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Synthesis, Characterisation And Antibacterial Study Of Mixed Ligand Morpholine Dithiocarbamato And 1,10-Phenanthroline Complexes Of Nickel(Ii) , Cobalt(Ii) , Copper(Ii) , Zin(Ii).

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Abstract: *A few mixed ligand complexes of the general formula [M (mordtc)(1,10-phen)] where M=Ni(II),Co(II),Cu(II), Zn(II)have been synthesised and characterized by electronic and infrared spectroscopy, and elemental analysis. The metal complexes were screened against gram positive bacteria (Streptococcus pneumonia and Staphylococcus aureus) and gram negative bacteria (Klebsiella subtilis and Escherichia coli) using Agar diffusion test. The complexes recorded a moderate activity against the screened pathogens.*
Keywords: *Antibacterial activity, Morpholine dithiocarbamate,1,10-phenanthroline*

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I. Introduction

Dithiocarbamates are a class of metal- chelating ,antioxidant compounds with various applications in medicines for the treatment of bacterial, fungal infections[1].They are used as accelerators in vulcanization, as high-pressure lubricants, in agricultural field as pesticides, analytical and organic chemistry fields[2,3].An extremely large number of dithiocarbamate complexes with transition and non transition metal ions have been reported[4].Many mixed ligand complexes of 1,10-phenanthroline have been reported[5-8] and most of these complexes have been screened for their antibacterial activity.Continuing our practical interest in the synthesis and study of new dithiocarbamato complexes this paper reports on the formation and study of mixed ligand complexes of some transition metal ion with morpholine dithiocarbamate and 1,10-phenanthroline metal complexes of dithiocarbamate with nitrogenous bases such as pyrolidine,picoline,1,10-phenanthroline with phosphine and its derivatives have been reported[9-17].Literature reports on dithiocarbamate complex containing 1,10-phenanthroline are scares[18].The resulting complexes where screened for their antibacterial study.

II. Experimental

The Micro analysis for carbon, hydrogen, nitrogen and sulphur in the synthesized ligand complex were done on an Elemental model Vario EL III at Sophisticated Test and Instrumentation Centre (SAIF), Kochi.Electronic spectra were recorded in DMF solution were recorded on a Thermo electron Nicolet evolution 300UV-Vis spectrophotometer. Infrared spectral data were obtained with a Thermo Nicolet, Avatar 370 FTIR Spectrometer in the frequency range 400-3000 nm using KBr pellet.

2.1 Preparation of [M(mdtc)$_2$]

The parent [Ni(mordtc)] (mordtc= morpholine dithiocarbamate) is prepared according to the previous reports .

2.2 General method preparation of[M(II) (morpholine dithiocarbamate)(1,10-Phenanthroline) complex]

[M(II)(morpholine dithiocarbamate)(1,10-phenanthroline)] complex is prepared by refluxing, 1,10-phenanthroline (1mmole) with Ni(II) morpholinedithiocarbamate complex (1mmole)in a mixture of chloroform and ethanol, Co(II) morpholinedithiocarbamatecomplex (1mmole)dissolved in methanol,Cu(II) morpholinedithiocarbamate complex(1 mmole) dissolved in dimethyl sulfoxide for 3 hours.The precipitate obtained is washed , filtered and dried.

2.3 Antibacterial activity

The in vitro antibacterial screening effects of newly synthesized metal complexes were tested against various bacterial strains, Streptococcus,Staphylococcus (Gram Positive) and Klebsella,E.coli(Gram Negative) The antibacterial activities were evaluated by disc diffusion method using nutrient agar medium for antibacterial activity. All bacteria were inoculated into Nutrient Broth (Difco) and incubated for 24 h. In the agar well diffusion method (Mueller-Hinton Agar (Oxoid) for bacteria), the dilution plate method was used to enumerate

microorganisms for 24 hr.Using a sterilized cork borer (6mmdiameter), wells were dug in the culture plates. Metal complexes were performed at the fixed concentration of 10 mg/ml and compounds dissolved in DMF. Compounds dissolved in DMF were added to these wells. The petri dishes were after incoculation at37°C for 24 hours, after which inhibitory zone were taken as a measure of antiibacterial activity.Amoxicillin was used as the reference drug in positive control.

