

SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION AND PRELIMINARY ANTIMICROBIAL STUDIES OF Fe(III) AND Ni(II) COMPLEXES OF TWO THIOLATES; 2,6-DIAMINO-3,5-DITHIODIPHENOYL PYRIDINE (DDPP) AND PHENOYLBENZYL MERCAPTAN (PBM)

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Abstract : Phenoylbenzyl mercaptan (PBM) was prepared by condensing benzoyl chloride with benzyl mercaptan in the presence of pyridine. Similarly, DDPP 2,6-diamino-3,5-dithiophenylpyridine was obtained by the condensation of 2,6-diamino-3,5-dithiopyridine with two moles of benzoyl chloride in the presence of pyridine. The Fe(III) and Ni(II) complexes of DDPP and Ni(II) complex of PBM were synthesized using the chloride salts. All isolated compounds were characterized on the basis of their melting points, electronic and infrared data. The ligands were also characterized based on their NMR spectral data. The data show the Fe(III) complex of DDPP to be a dinuclear, octahedral and cationic. While Ni(II) complex of DDPP is octahedral but neutral. On the other hand the Ni(II) complex of PBM is most probably square planar and cationic. All the isolated compounds showed varying degrees of activity against *Bacillus subtilis*, *Pseudomonas aeruginosa*, *Escherichia coli* and *Candida albicans*.

Introduction

Co-ordination chemistry of iron(III) is of much interest not only to the chemist but also to the biologist. This is much more due to the physiological role played by iron in living tissues (Spiro, 1980). For example, inorganic pharmaceuticals derived from iron range from the phospholipid-encapsulated iron(III) sulphate (Boccio et al., 2001) to the iron complexes of salicylic acid (Petrenfc and Vladimirov, 1998), and bis(salicyl)glycine (Muller and Burrows, 1998). Also, iron(III) complexes of pentaazamacrocyclic ligands $[\text{FeCl}_2\text{L}]^+$ have been known to protect cells from free radical damage (Byunghoon et al., 1999). In addition, carcinostatic properties have been reported for 4-ferrocenylbutanoic acid (Neuse, 1998). Of recent Rousin salts, $[\text{Fe}_2\text{S}_3(\text{NO})_4]^{2-}$ and $[\text{Fe}_7\text{S}_3(\text{NO})_7]^-$ as well as iron nitrosyl porphyrin complexes are being investigated for possible use in sensitizing tissues to radiotherapy and reduce toxic shocks (Ford, 1998).

Keywords : 2,6-diamino-3,5-dithiodiphenyl pyridine (DDPP), Phenoylbenzylmercaptan (PBM), antimicrobial, complexes, ligands.

Nickel(II) complexes of glycoside containing triamine ligands have shown high potency in inhibiting the growth of the pathogenic yeast, *Candida albicans* (Yano et al., 1998). Recently a new Ni(II) enzyme, acireductone dioxigenase (ARD) which catalyses oxidative breakdown of acireductone to 2- methylthiopropionate in *klebsiella pneumonia* was discovered (Szajna et al., 2004). In this dioxigenase, the sulfur atom is ligated to the Ni(II) centre. This has generated a lot of interest in ARD chemistry and its synthetic models are being prepared. Also current research is targeted towards ligands that coordinate through sulfur atom.

The present work reports on the synthesis of Fe(III) and Ni(II) complexes of two new ligands DDPP and PBM. These complexes have been characterized by means of their electronic, IR, NMR spectra as well as microanalysis and conductance measurements. Similarly ligands and complexes were screened for antibacterial and antifungal activities.

