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## Synthesis and IR, U.V., $^1\text{H}$ and $^{13}\text{C}$ -NMR studies of some tetra dentate schiff-bases derived from 4-carboxaldehyde-1-phenyl-2-pyrazoline-5-one and some diamines

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### ABSTRACT

Some Tetra dentate Schiff-base derived from 4-carboxaldehyde-3-methyl-1-phenyl-2-pyrazoline-5-one with ethylenediamine, hexamethylenediamine, benzidine, p-phenylenediamine and m-phenylenediamine. Tetradentate Schiff base have been synthesized and characterized using element, UV, IR,  $^1\text{H}$  &  $^{13}\text{C}$ -NMR spectroscopy elemental analysis, FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$ -NMR spectral studies. The use of all ligands and other's same kind ligands in the preparation of transition metal complexes is in progress.

**Key words:** Quaderidentate Schiff-base, Spectral studies

### INTRODUCTION

In recent years, considerable interest for the Co-ordination Ability of potentially Tetra dentate ligands has been established<sup>1-6</sup>. Such tetra dentate ligands used for monomeric metal complexes of ML type<sup>7-8</sup> and also Capable to form polymeric metal complexes<sup>9</sup>.

In continuation of our work on 2-pyrazolin-5-one derivatives, here we report the synthesis. FT-IR and  $^{13}\text{C}$ -NMR spectral studies of quadridentate Schiff-base ligand derived from 4-carboxaldehyde-3-methyl-1-phenyl-2-pyrazolin-5-one and ethylenediamine, hexamethylenediamine, benzidine, p-phenylenediamine and m-phenylenediamine.

### MATERIALS AND METHODS

#### Experimental

All chemical used were of reagent grade (BDH). melting point of all the compounds were taken in open glass capillary tubes on tempco melting point apparatus. The ligands were analyzed for carbon, hydrogen, and nitrogen using Carlo-Erba 1108 micro analyzer (CDRIC-Lucknow). The FT-IR spectra were recorded on perkin-Elmer, Spectrum-GX spectrophotometer in KBr pellets. The  $^{13}\text{C}$ -NMR spectra were recorded (CDRIC-Lucknow) on a Bruker DRX-300-FT-NMR spectrophotometer.

#### Synthesis of Ligands

The following general literature procedure is used for the preparation of Schiff-bases of 4-carboxaldehyde-3-methyl-1-phenyl-2-pyrazolin-5-one with ethylenediamine (CMPPZ-en), hexamethylenediamine (CMPPZ-hmda), benzidine (CMPPZ-bz), p-phenylenediamine (CMPPZ-ppd) and m-phenylenediamine (CMPPZ-mpd).

The Schiff-bases were synthesized through condensation reaction by mixing a hot ethanolic solution of 4-carboxaldehyde-3-methyl-1-phenyl-2-pyrazolin-5-one (0.02 mole) with ethanolic solution of diamines (0.01 moles)

for 2-3 hours on water bath. The crude product obtained was filtered, washed several times with hot water and with ethanol. The crude product was then recrystallized in ethanol.