III. Result and Discussion

All the complexes were stable in air and soluble in DMF , DMSO and insoluble in acetone, chloroform, and ether . The mixed ligand complexes shows the formula [M-(mordtc)(1,10-phen)].

3.1 Analytical Data of the Complexes

The analytical data (table 3.1) for the mixed ligand complexes obtained by the reaction of morpholine dithiocarbamate and 1,10-phenanthroline shows the formula [M-(mordtc)(1,10-phen)]

Table **3.**1: Analytical data of complexes

Complexes	Found (calculated) %					Colour
	C	H	N	S	Metal	
[Ni(mordtc)(1,10phe)]	49.67 (50.4)	4.15 (4.50)	10.11 (10.42)	15.20 (15.91)	14.21 (14.56)	Green
[Co(mordtc)(1,10phen)]	50.01 (50.1)	4.30 (4.50)	10.25 (10.42)	15.71 (15.90)	14.46 (14.61)	Dark green
[Co(mordtc)(1,10-phen)]	50.02 (50.4)	4.23 (4.50)	10.28 (10.30)	15.41(15. 72)	15.34 (15.57)	Dark brown
[Zn(mordtc)(1,10-phen)]	49.55 (49.1)	4.01 (4.43)	10.11 (10.25)	15.26 (15.65)	15.52 (15.96)	Yellow

3.2 Infrared Spectral Studies

The principal infrared bands of the mixed ligand complexes are presented in Table 3.2. In the present case $\bar{\upsilon}_{\mathbf{assymm(C\text{-}S)}}$(999-1019 cm^{-1}) has been obtained as a single band which indicates a bidentate nature of ligand. The band close to 1490 cm^{-1} is due to the stretching of C-N group of the NCS_2 moiety. Its position corresponds to a partial double bond character.The stretching frequency of C=N of 1,10 – phenanthroline ligand in complex appeared around 1600 cm^{-1} . The broad peak in range 3300-3400 cm^{-1} is attributed to aromatic C-H stretching. The infrared spectrum of the mixed ligand complexes are given in Fig:3.2.1, Fig:3.2.2 , Fig:3.2.3.Fig:3.2.4

Table3.2.Infrared spectral data of [M(mordtc)(1,10-phen)] complexes

Complex	$\bar{\upsilon}_{(C\text{-}N)}$ cm^{-1}	$\bar{\upsilon}_{(C\text{-}S)}$ cm^{-1}		$\bar{\upsilon}_{(M\text{-}N)}$ cm^{-1}	$\bar{\upsilon}_{(C=N)}$ cm^{-1}
		$\bar{\upsilon}_{assymm}$	$\bar{\upsilon}_{symm}$		
[Ni(mordtc)(1,10-phen)]	1492	1015	592	541	1636
[Cu(mordtc)(1,10-phen)]	14478	1006	654	544	1644
[Co(mordtc)(1,10-phen)]	1479	999	655	547	-
[Zn(mordtc)(1,10-phen)]	1461	1019	635	543	1622

