

**SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL STUDIES
OF METAL CHELATES DERIVED FROM 4-CARBOXALDEHYDE-1-
PHENYL-2-PYRAZOLINE-5-ONE AND META PHENYLENE
DIAMINES**

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ABSTRACT

Some Tetra dentate Schiff-base derived from 4-carboxaldehyde-3-methyl-1-phenyl-2- pyrazoline-5-one with meta phenylene diamine. Form a stable complex with transition metal ions such as VO (III), Cr (II), Mn (II) and Fe (II) in ethanol. Tetradentate Schiff base have been synthesized and characterized by using UV, IR, ¹H & ¹³C-NMR spectral studies. The biological activities of the all metal complexes were measured against bacteria, yeast and fungi.

KEYWORDS: Quateridentate Schiff-base, Metal Complexes, Spectral studies, Biological Studies.

INTRODUCTION

The presence of unsaturation is typical of planar quadridentate ligands and this unsaturation is most commonly provided by imine bonds. Whereas, planar tridentates are often formed by the condensation of amines with aldehyde. The corresponding planar quadridentate ligands can arise from the condensation of two molecules of an aldehyde with a diamine.^[3-5,15] Metal Schiff-base complexes have been known since the mid-nineteenth century,^[1] and even before the general preparation of Schiff-base ligands themselves. However, there was no comprehensive, systematic study of this potential ligand until the preparative work of Pfeiffer and associates.^[1-14] Since Pfeiffer's initial contributions,^[1-14] the interest in quadridentate Schiff-base complexes has increased significantly.

Schiff bases derived from m-phenylenediamines can only coordinate one nitrogen atom to any metal cation, giving dimeric complexes. The Cr(II) and Fe(II) complexes with H₂ac-m-

phen have been prepared and their dimeric structure has been established by mass spectrometry.^[16] The magnetic susceptibility measurements as a function of temperature have shown the existence of weak antiferromagnetic interactions for Schiff base complexes derived from *m*-phenylenediamine or 2,6-diaminopyridine and acetylacetone with Mn(II), VO(II), Cr(II) and Fe(II) and consequently these complexes have been formulated as dimers.^[17]

In continuation of our work on 2-pyrazolin-5-one derivatives, here we report the synthesis. Ft- Ir and ¹³C-NMR spectral studies of quadridentate Schiff-base ligand derived from 4-carboxaldehyde-3-methyl-1-phenyl-2-pyrazolin-5-one.

MATERIALS AND METHODS

All the chemicals used in the present study were of best quality. Ethylacetoacetate, phenylhydrazine, sodiumacetate, phosphorylchloride, [SD's fine chemicals Ltd., British Drug House, Qualigens-Glaxo, Mumbai] were used. Dioxane and N, N'-dimethylformamide (DMF) [Qualigens- Glaxo, Mumbai] were used after purification. Absolute ethanol from Alembic Chemical Works Co. Ltd., Baroda was used after distillation. All diamines were obtained from [SD's fine chemicals Ltd., British Drug House, Qualigens-Glaxo, Mumbai] Baroda and were used without further purification. Cr(III), Mn(II), Co(II), Ni(II) and Cu(II) metal acetates [SD's fine chemicals Ltd., British Drug House, Qualigens-Glaxo, Mumbai] were used. Vanadylsulphate, ferrous sulphate and anhydrous ferric chloride [SD's fine chemicals Ltd., British Drug House, Qualigens-Glaxo, Mumbai] were used in the preparation of VO(II), Fe(II) and Fe(III) chelates respectively.

The ligands used in the present study were prepared in three steps

- (a) Preparation of 1-phenyl-3-methyl-2-pyrazolin-5-one.^[1]
- (b) Preparation of 4-formyl-1-phenyl-3-methyl-2-pyrazolin-5-one.^[1,2]
- (c) Preparation of the Schiff bases.^[1,3]

(a) Preparation of 1-phenyl-3-methyl-2-pyrazolin-5-one [PMP]

1-phenyl-3-methyl-2-pyrazolin-5-one was obtained by condensing phenyl hydrazine (0.1 mole) with ethylacetoacetate (0.1 mole) in ethanol, containing few drops of concentrated sulphuric acid.^[1-5]

(b) Preparation of 4-formyl-1-phenyl-3-methyl-2-pyrazolin-5-one [H₂PMFP]