EXPERIMENTAL

Reagents/Instruments

Nickel (II) chloride and iron (III) chloride were products of Fluka, Switzerland. Benzoylchloride, benzylmercaptan and 2,6-diamino-3,5-dithiopyridine were obtained from BDH (England) and were used as supplied. The melting points were measured using a 4017 model of John-Fisher melting point apparatus (USA). The electronic spectra were obtained on CECIL CE 9050 spectrophotometer, FTIR data were recorded as Nujol Mulls on Buck Scientific model 500 IR Spectrophotometer. Proton and carbon-13 NMR spectra were run with YH 200 MHz Varian Mercury NMR spectrometer using CDCl_3 and DMSO as solvents respectively. The proton NMR peaks were observed at 200 MHz whereas the carbon-13 spectra were observed at about 50 MHz. All the spectroscopic analysis was performed at the Central Analytical Laboratory of Obafemi Awolowo University, Ile-Ife, Nigeria. Elemental analysis was done using LECO-CHNS 932 microanalysis apparatus at Department of Pure and Applied Chemistry, University of Strathclyde, UK. Conductance measurement for the compounds were made at 28°C using a Milwaukee CD 600 Conductivity meter with a cell constant of 1.0 cm^{-1} . Standard solutions were prepared in nitrobenzene.

Preparation of Ligands

Synthesis of 2,6-diamino-3,5-dithiodiphenoyl pyridine (DDPP)

Standard method is as described in Reference (Vogel, 1989). 5.8 mL (0.05 mole) benzoyl chloride, 2.925 g (0.025 mole) 2,6-diamino-3,5-dithiopyridine and about 5 mL of pyridine were mixed in a 500 mL round-bottomed flask. The mixture was heated with stirring in a water bath until HCl fumes ceased. Then 2 mL of distilled water and about 2 mL pyridine were added to eliminate the excess of the reagent. Pale green solid was separated and was recrystallized with dilute ethanol. The yield was 56 %.

Synthesis of Phenolylbenzylmercapttn (PBM)

2.9 mL (0.025 mole) benzoyl chloride, 2.33 mL (0.025 mole) benzylmercaptan and about 5 mL of pyridine was mixed in a 500 mL round-bottomed flask. The mixture was heated with

stirring over a water bath until HCl fume ceased. Then about 2 mL of distilled water and about 2 mL of pyridine were added to eliminate excess reagent. The mixture was allowed to cool and white needle like crystals separated. The product was recrystallized with absolute ethanol. The yield was 87.9 %.

Preparation of Complexes

Synthesis of Fe(III) and Ni(II) Complexes of DDPP

1.623 g (0.01 mole) of FeCl_3 was dissolved in 10 mL absolute ethanol and mixed with 0.009 g (0.02 mole) of DDPP previously dissolved in 10 mL of absolute ethanol. The mixture was refluxed for 30 minutes. A pale green product separated which was washed with absolute ethanol and dried at room temperature. The Ni(II) complex was prepared similarly.

Synthesis of Ni(II) Complex of PBM.

1.297 g (0.01 mole) of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ earlier dissolved in absolute ethanol was added to 0.01 g (0.02 mole) of PBM also dissolved in ethanol. The mixture was refluxed for 30 minutes. The solution was allowed to cool and dirty white needle-like crystals separated. The product was washed with absolute ethanol and dried at room temperature. The Fe(III) complex was not isolated.

Conductance Measurement

Conductance measurement for the compounds were made at 28 °C using a Milwaukee CD 600 Conductivity meter with a cell constant of 1.0 cm^{-1} . Standard solutions were prepared in nitrobenzene.

Spectroscopic Analyses

The electronic spectra were obtained on CECIL CE 9050 spectrophotometer, FTIR data were recorded as Nujol Mulls on Buck Scientific model 500 IR Spectrophotometer. Proton and carbon-13 NMR spectra were run with YH 200 MHz Varian Mercury NMR spectrometer using CDCl_3 and DMSO as solvents respectively. The proton NMR peaks were observed at 200 MHz whereas the carbon-13 spectra were observed at about 50 MHz. All the spectroscopic analysis was performed at the Central Analytical Laboratory of Obafemi Awolowo University, Ile-Ife, Nigeria

Antimicrobial studies of 2,6-diamino-3,5-dithiodiphenyl pyridine (DDPP) and phenylbenzylmercaptan (PBM) and their respective Fe(III) and Ni(II) complexes.