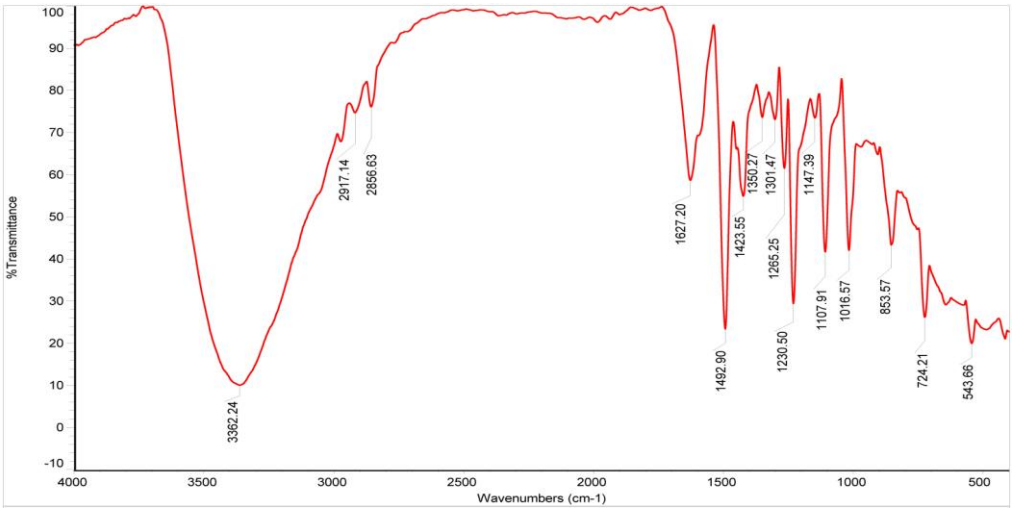

Fig:3.2.1 IR Spectrum of [Ni(mordtc) (1,10-phen)]

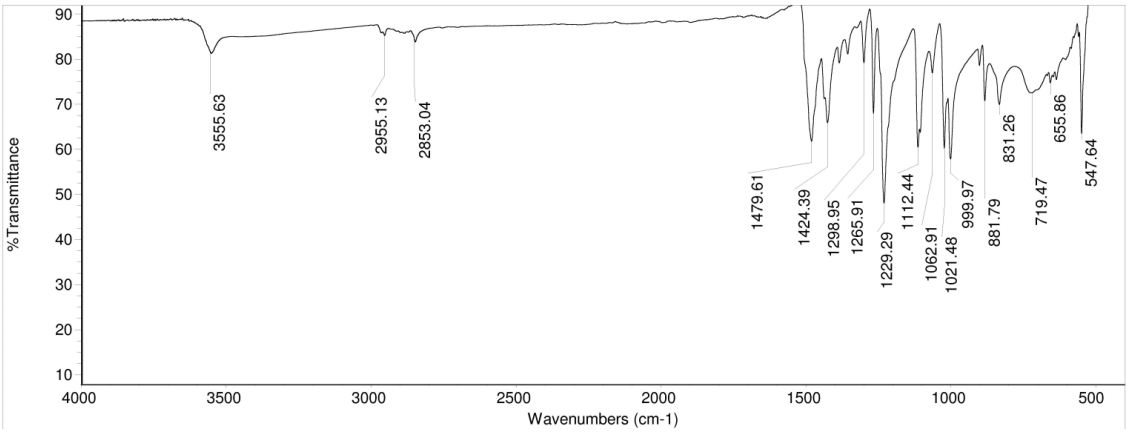

Fig:3.2.2.IR Spectrum of [Co(mordtc) (1,10-phen)]