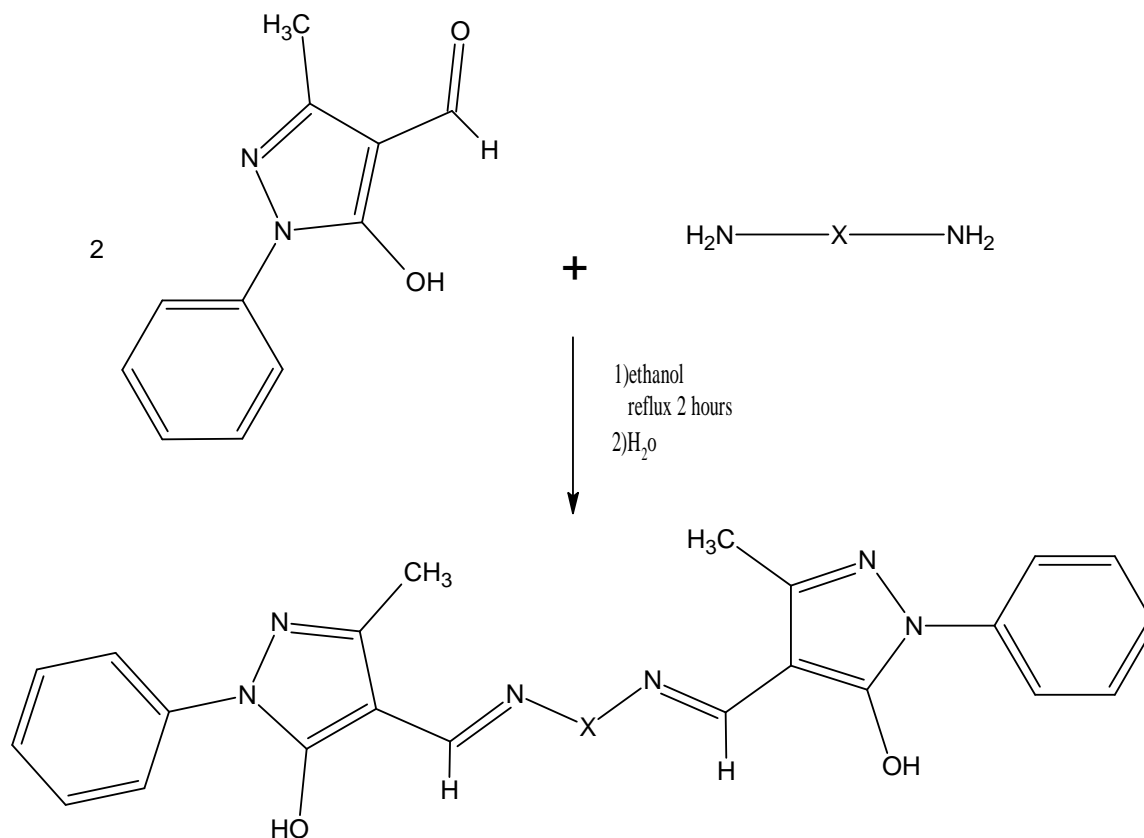
The physical and analytical data of all the ligands in the study are listed in Table-1.

**TABLE -I PHYSICAL PROPERTIES OF SCHIFF BASE LIGANDS**

Ligands	Melting Point °C	Colour	Carbon	Hydrogen	Nitrogen	Yield %
H2PMFP-END	210	Yellowish Brown	67.39 (67.28)	5.77 (5.60)	19.20 (19.62)	68
H2PMFP-HMD	216	Reddish Brown	69.82 (69.42)	6.71 (6.61)	17.19 (17.35)	65
H2PMFP-MPD	206	Yellowish Brown	70.32 (70.58)	5.45 (5.14)	17.72 (17.64)	53
H2PMFP-PPD	182	Parrot green	70.68 (70.58)	5.60 (5.34)	17.30 (17.64)	64
H2PMFP-BZ	207	Brown	74.05 (73.91)	5.47 (5.18)	15.38 (15.22)	59

### RESULTS AND DISCUSSION

The quadridentate Schiff-base ligand under present study may have following tautomeric form (1) and (2).