The antimicrobial properties of two ligands ; 2,6-diamino-3,5-dithiodiphenyl pyridine (DDPP) and phenylbenzylmercaptan (PBM) and their respective Fe(III) and Ni(II) complexes were determined against *Staphylococcus aureus* (ATCC 25923), *Bacillus subtilis* (ATCC 6633), *Pseudomonas aeruginosa* (ATCC 27853), *Escherichia coli* (ATCC 25922) and *Candida albicans* (ATCC 2091) obtained from BDCP IntaceEED, Nsukka, Nigeria using the agar-well diffusion method (Chah et al., 2006). Briefly, each Mueller-Hinto agar (and Sabouraud dextrose agar for *Candida albicans*) plate was inoculated with 0.1 mL of 3 hours broth culture of each test

stirring over a water bath until HCl fume ceased. Then about 2 mL of distilled water and about 2 mL of pyridine were added to eliminate excess reagent. The mixture was allowed to cool and white needle like crystals separated. The product was recrystallized with absolute ethanol. The yield was 87.9 %.

Preparation of Complexes

Synthesis of Fe(III) and Ni(II) Complexes of DDPP

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Synthesis of Ni(II) Complex of PBM.

1.297 g (0.01 mole) of $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ earlier dissolved in absolute ethanol was added to 0.01 g (0.02 mole) of PBM also dissolved in ethanol. The mixture was refluxed for 30 minutes. The solution was allowed to cool and dirty white needle-like crystals separated. The product was washed with absolute ethanol and dried at room temperature. The Fe(III) complex was not isolated.

Conductance Measurement

Conductance measurement for the compounds were made at 28 °C using a Milwaukee CD 600 Conductivity meter with a cell constant of 1.0 cm^{-1} . Standard solutions were prepared in nitrobenzene.

Spectroscopic Analyses

The electronic spectra were obtained on CECIL CE 9050 spectrophotometer, FTIR data were recorded as Nujol Mulls on Buck Scientific model 500 IR Spectrophotometer. Proton and carbon-13 NMR spectra were run with YH 200 MHz Varian Mercury NMR spectrometer using CDCl_3 and DMSO as solvents respectively. The proton NMR peaks were observed at 200 MHz whereas the carbon-13 spectra were observed at about 50 MHz. All the spectroscopic analysis was performed at the Central Analytical Laboratory of Obafemi Awolowo University, Ile-Ife, Nigeria

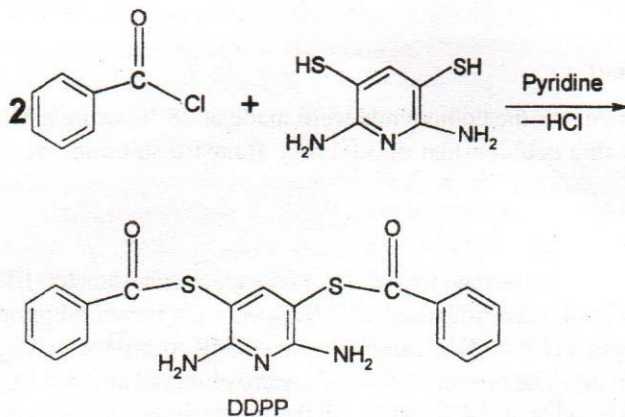
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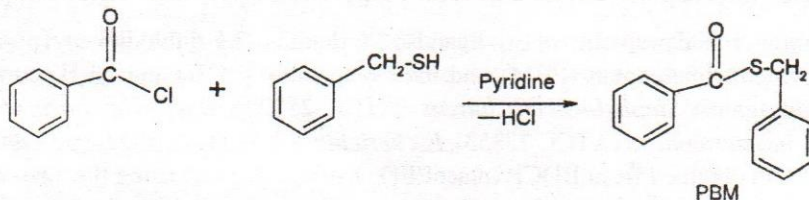
organism. Wells (7 mm in diameter and 2.5 mm deep) were cut into the inoculated agar and labelled from one to seven. 50 μL of 20 mg/mL of DDPP, PBM, $[\text{Fe}_2\text{XL}_2]^{3+}$, $[\text{NiLX}_2]$, $[\text{Ni}(\text{PBM})_2]^{2+}$ were placed in wells labelled 1 to 6; and 20% v/v dimethylsulfoxide (DMSO) was delivered into the 7th well. The set up was left on the laboratory bench for one hour for the solutions and DMSO to diffuse into the media. The plates were then incubated at 37°C for 24 hours. Assessment of antibacterial activity was based on the measurement of the diameter of inhibition zone (IZD) around the wells. The experiment was replicated three times and the mean IZD was recorded to the nearest whole millimetre.