A mixture of 1-phenyl-3-methyl-2-pyrazolin-5-one (0.5 mole, 17.4 g) and 20 mL of DMF was cooled to 0°C. Then 11.0 mL (0.60 mole, ~ 18.49 g) of phosphoryl chloride was added dropwise at such a rate as to maintain the temperature between 10 ° to 20 ° C. After the addition was complete, the reaction mixture was heated on the steam bath for 1.5 hours. The mixture was then poured into 900 mL of ice-water mixture. The resulting mixture was allowed to stand overnight at room temperature. The solid product was collected by filtration, washed several times with water and recrystallized from ethanol.

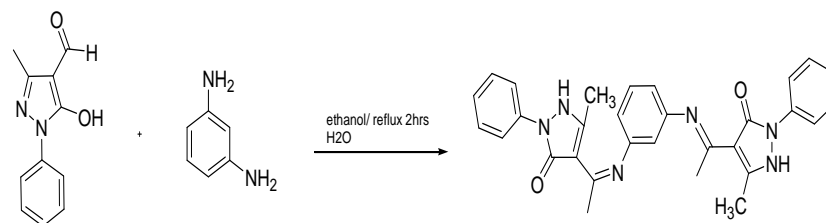
(c) Preparation of the tetradentate Schiff base ligands: An identical procedure has been used in the preparation of all the Schiff bases used in the present study. The Schiff bases were prepared by refluxing (2 hours) the 4-formyl-1-phenyl-3-methyl-2-pyrazolin-5-one (0.01 mole, 2.02 g) and diamines (m-phenylenediamine 0.005 mole, 0.35 in 150 ml ethanol. The Schiff bases thus obtained were filtered and recrystallized from ethanol.

The physical properties and elemental analysis of the metal chelates are listed in Table.

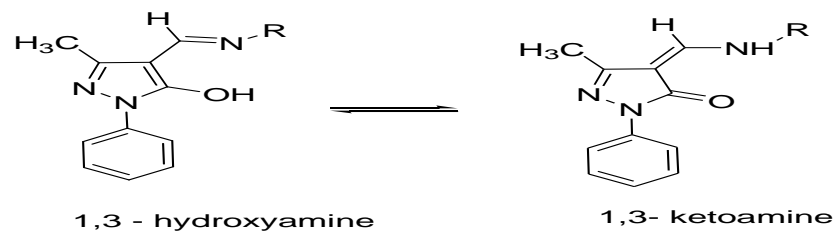
Physical and analytical data of metal complexes

Chelates	Colour	Empirical formula	Found (Calculated) %				$\Delta m \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$ in DMF	μ_{eff} in B. M.
			Metal	Carbon	Hydrogen	Nitrogen		
[VO(PMFP-MPD)(H ₂ O)]	Yellowish green	VOC ₂₈ H ₂₄ O ₃ N ₆	11.75 (11.96)	60.28 (60.11)	4.42 (4.29)	15.22 (15.02)	5.79	167
[Cr(PMFP-MPD)(H ₂ O)OAc]	Reddish brown	CrC ₃₀ H ₂₇ O ₅ N ₆	8.80 (8.62)	59.55 (59.70)	4.69 (4.51)	13.77 (13.93)	18.19	3.92
[Mn(PMFP-MPD)(H ₂ O) ₂]	Yellowish brown	MnC ₂₈ H ₂₆ O ₄ N ₆	9.88 (9.72)	59.68 (59.47)	4.82 (4.63)	14.70 (14.86)	11.27	5.74
[Fe(PMFP-MPD)(H ₂ O) ₂]	Reddish brown	FeC ₂₈ H ₂₆ O ₄ N ₆	9.98 (9.86)	59.48 (59.37)	4.82 (4.63)	14.98 (14.84)	12.17	4.79

RESULT AND DISCUSSION



The quadridentate Schiff-base ligand under present study may have following tautomeric form