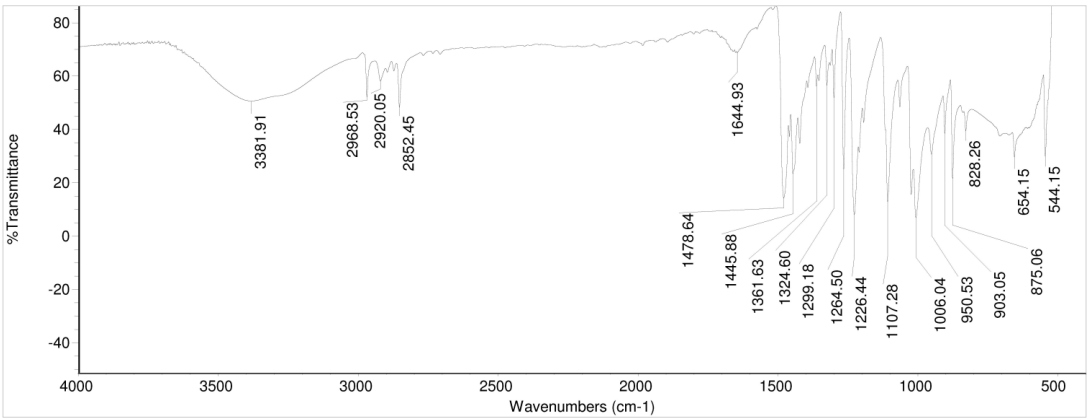

Fig:3.2.3 IR Spectrum of [Cu(mordtc) (1,10-phen)]

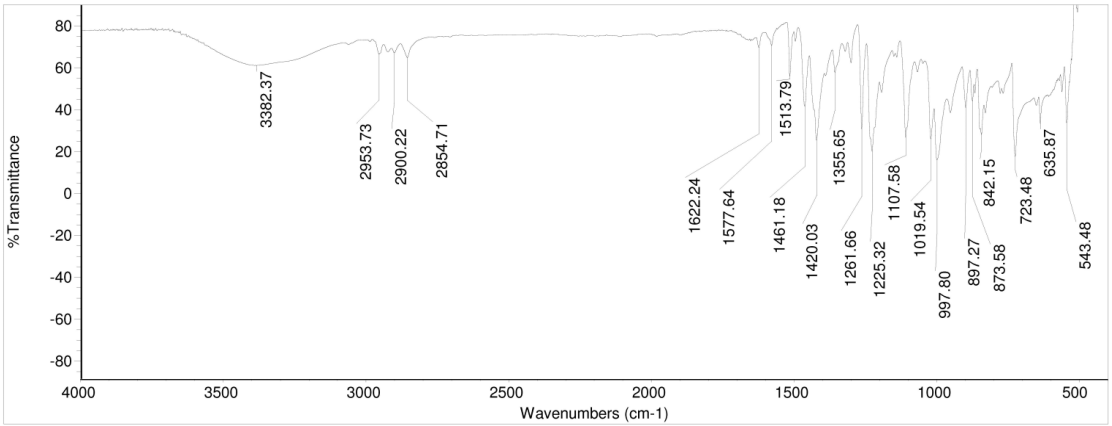

Fig:3.2.4 .IR Spectrum of [Zn(mordtc) (1,10-phen)]

3.3 ***Electronic Spectra***

Most of the dithiocarbamate complexes show bands at approximately 254nm and 274 nm although precise assignments of these bands are yet to be determined. The bands near 260 and 290 nm are due to the intraligand $\pi \rightarrow \pi^*$ transitions mainly located on N-C=S and S-C=S group [respectively[19]].The band at 350 nm is due to the transition of the type $n \rightarrow \pi^*$ located on sulfur atom.Intense band in the 390-450 nm region to either metal→ligand or ligand→metal charge [transfer[20]].In addition to these charge tansfer bands , the electronic spectra show a weak bands at 490 nm and 650 nm due to the d-d transitions. The results were tabulated in Table 3.3 and the spectrum are given in Fig:3.3.1, Fig:3.3.2, Fig:3.3.3.Fig:3.3.4, Fig:3.3.5

Table 3.3 Electronic spectra of the mixed ligand complexes

Complexes	Absorption maxima (nm)	Band Assignment
[Ni(mordtc)(1,10-phen)]	280 298	$\pi\rightarrow\pi^*$ Intraligand Transition $\pi\rightarrow\pi^*$ Intraligand Transition
[Co(mordtc)(1,10-phen)]	330 475 458 675	$n\rightarrow\pi^*$ Transition Ligand-Metal charge Transition Ligand-Metal charge Transition d-d Transition
[Cu(mordtc)(1,10-phen)]	254 274	$\pi\rightarrow\pi^*$ Intraligand Transition $\pi\rightarrow\pi^*$ Intraligand Transition
[Zn(mordtc)(1,10-phen)]	260 287	Intraligand Transition Intraligand Transition