Results and Discussion

The synthesis of these ligands was based on the well-known condensation reaction of acyl chlorides with thiols (Vogel, 1989). The reaction of benzoyl chloride with 2,6-diamino-3,5-dithiopyridine afforded 2,6-diamino-3,5-dithiodiphenylpridine herein after denoted DDPP according to Scheme (1). Also the reaction of benzylmercaptan with benzoyl chloride yielded phenylbenzoyl mercptan (PBM) as seen in scheme (2). Reaction of FeCl_3 and $\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$ with either DDPP or PBM afforded the complexes.



Scheme 1: Synthesis of DDPP



Scheme 2: Synthesis of PBM

Physical Properties

The physical properties of these ligands and their complexes are presented in Table-1.

Table-1 : Physical Properties of the Ligands and Complexes

Compound	Colour	Melting Point (°C)	Yield (%)	Molar conductivity (cm ² Ohm ⁻¹ mole ⁻¹)
DDPP	Pale Green	178 - 180	56	-
PBM	White	115 - 117	87.9	-
[Fe:XL ₂] ⁵⁺	Pale Green	220 - 223	70	77.60
[NiLX ₂]	Dirty Green	195 -197	65	4.15
[Ni(PBM) ₂] ²⁺	Dirty White	124 - 126	60	43.70

Legend : L = DDPP; X = Cl

Analytical Data

The analytical data of these ligands are presented in Table-2.

There is a good agreement between what is expected and what was observed as regards the analytical data. The crystalline solids were found to be stable and on storage for about 24 months their nature did not changed. The conductance indicates that the nickel(II) complex of DDPP is most probably non-ionic as the value shows that it did not dissociate. The values found for other complexes show [Ni(PBM)₂]²⁺ to be a 2:1 electrolyte and Fe(III) complex of DDPP to be a 5:1 electrolyte.

Table-2 : Analytical Data of the Ligands

Compound	Molecular Mass		%C		%H		%N		%S	
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
DDPP	366	360	62.30	62.46	4.10	4.38	11.48	10.89	17.49	19.12
PBM	228	231	73.68	71.50	5.26	6.10	-	-	14.03	15.01

Spectroscopic Studies

Table-3 describes the electronic spectral results of these ligands and their complexes. DDPP and PBM showed sharp intense bands at 246.8 nm and 257.0 nm respectively. These bands have been assigned specifically to $\pi \rightarrow \pi^*$ transitions of aromatic rings. The electronic data of [Fe₂XL₂]⁵⁺ shows two bands in the regions 234 nm and 344.0 nm. The band at 234 nm is mainly due to ligand transition whereas the metal $d \leftarrow d$ transition likely results in the broad band at 344.0 nm with low extinction. However, for most octahedral Fe(III) complexes, bands in this area are due to charge transfer phenomenon which masks the $d \leftarrow d$ transition (Szajna et al., 2004). The Ni(II) complexes have absorption bands similar to that of Fe(III). The peaks between 246 nm to 258 nm results from $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transfer in the ligands but shifts to slightly higher wavelength are due to complexation which distorts the $\pi \rightarrow \pi^*$ transitions. The bands at 345-348 nm (28985.50 – 28735.63 cm⁻¹) have been ascribed to ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ in an octahedral field. The same observation has been made for hydrazone complexes of Ni(II) (Agarwal and Prasad, 2005; Lee, 1998).