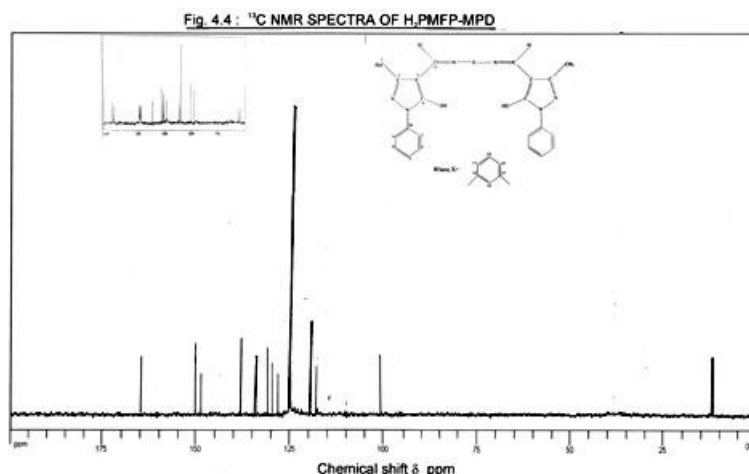


FT-IR SPECTRA

The FT-IR spectra of Schiff-base ligands (PMFP-MPD) show broad band on the 3480-3090 cm^{-1} . The low energy shift may be due to intramolecular or intermolecular hydrogen bonding and also suggest the presence of the enol form at least in the solid state. The Schiff-base ligands (PMFP-MPD) show band in the region 1250-1225 cm^{-1} , which may be due to 1H spectra. The FT-IR spectra of ligands (PMFP-MPD) show bands in the region 1350-1280 cm^{-1} , which may be due to $\nu_{\text{C-O}}$. The FT-IR spectrum of ligands show bands in the region 1642-1668 cm^{-1} which may be due to $\nu_{\text{C=N}}$ (azomethine). The FT-IR spectrum of ligands show bands in the region 1606-1594 cm^{-1} which may be due to C=N (pyrazolin ring).^[15] The important infrared vibrational frequencies of all ligands are listed in Table.

H ₂ PMFP-MPD	[VO(PMFP-MPD)(H ₂ O)]	[Cr(PMFP-MPD)(H ₂ O)OAc]	[Mn(PMFP-MPD)(H ₂ O) ₂]	[Fe(PMFP-MPD)(H ₂ O) ₂]	Assignment
3300 – 3100 (m.br)	-	-	-	-	$\nu_{\text{O-H}}$ (enolic)
-	3500 - 3250 (m.vb)	3450 – 3300 (m.vb)	3400–3200 (m.vb)	3400 – 3250 (m.vb)	$\nu_{\text{O-H}}$ (Coordinated water)
3088 (m.br)	3087 (m.vb)	3086 (m.vb)	3087 (m.vb)	3086 (m.vb)	Aryl $\nu_{\text{(C-H)}}$
2923 (w.br)	2924 (w.br)	2923 (w.br)	2924 (w.br)	2924 (w.br)	Saturated $\nu_{\text{(C-H)}}$
1662 (s.s)	1620 (s.s)	1611 (s.s)	1625 (s.s)	1617 (s.s)	$\nu_{\text{(C=N)}}$ (azomethine)
1594 (s.br)	1595 (s.br)	1594 (m.br)	1596 (s.s)	1593 (s.br)	$\nu_{\text{(C=N)}}$ (Pyrazolin)
1546 (s.s.)	1547 (s.s.)	1548 (s.s.)	1548 (s.br)	1548 (s.s.)	Pyrazolin ring stretch
1497 (s.s)	1496 (s.s.)	1497 (s.br)	1496 (s.s.)	1497 (s.s.)	Phenyl ring $\nu_{\text{(C=C)}}$
1554 (w.sh)	1556 (m.sh)	1556 (m.sh)	1555 (m.sh)	1555 (m.sh)	Pyrazolin ring stretch
1282 (s.s)	1296 (m.s)	1321 (m.s)	1319 (m.br)	1292 (m.br)	$\nu_{\text{(C-O)}}$ (enol)
1225 (m.s)	-	-	-	-	$\delta_{\text{O-H}}$ (enol)
1114 (w.sh)	1114 (w.sh)	1113 (w.sh)	1112 (w.sh)	1113 (w.sh)	Pyrazolin ring breathing
1005 (w.sh)	1006 (m.s)	1007 (m.br)	1005 (m.s)	1006 (m.br)	CH ₃ rocking
967 (m.s)	967 (m.s)	968 (m.s)	967 (m.sh)	968 (m.br)	C-C ₆ H ₅ stretch
912 (m.s)	914 (m.s)	912 (m.s)	913 (m.s)	913 (m.s)	C-CH ₃ stretch
-	803 (m.br)	822 (m.br)	830 (m.br)	822 (m.br)	$\nu_{\text{(O-H)}}$ (wagging mode of coordinated)
	520 (m.vb)	510 (m.vb)	510 (m.vb)	510 (m.vb)	$\nu_{\text{(M-O)}}$
	462 (m.br)	485 (m.br)	485 (m.br)	480 (m.br)	$\nu_{\text{(M-N)}}$
	$\nu_{\text{v=O}}$ (str) : 962	ν_{COO^-} : 1575			