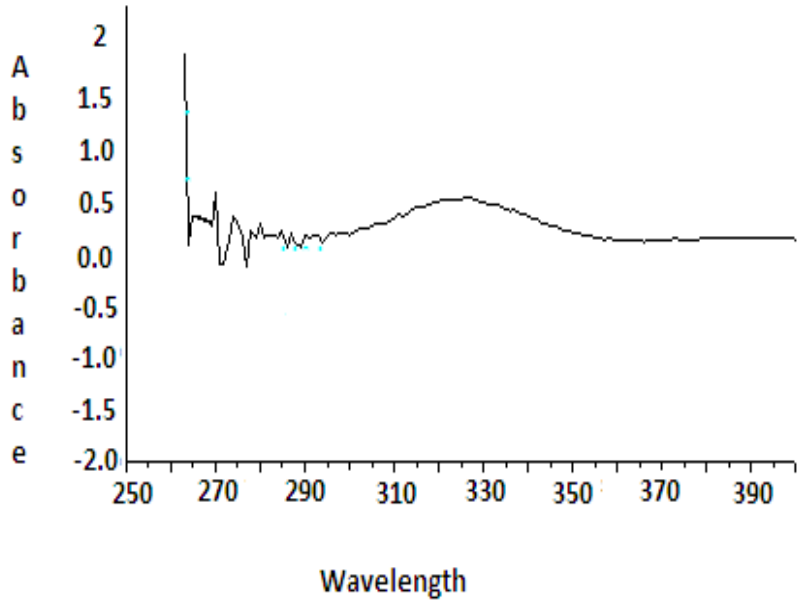

Fig:3.3.1 UV Spectrum of [Ni(mordtc)(1,10phen)]

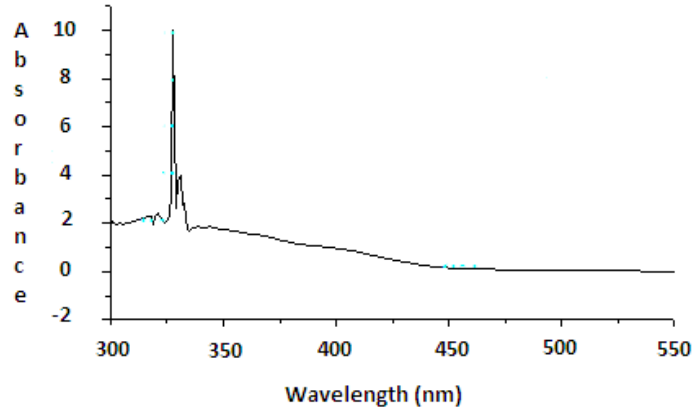

Fig.3.3.2: UV Spectrum of [Co(mordtc) (1,10phen)]

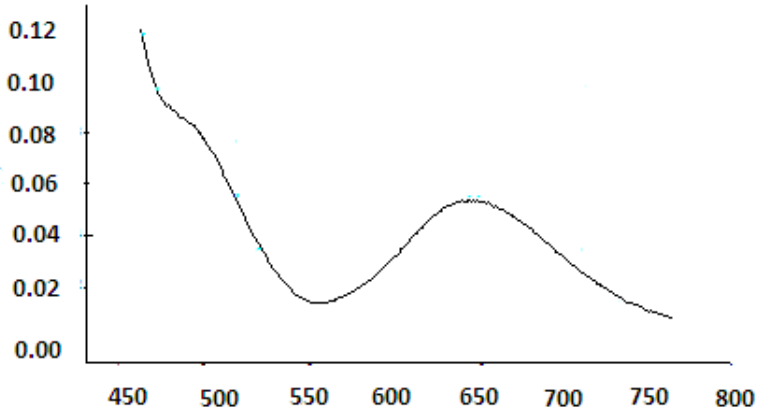

Fig.g:3.3.3spectrum of [Co(mordtc) (1,10phen)]