Table-3 : Electronic Spectral Data (nm) of Compounds

Compound	ν_1	ν_2
DDPP	246.8 (1.696)	-
PBM	257.0 (2.673)	-
$(\text{Fe}_2\text{XL}_2)^{5+}$	234 (2.581)	344.0 (1.453)
$[\text{NiXL}_2]$	258 (3.092)	345.2 (2.046)
$[\text{Ni}(\text{PBM})_2]^{2+}$	246.6 (2.854)	348.0 (1.328)

Legend : L = DDPP; X = Cl

Table-4 show the peaks and assignments of the IR absorptions of the ligands and complexes. In the ligands and their complexes, the most significant peaks are those of $\nu(\text{NH}_2)$ which appears at 3455 cm^{-1} in DDPP, 3430.9 cm^{-1} in $[\text{Fe}_2\text{XL}_2]^{5+}$ and at 3354.66 cm^{-1} in $[\text{NiXL}_2]$. The

Table-4 : Infrared Absorption Frequencies (cm^{-1}) in Nujol Mulls of DDPP, its Fe(III) and Ni(II) Complexes and PBM and its Ni(II) Complex

DDP	$[\text{Fe}_2\text{XL}_2]^{5+}$	$[\text{NiXL}_2]$	PBM	$[\text{Ni}(\text{PBM})_2]^{2+}$	Assignment
3455 (br)	3430.9 (br) 3142 (sh)	3354.66 (br) 3121.14(sh)			$\nu(\text{N} - \text{H})$
2853.19 (s) 2800 (s)	2890 (s) 2805 (s) 2349 (w)	2891 2851 2327.54	2918.84 (s) 2858.64 (w)	2918.85 (s) 2857.45 (s) 2675.93	$\nu(\text{C} - \text{H})$
164.97 (s)	1628.8 (br)	1602 (br)	1700 (w) 1669.26 (m) 1650 (w)	1694.68 1619.51 1454.52	$\nu(\text{C} = \text{O})$
1461.62 (s) 1377.30 (s) 1289.10 (w)	1462.33 (s) 1377.35 (s) 1287.56 (w)	1462 (s) 1377.66 (s)	1453.03		$\nu(\text{C} - \text{C})$ of ring
1255 (w) 1125.80 (w)	1028.59 (w)	1157 (w) 1034.69 (s)			$\nu(\text{C} - \text{N})$
			1400 (m) 1325 (m) 1215	1377.60 1287.24	γ (ring) ω (CH_2)
935.09 (w)			999.31 (m) 914.09 (s)	915.37 (s)	ω (C - H)
			1127.08 (m) 1069.69 (m)	1176.54 1028.11	γ (CH_2) ring vibration
760 (W) 710.40(s)	721.73 (w)	721.98 (w)	804.45 (s) 706.83 (s)	804.36 (s) 750 (w) 710 (s)	ν (C - S)
690.09 (m) 547.05 (w)			537.50 (s)		Ring breathing
	512.50 (w) 451.20 (w) 409.52 (w)	543.30 (w) 415.35 (w) 395.16 (w)		412.12 (w) 339.50 (w)	$\nu(\text{M} - \text{O})$, $\nu(\text{M} - \text{N})$, or $\nu(\text{M} - \text{s})$

s = strong, m = medium, br = broad, sh = shoulder, w = weak

shifts in the peaks, suggest the participation of N-H in bonding to the metals. As expected, the spectrum of PBM does not show any peak for N-H. $\nu(\text{C}=\text{O})$ is seen at 1694.97 cm^{-1} in DDPP and at 1669.26 cm^{-1} and 1700 cm^{-1} in PBM. However $[\text{Fe}_2\text{XL}_2]^{5+}$ and $[\text{NiXL}_2]$ have the $\nu(\text{C}=\text{O})$ centered at 1628.8 cm^{-1} and 1602 cm^{-1} respectively suggesting likely ligation through the oxygen atom of the carbonyl group. The peaks at 760 cm^{-1} and 710.40 cm^{-1} for DDPP and

708.83 cm^{-1} for PBM is likely due to $\nu(\text{C} - \text{S})$ stretch. In $[\text{Fe}_2\text{XL}_2]^{3+}$ this peak shifted to 721.73 cm^{-1} and in $[\text{NiLX}_2]$, it shifted to 721.98 cm^{-1} . In $[\text{Ni}(\text{PBM})_2]^{2+}$, this peak was not observed. These results also indicate the lone pair electrons on the S atom to have participated in bonding to the metals.