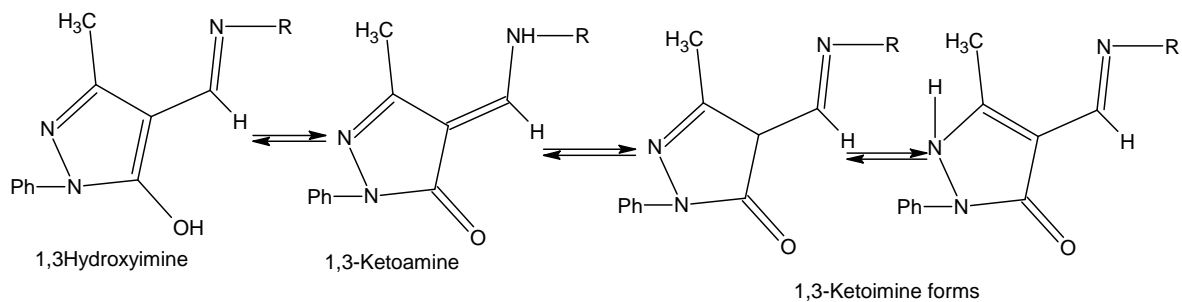


Figure-1 Tautomeric forms of 4-formylpyrazolone schiff-bases

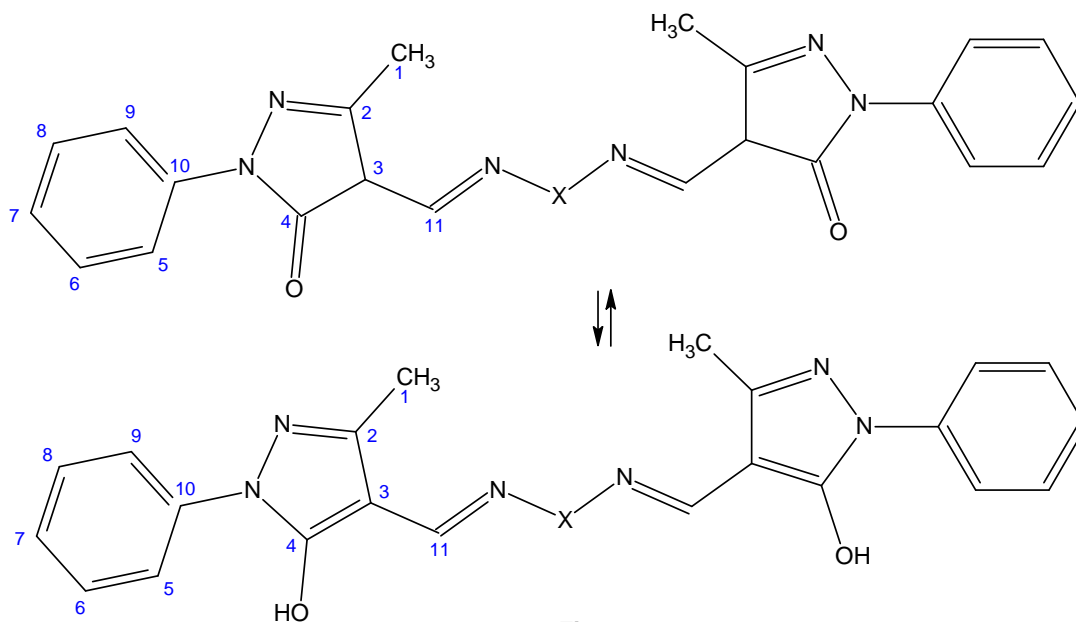


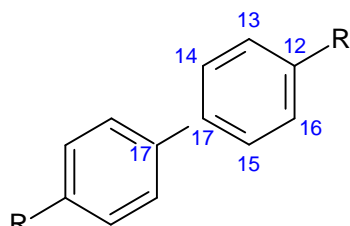
Figure-2

Where

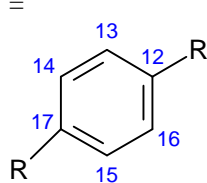
X= -CH<sub>2</sub>-CH<sub>2</sub>-

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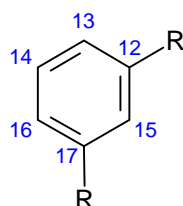
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**FT-IR SPECTRA**

The FT-IR spectra of Schiff-base ligands (CMPPZ-en),(CMPPZ-hmda),(CMPPZ-bz),(CMPZ-ppd),(CMPPZ-mpd) show broad band on the 3480-3090  $\text{cm}^{-1}$ . The low energy shift may be due to intramolecular or intermolecular hydrogen bonding and also suggest the presence of the enol form (structure-2) at least in the solid state.

The Schiff-base ligands CMPPZ-en),(CMPPZ-hmda),(CMPPZ-bz),(CMPZ-ppd),(CMPPZ-mpd) show band in the region 1250-1225  $\text{cm}^{-1}$ , which may be due to  $^1\text{H}$  spectra. The FT-IR spectra of ligands (CMPPZ-en),(CMPPZ-hmda),(CMPPZ-bz),(CMPZ-ppd),(CMPPZ-mpd) show bands in the region 1350-1280  $\text{cm}^{-1}$ , which may be due to  $\nu_{\text{C-O}}$ . The FT-IR spectrum of ligands show bands in the region 1642-1668  $\text{cm}^{-1}$  which may be due to  $\nu_{\text{C=N}}$  (azomethine) 14. The FT-IR spectrum of ligands show bands in the region 1606-1594  $\text{cm}^{-1}$  which may be due to C=N (pyrasolin ring) 15. The important infrared vibrational frequencies of all ligands are listed in Table-11.