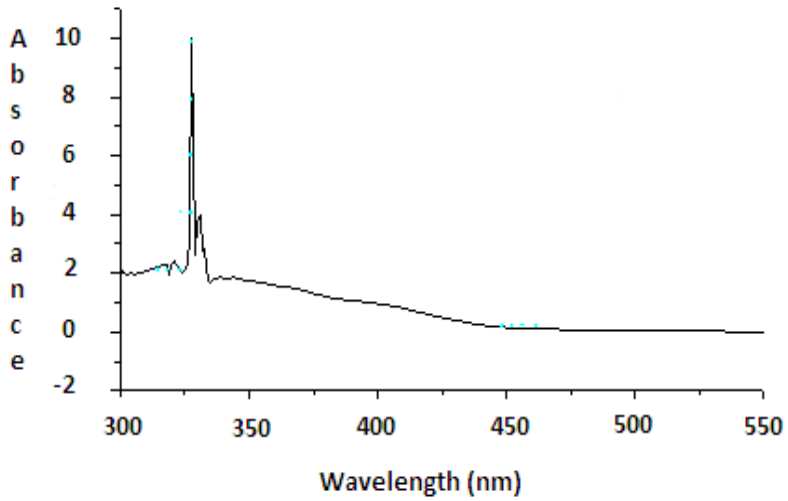

Fig.:3.3.4 UV Spectrum [Cu(mordtc)(1,10-phen)]

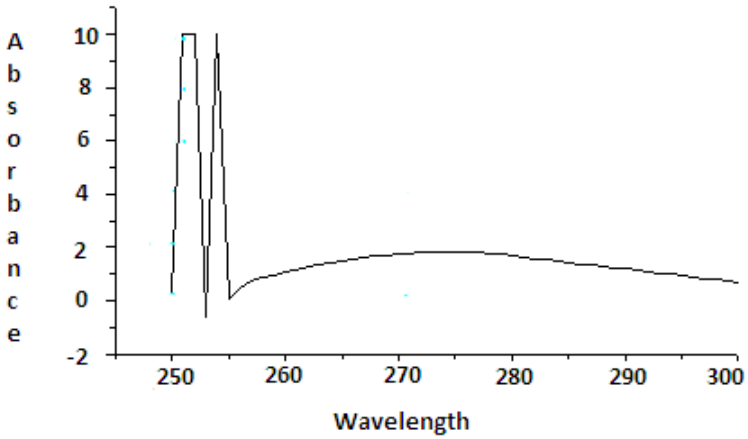

Fig:3.3.5 UV Spectrum of [Zn(mordtc)(1,10-phen)]

3.4 Antibacterial screening

The result concerning in vitro antibacterial activity of complexes together with inhibition zone diameter (mm) are presented in Table 4. All the complexes showed significant antibacterial activity against Streptococcus, Staphylococcus (Gram Positive) and Klebsella, E.coli (GramNegative) Ni(II), Cu(II) ,Co(II) complexes displayed good antibacterial activity against the tested bacteria.Tweedy's chelation therapy[21 predicts that chelation reduces the polarity of metal atom because of partial sharing of its +ve charge with donor group and possible electron delocalisation occur the whole ring.This will increases the lipophilic characters of chelates favouring its permiation through lipid layer of bacterial membrane. The results for the complexes are listed in Table3.4. Histogram representation of the antibacterial screening of the mixed ligand complexes are given in Fig:3.4.1