Table-5 : ^1H NMR Data of the Ligands

DDPP	
^1H (δ)	Assignments
7.95 (10H, m)	Aromatic protons on the side rings
7.52 (1H, s)	Proton in the middle pyridine ring
7.6 (4H, s)	Protons on the two amino groups of the pyridine ring
PBM	
7.8 (5H, m)	aromatic protons on A side rings
7.5 (5H, m)	aromatic protons on B ring
2.5 (2H, s)	($\text{CH}_2 - \text{S}$) protons

Table-6 : ^{13}C NMR Data of the Ligands

Position	$^{13}\text{C}(\delta)$	Structure Showing Carbon Numberings for DDPP	
C1, C15	129.271		
C2, C16	129.931		
C3, C17	129.472		
C4, C18	129.962		
C5, C19	129.986		
C6, C14	129.992		
C9	131.411		
C8, C10	133.581		
C11, C12	133.621		
C7, C13	168.017		
Position	$^{13}\text{C}(\delta)$		Structure Showing Carbon Numberings for PBM
C8	40.0		
C2, C11	129.188		
C1, C10	129.224		
C3, C12	129.977		
C4, C13	130.011		
C5, C14	131.449		
C9	133.328		
C6	133.482		
C7	168.063		

The Proton and Carbon-13 NMR spectra of the ligands are shown in Table-5 and 6 respectively. For DDPP, the peak at 7.6 ppm and integrated for 4 protons is due to two $-NH_2$ protons. The peak centered at 7.52 ppm has been assigned to the protons of the pyridine ring whereas the peak centered at 7.95 ppm is due to the 10 aromatic protons in the side.

For PBM, the peak at 2.5 ppm is due to the $S-CH_2$ group. The peaks centered at 7.5 ppm and 7.90 ppm are assigned to the five aromatic proton on the B ring bearing the carbonyl group and the A ring bearing the $-CH_2-$ group respectively. The absence of any bands between 3.5-3.8 ppm suggests the absence of S-H protons. The results are in conformity with the structures suggested for the ligands.

The ^{13}C NMR spectra of DDPP and PBM are shown in Table-7. For DDPP, the aromatic carbons on the two symmetrical side rings appear between 129.271 to 129.992 ppm. The $C=O$ carbon appear at 168.017 ppm. The peaks at 39 - 40.998 ppm are due to the solvent. Similar observations were made for PBM. The aromatic carbons appear between 129.188 to 133.482 ppm. The $C=O$ carbon shows at 168.063 ppm. The ^{13}C spectral results are in agreement with structures given for the ligands.

Antimicrobial properties

Antimicrobial properties of DDPP, its Ni(II) and Fe(III) complexes, and PBM and its Ni(II) complexes are presented in Table-7. The results indicate that the ligands and their metal complexes did not inhibit the growth of *E. coli* strain used in this study. At a concentration of 20 mg/mL DDPP showed activity against *S. aureus*, *B. subtilis*, *P. aeruginosa* and *C. albicans* while PBM showed the same pattern of activity but not on *B. subtilis*. Overall PBM with inhibition zone diameter of 20 against 16 for DDPP is a better agent for combating *S. aureus* than DDPP. $[NiLX_2]$ shows the same range of activity as the ligand. $[Ni(PBM)_2]^{2+}$ showed mild activity against *B. subtilis*, *S. aureus* and *C. albicans* and appears a better antimicrobial agent than the ligand PBM in suppressing the growth of *B. subtilis*. Apart from this, complexation did not impart better antimicrobial properties for the other cases. The suggested structures of the complexes are given in Figure-1. below