**Table-II UV and IR (cm-1) spectral data of the ligands**

Assignment	H2PMFP-END	H2PMFP-HMD	H2PMFP-MPd	H2PMFP-PPD	H2PMFP-BZ
$V_{\text{max}}$ (nm)	260	270	265	252	250
$E_1$	38,461	37037	37,735	39,682	40,000
$V_{\text{max}}$ (nm)	350	-	-	310	-
$E_2$	28,571	-	-	32,258	-
$V_{\text{O-H}}$ (enolic)	3400-3100 (m,vb)	3080-3090 (m,br)	3300-3100(m,br)	3400-3120 (s,br)	3450-3220(s,br)
$V_{\text{O-H}}$ (Co-ordinated water)	-	-	-	-	-
Aryl $V_{\text{(C-H)}}$	3059 (m,vb)	3061 (m,br)	3088(m,br)	3045(m,br)	3045(w,br)
Saturated $V_{\text{(C-H)}}$	2942 (w,br)	2921 (w,br)	2923(w,br)	2919(w,br)	2917(w,br)
$V_{\text{(C=N)}}$ (azomethelene)	1668 (s,s)	1666 (s,s)	1662(s,s)	1648(s,s)	1642 (s,sh)
$V_{\text{(C=N)}}$ (pyrasolin)	1606 (s,s)	1594 (s,br)	1594(s,br)	1595(s,br)	1596(s,s)
Pyrasolin ring stretch	1547 (s,s)	1545 (s,s)	1546(s,s)	1544(s,s)	154(s,s)4
Phenyl ring $V_{\text{(C-C)}}$	1497 (s,s)	1498 (s,s)	1497(s,s)	1485(s,s)	148(s,s)9
Pyrasolin ring stretch	1455 (s,s)	1456 (w,sh)	1554(w,sh)	1446(w,sh)	1455(w,sh)
$V_{\text{(C=O)}}$ (enol)	1340 (s,s)	1345 (s,s)	1282(s,s)	1307(s,s)	1279(s,s)
$V_{\text{O-H}}$ (enol)	1225 (m,s)	1227 (m,s)	1225(m,s)	1250(m,s)	1226(m,s)
Pyrasolin ring breathing	1114 (m,br)	1116 (w,sh)	1114(w,sh)	1112(w,sh)	1112(w,sh)
$\text{CH}_3$ rocking	1004 (m,br)	1002 (w,sh)	1005(w,sh)	9001(w,sh)	1002(w,sh)
C-C <sub>6</sub> H <sub>5</sub> stretch	980 (m,br)	975 (m,s)	967(m,s)	964(m,s)	964(m,s)
C-CH <sub>3</sub> stretch	930 (m,br)	906 (m,s)	912(m,s)	906(m,s)	907(m,s)
$V_{\text{O-H}}$ (wagging mode of co-ordinated water)	-	-	-	-	-
$V_{\text{(M-O)}}$	-	-	-	-	-
$V_{\text{(M-N)}}$	-	-	-	-	-

The absence of  $^{13}\text{C}$ -NMR shift due to carbon atom of C=O (pyrazolin ring) also suggest enol-form of the Schiff-base.

 **$^{13}\text{C}$ -NMR Spectra**

An attempt has been made to characterized ligands by  $^{13}\text{C}$ -NMR spectral studies. The assignment of  $^{13}\text{C}$ -NMR shift has been made reported value for 2-pyrasolin-5-one derivatives<sup>16-18</sup>.

The  $^{13}\text{C}$ -NMR spectral data of 2-pyrasolin-5-one derivatives are presented in Table-3.

**Table-III  $^1\text{H}$  and  $^{13}\text{C}$  NMR Spectral data of the ligands in  $\delta\text{ppm}$  relative to TMS**