Table 4. Antibactetrial Screening

Test Compounds	*Escherichia Coli* cm	*Klebsiella subtilis* cm	*Staphylococcus aureus* cm	*Streptococcus Pneumoniae* cm
[Ni(mordtc)(1,10-phen)]	1.2	1.25	0.85	0.9
[Co(mordtc)(1,10-phen)]	1.4	1.4	1	0.95
[Cu(mordtc)(1,10-phen)]	0.8	1.25	0.85	0.9
[Zn(mordtc)(1,10-phen)]	1.35	1.35	0.6	1.1
Standard	1.1	1	0.7	1

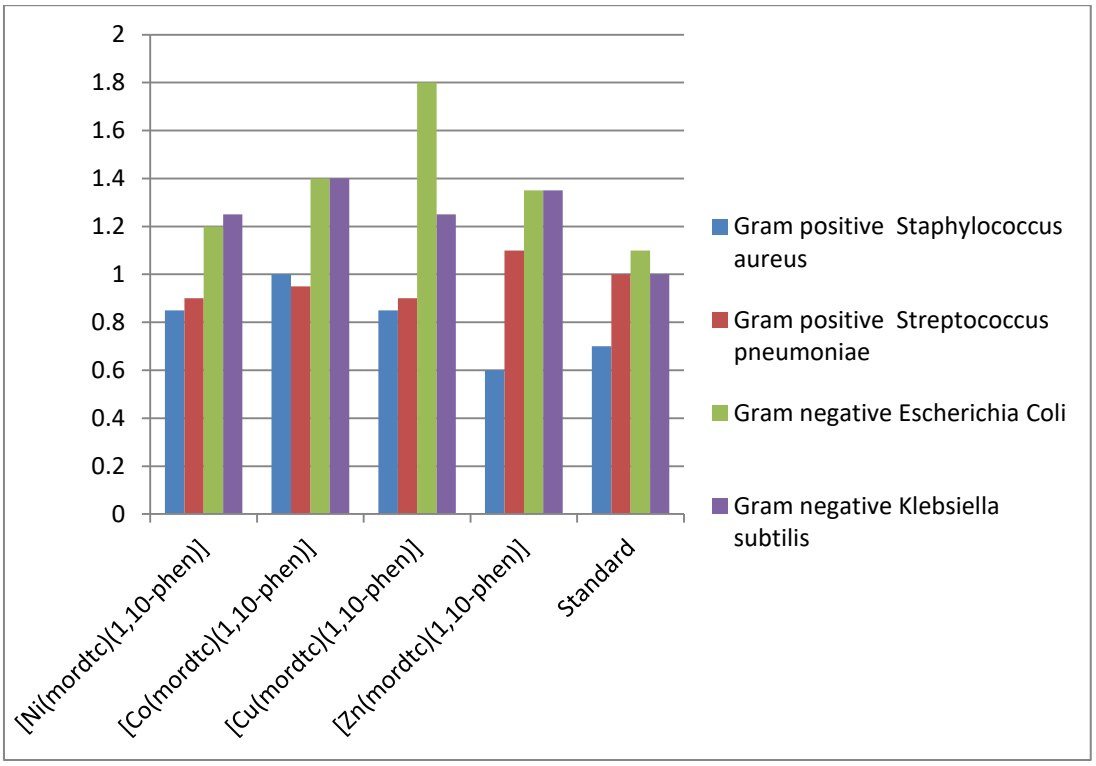

Fig:3.4.1 Histogram representation of the antibacterial screening of the mixed ligand complexes.

IV. Conclusion

In the present project attempt to synthesis , characterise and study antibacterial activity of Ni(II),Co(II),Cu(II), Zn(II) complexes with morpholine dithiocarbamate and 1,10-phenanthroline as ligands the analytical data and spectroscopy studies suggest that the complexes were of general formula [M (mordtc)(1,10-phen)] where M =Ni(II),Co(II),Cu(II), Zn(II).Account to the IR data morpholine dithiocarbamate showed bidentate coordination through both sulfur atoms.The biological activity test results showed that mixed ligand complex have significant antibacterial activity against bacteria.We think that Zn complex might be effective as an antibacterial agent.

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