Table-7 : Antimicrobial Properties of DDPP, PBM and their Metal Complexes

Microorganism	Mean inhibition zone diameter (\pm sem)*				
	DDPP	PBM	$[Fe_2XL_2]^{5+}$	$[NiLX_2]$	$[Ni(PBM)_2]^{2+}$
Staphylococcus aureus (ATCC 25923)	16 \pm 0.02	20 \pm 0.2	0	16 \pm 0.01	15 \pm 0.07
Bacillus subtilis (ATCC 6633)	13 \pm 0.02	0	11 \pm 0.05	14 \pm 0.02	0
Pseudomonas aeruginosa (ATCC 27853)	10 \pm 0.01	11 \pm 0.00	0	11 \pm 0.00	11 \pm 0.01
Escherichia coli (ATCC 25922)	0	0	0	0	0
Candida albicans (ATCC 2091)	12 \pm 0.04	12 \pm 0.05	0	12 \pm 0.03	12 \pm 0.08

*mean of three replicates (measured in mm)

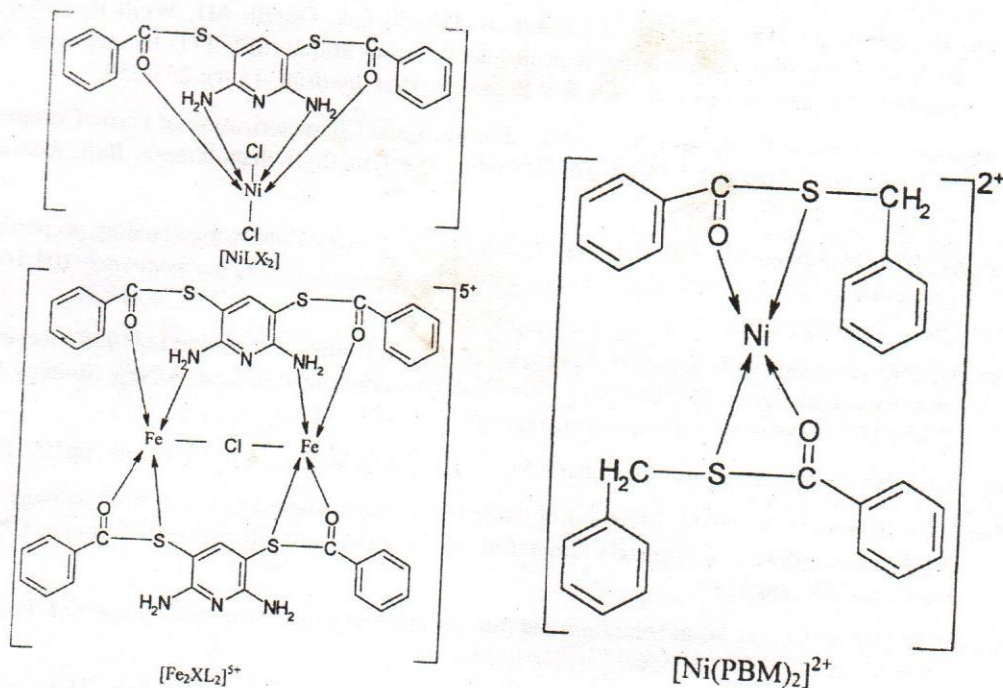


Figure-1 : Suggested Structures of Complexes $[NiLX_2]$, $[Fe_2XL_2]^{5+}$, $[Ni(PBM)_2]^{2+}$

Conclusion

Two new thiolates and their Fe(III) and Ni(II) complexes have been successfully prepared and partially characterized. The ligands most probably coordinated to the metals from the sulfur atom and the carbonyl oxygen and for the DDPP ligand the amino groups are also coordinated. The iron complex $[Fe_2XL_2]^{5+}$ where the iron indicates an octahedral geometry. The same octahedral geometry has been indicated by the $[NiLX_2]$ complex where the ligand is hexadentate overall. PBM is bidentate and for $[Ni(PBM)_2]^{2+}$ a probable square-planar geometry is indicated. The ligands have shown moderate activity against some multi-drug resistant microbes.

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