³C-NMR Spectra: An attempt has been made to characterize ligands by ¹³C-NMR spectral studies. The assignment of ¹³C-NMR shift has been made reported value for 2-pyrazolin-5-one derivatives.^[18-20]

 ^{13}C NMR spectral data of SCHIFF BASE ligands

Ligand	Types of Carbon Atoms Chemical shift (δ) ppm												
	C ₁	C ₂	C ₃	C ₄	C ₅ , C ₉	C ₆ , C ₈	C ₇	C ₁₀	C ₁₁	C ₁₂ , C ₁₇	C ₁₃ , C ₁₆	C ₁₄	C ₁₅
H ₂ PMFP - MPD	12.8	149.5	101.5	165.2	129.5	118.1	124.2	139.1	150.2	134.8	120	129.1	130.6

Thermal Decomposition Data of the Schiff-Base Chelates.

Metal Chelates	*(% Weight loss) step									Decomp. temp. °C	Activation energy
	I	II	III	IV	V	VI	VII	VIII	IX		
[VO(PMFP- MPD)(H ₂ O)]	I	180	200	220	240	260	-	-	-		12.45
		* (3.20)	(3.24)	(3.90)	(4.2)	(6.4)					
	II	280	300	320	340	360	380	400	420	258	26.58
		* (8.4)	(14.2)	(28.4)	(30.4)	(32.6)	(34.2)	(36.4)	(38.6)		
[Cr(PMFP- MPD)(H ₂ O)OAc]	I	180	200	220	240	260	280	300	-		14.27
		* (2.4)	(2.94)	(3.0)	(3.4)	(8.4)	(10.4)	(16.40)			
	II	320	340	360	380	400	420	440	460	271	26.97
		* (18.4)	(20.4)	(21.3)	(21.9)	(22.38)	(28.4)	(34.4)	(36.4)		
[Mn(PMFP- MPD)(H ₂ O) ₂]	I	200	220	240	260	-	-	-	-		33.20
		* (6.32)	(7.8)	(7.9)	(8.0)						
	II	280	300	320	340	360	380	400	420	260	149.4
		* (8.2)	(8.9)	(11.4)	(16.2)	(24.29)	(25.72)	(26.67)	(27.62)		
[Fe(PMFP- MPD)(H ₂ O) ₂]	I	180	200	220	240	260	-	-	-		36.55
		* (2.80)	(6.10)	(6.20)	(6.40)	(6.42)					
	II	280	300	320	340	360	380	400	420	267	8.33
		* (10.10)	(12.15)	(10.08)	(11.44)	(11.91)	(12.38)	(14.29)	(15.24)		
[Fe(PMFP- MPD)(H ₂ O) ₂]	III	540	560	580	600	620	640	660	680		6.22
		* (47.62)	(51.43)	(52.86)	(55.24)	(59.05)	(60.96)	(63.34)	(64.77)		

Electronic Spectra

Electronic Spectral Data of the Vo(II) Chelates

Metal Chelates	Observed transition energies (cm ⁻¹)					Radial parameters (cm ⁻¹)		
	<i>b</i> ₂	<i>e</i>	<i>b</i> ₂ <i>b</i> ₁	<i>b</i> ₂	<i>a</i> ₁	D _{qxy}	-D _s	D _t
[VO(PMFP-MPD)H ₂ O]	10,330 (13)		17,606 (14)	25,974 (51)		1,760	2,671	463

*(ϵ) = Molar extinction coefficient in litre mole⁻¹ cm⁻¹.