$^1\text{H}$ ( $^{13}\text{C}$ )	END	HMDA	BZ	PPD	MPD
1	2.30(S,6H) (12.3)	2.25(S,6H) (12.4)	2.34(S,6H) (12.6)	2.33(S,6H) (12.6)	2.34(S,6H) (12.8)
2	- (148.2)	- (148.2)	- (148.4)	- (148.5)	- (149.5)
3	- (99.3)	- (98.2)	- (101.6)	- (100.1)	- (101.5)
4	- (164.8)	- (165.0)	- (164.9)	- (164.9)	- (165.2)
5	11.37(S,2H) -	11.33(S,2H) -	11.38(S,2H)	11.38(S,2H)	11.39(S,2H)
6,10	7.33(m,4H) (128.6)	7.34(m,4H) (129.6)	7.38(m,4H) (128.8)	7.38(m,4H) (128.7)	7.38(m,4H) (129.5)
7,9	8.00(m,4H) (117.3)	7.92(m,4H) (119.2)	8.10(m,4H) (117.6)	8.10(m,4H) (117.5)	7.98(m,4H) (118.1)
8	7.12(m,2H) (123.2)	7.11(m,2H) (123.2)	7.10(m,2H) (123.7)	7.10(m,2H) (127.7)	7.13(m,2H) (124.2)
11	(139.5)	(139.6)	(139.1)	(137.8)	(139.1)
12					
13	- (157.3)	- (153.4)	- (149.0)	- (153.1)	- (156.2)
14	3.45(t,4H)	2.72(b,4H)	-	-	-
15,18	- - 23 -	2.77(m,4H) (15)	7.0(m,2H)	6.92(m,2H)	6.89(m,2H)
16,17	-	2.80(m,4H)	7.42(m,4H)	7.12(m,4H)	6.89(m,2H) (16)
17	-	-	-	-	7.0(m,2H) (134.8)

**Biological Activity**

The biological activities of the metal complexes were measured against bacteria, yeast and fungi following literature methods.<sup>37</sup> 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.<sup>37</sup>

The effect of ligand and its metal complexes on the growth of test microorganisms is given in Table-IV (1-6). 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.

**TABLE IV-1 EFFECT OF LIGAND AND ITS METAL CHELATES ON THE GROWTH OF MICROORGANISMS**

Incubation time (in hour)/ Compound <sup>a</sup>	% 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 <sup>b</sup>	38	50	57	60	64	86	100	100	40	42	53	58	78	100	100	100
H <sub>2</sub> PMFP-END	31	47	48	49	52	60	64	69	35	40	44	48	60	70	72	72

**TABLE IV-2**

Incubation time (in hour)/ Compound <sup>a</sup>	% 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 <sup>b</sup>	32	56	60	66	74	100	100	100	24	38	42	50	72	100	100	100
H <sub>2</sub> FMFP-HMD	28	42	44	47	50	70	72	72	20	36	40	44	58	62	66	66

<sup>a</sup>Concentration of each compound was 500 ppm; <sup>b</sup>Control does not contain any test compound.

**TABLE IV-3**

Compound <sup>a</sup>	<i>A. niger</i>		<i>T. longibrachiatum</i>	
	% Sugar utilized	% Growth <sup>b</sup>	% Sugar utilized	% Growth <sup>b</sup>
Control <sup>c</sup>	97.83	100	98.66	100
H <sub>2</sub> PMFP-END	50.83	51	60.83	61

**TABLE IV-4**

Compound <sup>a</sup>	<i>A. niger</i>		<i>T. longibrachiatum</i>	
	% Sugar utilized	% Growth <sup>b</sup>	% Sugar utilized	% Growth <sup>b</sup>
Control <sup>c</sup>	95.4	100	95.8	100
H <sub>2</sub> PMFP-HMD	59.16	60	56.66	57

<sup>a</sup>Concentration of each compound was 500 ppm.

<sup>b</sup>Growth after 40 hours.

<sup>c</sup>Control does not contain any test compound.

TABLE IV-5

Incubation time (h)	R. Minuta % Growth <sup>b</sup>		P. stipitis % Growth <sup>b</sup>	
	24	48	24	48
Compound <sup>a</sup>				
Control <sup>c</sup>	60	100	46	100
H <sub>2</sub> PMFP-END	56	92	36	78

TABLE IV-6

Incubation time (h)	R. Minuta % Growth <sup>b</sup>		P. stipitis % Growth <sup>b</sup>	
	24	48	24	48
Compound <sup>a</sup>				
Control <sup>c</sup>	37	100	41	100
H <sub>2</sub> FMFP-HMD	33	67	35	76

<sup>a</sup>Concentration of each compound was 500 ppm<sup>b</sup>Growth after 40 hours.<sup>c</sup>Control does not contain any test compound.

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