ Zn)	00	00	16	11.3	8.3	5.3	18.3	16.6
Gentamycin		35		45		--		--
Ketoconazole		--		--		16		19

The antibacterial activities of these complexes are show at the concentrations 1000 ppm and 2000 ppm. These activity increases with increase in concentration against E-Coli and B Subtilis. This is because that these complexes are highly effective for *E.coli* and *B. subtilis* due to binding. Because they have affinity with both bacteria. $[\text{Zn}(\alpha\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ and $[\text{Zn}(\beta\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ complexes are also observed active at the concentration 1000 ppm against both bacteria E-Coli and B Subtilis. But The $[\text{Zn}(\text{OPD})(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ complex have been inactive at the concentration 1000 ppm against *E. Coli* and *B. Subtilis* and $[\text{Zn}(\gamma\text{-pic})_2(\text{S}_2\text{C}=\text{C}(\text{CN})\text{COOMe})]$ complex have also been inactive at both concentration 2000 ppm and 1000 ppm respectively.

The antifungal activity result show that complex $[Zn(OPD)(S_2C=C(CN)COOMe)]$ are found inactive at concentration 1000 ppm against fungi *Aspergillus niger* and this complex are also found inactive at both concentration 2000 ppm and 1000 ppm against *Aspergillus fumigates*. These complexes $[Zn(\alpha\text{-pic})_2(S_2C=C(CN)COOMe)]$, $[Zn(\beta\text{pic})_2(S_2C=C(CN)COOMe)]$ and $[Zn(\gamma\text{-pic})_2(S_2C=C(CN)COOMe)]$ are observed active at concentration 2000 ppm and 1000 ppm against *Aspergillus niger* and *Aspergillus fumigates*. The activity increase with increase in concentration against *Aspergillus niger* and *Aspergillus fumigates*.

These results suggest that the nature of different nitrogen donor ligand coordinated to metal ion play significant role in the inhibition activity.

CONCLUSION

On the basis of foregoing discussions and earlier literature, following structure of the complexes has been proposed tentatively.

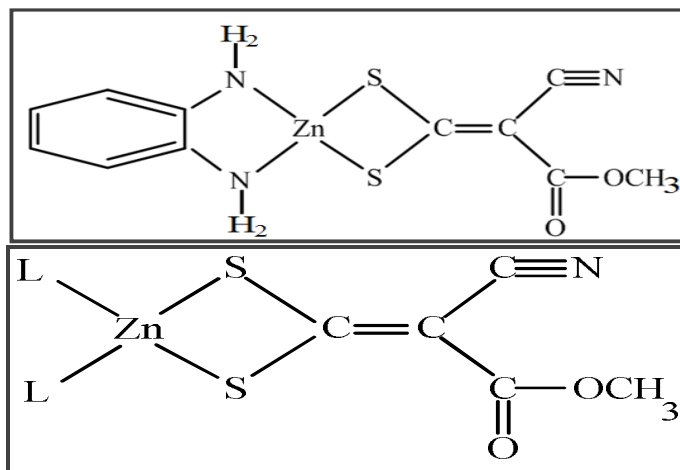


Figure 1. The structure of mixed ligand complexes of dithiolate of zinc(II).
 $C_6H_4N_2$ = O-Phenylene diammine, L= Pyridine, α -Picoline, β -Picoline, γ -Picoline

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