Electronic Spectral Data of the Cr(III) Chelates

Metal Chelates	Observed transition energies (cm ⁻¹)						
	<i>4A</i> _{2g}		<i>4T</i> _{2g} (F)		<i>4A</i> _{2g}	<i>4T</i> _{1g} (F)	
	<i>4B</i> _{1g}	<i>4E</i> _g	<i>4B</i> _{1g}	<i>4B</i> _{2g}			
[Cr(PMFP-MPD(H ₂ O)OAc)]		15,974 (28)			18,622 (36)		27,933 (52)

Electronic Spectral Data of the Six-Coordinate mn(ii) Chelates

Metal Chelates	Observed transition energies (cm ⁻¹)		
	<i>6A</i> _{1g} → <i>4E</i> _g , <i>4A</i> _{1g}	<i>6A</i> _{1g} → <i>4T</i> _{1g} (G)	<i>6A</i> _{1g} → <i>4T</i> _{2g}
[Mn(PMFP-MPD)(H ₂ O) ₂]	16,179 (15)	18,949 (22)	25,320 (28)

Electronic Spectral Data of the Six-Coordinate Fe(II) Chelates

Metal Chelates	Observed transition energies (cm ⁻¹)		B (cm ⁻¹)	β	C (cm ⁻¹)
	Charge transfer	<i>5T</i> _{2g} → <i>5E</i> _g			
[Fe(PMFP-MPD)(H ₂ O) ₂]	28,980 (102)	11,947 (22)	646	0.6106	2,584

Biological Activity

The biological activities of the metal complexes were measured against bacteria, yeast and fungi following literature methods.³⁷ Nutrient broth, Sabouraud's dextrose broth and yeast extract peptone dextrose (YEDP) medium with and without the indicated samples were used for growth studies of bacteria (*E. coli* and *B. subtilis*), fungi (*A. niger* and *T. longibrachiatum*) and yeast (*P. stipitis* and *R. minuta*), respectively. The concentration of the test compounds was kept constant at 500 ppm during all the experiments. For the inoculation into test media containing the sample, cultures were pregrown in the same media without the samples (control) to be tested, and 24 h old cultures were used to inoculate the test media for bacterial and yeast cultures. Similarly, a fungal inoculum was prepared by harvesting spores from

nutrient-agar plates in sterile distilled water. The culture flasks were incubated on a rotary shaker at room temperature. After 48 h, the optical density of the bacterial and yeast cultures was determined at 660 nm using an Equiptronics digital spectrophotometer. For the fungal cultures the flasks were harvested after 40 h and dry cell mass was determined gravimetrically.

An attempt has been made to evaluate the biological activities of the synthesized ligand and its metal complexes against bacterial (*E. Coli* and *B. Subtilis*), fungal (*A. Niger* and *T. Longibrachiatum*) and yeast (*P. Stipitis* and *R. Minuta*) cultures using literature methods.³⁷ The effect of ligand and its metal complexes on the growth of test microorganisms is given in Table 8. The results suggest that the synthesized compounds show 30 % to 53 % inhibitory effect on the growth of bacterial, 44 % to 71 % inhibitory effect on the growth of fungal and 15 % to 51 % inhibitory effect on the growth of yeast cultures.

Effect of Ligand and Its Metal Chelates on the Growth of Microorganisms

Incubation time (in hour)/Compound ^a	% Growth of <i>E.coli</i>							% Growth of <i>B.subtilis</i>								
	20	24	28	32	36	40	44	48	20	24	28	32	36	40	44	48
Control ^b	40	59	63	67	73	100	100	100	31	45	48	60	81	100	100	100
H ₂ PMFP-MPD	35	50	52	54	57	62	70	70	32	38	44	48	54	68	84	84
[VO(PMFP-MPD)(H ₂ O)]	30	40	47	50	55	55	55	55	30	35	37	39	45	50	56	56
[Cr(PMFP-MPD)(H ₂ O)OAc]	27	40	42	44	48	53	59	59	20	28	32	33	40	54	64	64
[Mn(PMFP-MPD)(H ₂ O) ₂]	28	42	44	46	50	57	58	58	30	36	38	40	50	65	72	72
[Fe(PMFP-MPD)(H ₂ O) ₂]	24	40	42	44	46	52	60	60	30	35	37	39	45	70	72	72
[Fe(PMFP-MPD)(H ₂ O)OAc]	25	42	44	46	48	57	63	63	27	32	33	33	40	60	68	68
[Co(PMFP-MPD)(H ₂ O) ₂]	30	40	44	47	50	52	59	59	30	36	40	44	50	60	64	64
[Ni(PMFP-MPD)(H ₂ O) ₂]	28	45	47	49	50	52	54	54	28	30	33	33	33	55	60	72
[Cu(PMFP-MPD)(H ₂ O) ₂]	20	28	32	37	42	50	52	52	18	30	33	40	50	68	76	76

^aConcentration of each compound was 500 ppm; ^bControl does not contain any test compound

Effect of Ligand and Its Metal Chelates on The Growth of Microorganisms

Compound	T. longibrachiatum		A. Niger	
	% Sugar utilized	% Growth ^b	% Sugar utilized	% Growth ^b
Control ^c	98.46	100	98.66	100
H ₂ PMFP-MPD	55.00	56	55.00	57
[VO(PMFP-MPD)(H ₂ O)]	50.83	51	50.83	51
[Cr(PMFP-MPD)(H ₂ O)OAc]	34.66	35	34.16	35
[Mn(PMFP-MPD)(H ₂ O) ₂]	35.6	36	35.00	36
[Fe(PMFP-MPD)(H ₂ O) ₂]	40.00	41	36.66	37

^aConcentration of each compound was 500 ppm.

^bGrowth after 40 hours.

^cControl does not contain any test compound.

Effect of Ligand and Its Metal Chelates on the Growth of Microorganisms

Incubation time (h)	R. Minuta % Growth ^b		P. stipites % Growth ^b	
	24	48	24	48
Compound ^a				
Control ^c	47	100	43	100
H ₂ PMFP-MPD	36	78	38	55
[VO(PMFP-MPD)(H ₂ O)]	30	70	29	43
[Cr(PMFP-MPD)(H ₂ O)OAc]	34	60	27	49
[Mn(PMFP-MPD)(H ₂ O) ₂]	28	68	32	48
[Fe(PMFP-MPD)(H ₂ O) ₂]	32	64	33	46

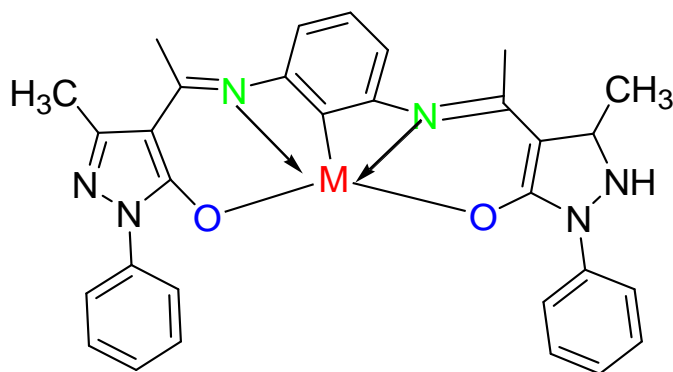
^aConcentration of each compound was 500 ppm.

^bGrowth after 40 hours.

^cControl does not contain any test compound.

CONCLUSION

Describes in detail, the information obtained by different physico-chemical methods and its interpretation with respect to the structure of metal chelates. The conductivity, magnetic, electronic spectral and thermogravimetric data suggest six coordinate octahedral stereochemistry for all the metal chelates. The IR spectral data suggest quadridentate nature of the ligands and show coordination to the metal ions through the nitrogen atoms of the azomethine groups and the enolic oxygen of the 5-OH groups. The rest of the coordination positions have been occupied by either the water molecules or by acetate (CH₃COO⁻) and water molecule.



M=VO(II), Cr(III), Mn(II) and Fe(II)

For VO(II), Mn(II) and Fe(II) X=Z=(H₂O)

For Cr(III) X= (H₂O) Z= OAc

Describes the studies on antimicrobial activities of the Schiff bases ligands and their metal chelates. All the ligands and their metal chelates are tested for their antibacterial, antifungal and antiyeasts activity against *Escherichia coli*, *Bacillus subtilis* and *Aspergillus niger*, *Trichoderma longibrachiatum* and *Rhodotorula Minuta*, *Pichiastipitis* respectively using standard literature procedures. It was observed that all the synthesized ligands and their metal chelates affect the growth of microorganisms and resulted into inhibitory effect. The antimicrobial activity of the metal chelates was found higher than that of the corresponding ligands.

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