

## Spectroscopic Studies of Some Tridentate Schiff Bases and their Metal Chelates

M.Y. KHUHAWAR, M.B. RIND, A.K. TALPUR AND A.G. BHATTI  
*Institute of Chemistry, University of Sindh, Jamshoro, Sindh, Pakistan*

(Received July 7, 1993, revised March 16, 1994)

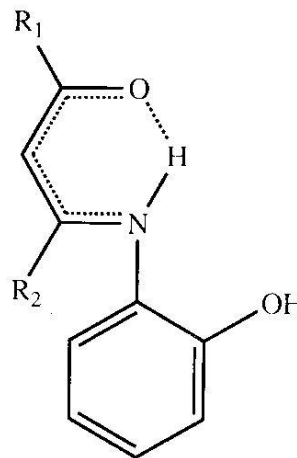
**Summary:** New tridentate ligands isopropanoylacetone-2-imino-phenol ( $H_2PAP$ ), trifluoroisopropanoylacetone-2-imino-phenol ( $H_2F_3PAP$ ), acetylmesityl oxide-2-imino-phenol ( $H_2AMP$ ) and trifluoroacetylmesityloxide-2-imino-phenol ( $H_2F_3AMP$ ) have been prepared and characterized by elemental microanalysis, IR,  $^1H$ -NMR and mass spectroscopic techniques. Their reactions towards copper(II), nickel(II), cobalt(II), iron(II) and chromium(III) have been studied spectrophotometrically. The reactions with metal ions are rapid with molar absorptivities in the range of 100-8000  $l.mole^{-1} cm^{-1}$  in visible region.

### Introduction

A number of studies have been reported on tetradentate Schiff bases [1,2] but some studies are also reported on bifunctional tridentate Schiff bases derived by the condensation of 2-aminophenol with  $\beta$ -diketones and salicylaldehyde [3-6]. The tridentate Schiff bases react with a number of metal ions to form coloured metal chelates [7-10]. Thus in the present work four new tridentate Schiff bases have been prepared and their reactions towards copper (II), nickel(II), cobalt(II), iron(II) and chromium (III) have been studied spectrophotometrically.

### Results and Discussion

The results of elemental microanalysis agreed reasonably to the expected values (Table 1) (Fig. 1). The mass spectra of the reagents  $H_2PAP$  and  $H_2F_3PAP$  indicated molecular ion peaks  $M^+$  at  $m/e$  (rel. intensity %) 219 (16) and 273 (3) respectively at corresponding to their expected molecular weights. The base peak in the case of both reagents  $H_2PAP$  and  $H_2F_3PAP$  were obtained at  $m/e$  176 (100) and 230 (100) respectively due to the loss of isopropyl groups. The diagnostic peaks in the case of  $H_2PAP$  and  $H_2F_3PAP$  were obtained at  $m/e$  134(22) and 188 (9) respectively corresponding to  $M-[(CH_3)_2CHCOCH_2]^+$  and support that condensation has occurred at the carbonyl group adjacent to methyl or trifluoromethyl groups. The reagent  $H_2F_3AMP$  indicates molecular ion peak  $M^+$  at  $m/e$  285 (20). The base peak is obtained at  $m/e$  270 (100) due to loss of fragment corresponding to  $-CH_3$  group. A signal at  $m/e$  230 (12) is assigned due to loss of fragment corresponding to isobutene from



- (I)  $H_2PAP = R_1 = (CH_3)_2CH-$ ,  $R_2 = CH_3$   
 (II)  $H_2F_3PAP = R_1 = (CH_3)_2CH-$ ,  $R_2 = CF_3$   
 (III)  $H_2F_3AMP = R_1 = CF_3$ ,  $R_2 = (CH_3)_2C=CH-$

Fig. 1: Structural diagram of the reagents.

molecular ion peak. Diagnostic peak is observed at  $m/e$  200 (12) due to the loss of  $[CF_3CO]^+$  and support that the condensation has occurred at the carbonyl group adjacent to isobutene.

$^1H$ -NMR of  $H_2F_3PAP$  and  $H_2PAP$  indicate a peak at  $\delta$  12.268 and 11.877 ppm respectively, due to  $NH/OH$  groups. The reagent  $H_2F_3PAP$  and  $H_2PAP$  indicate a doublet at  $\delta$  1.32 and 1.37 ppm and a multiplet at  $\delta$  2.733 and 2.496 ppm respectively due to the presence of a isopropyl group in each of the ligand molecule.  $H_2F_3PAP$  and

Table 1: Results of Elemental Micro-Analysis

Compound	Mol.Formula	M.P.	Expected			Found		
			C	H	N	C	H	N
1. Trifluoroacetyl-mesityloxyde-2-isinophenol	C <sub>14</sub> H <sub>14</sub> NO <sub>2</sub> F <sub>3</sub>	158	58.94	4.91	4.91	58.64	5.04	4.91
2. Trifluoroacetyl-sesityl oxide-2-isinophenol	C <sub>14</sub> H <sub>12</sub> NO <sub>2</sub> F <sub>3</sub>	-	48.46	3.46	4.04	48.32	3.52	4.28
3. Acetylsesityl-oxide-2-isinophenol	C <sub>14</sub> H <sub>16</sub> NO <sub>2</sub>	-	73.04	6.95	6.08	71.74	6.85	5.59
4. Trifluoroisopropanoylacetone-2-isinophenol	C <sub>13</sub> H <sub>13</sub> NO <sub>2</sub> F <sub>3</sub>	174	57.37	5.12	5.12	57.14	5.43	5.13
5. Isopropanoyl-acetone-2-isinophenol	C <sub>13</sub> H <sub>17</sub> NO <sub>2</sub>	150	71.23	7.76	6.39	71.01	7.46	6.23
6. Trifluoroisopropanoylacetone-isinophenol Copper(II)	C <sub>13</sub> H <sub>13</sub> NO <sub>2</sub> F <sub>3</sub> Cu	300	46.57	3.88	4.17	47.71	3.84	4.03
7. Isopropanoyl-acetone-2-isinophenol copper(II)	C <sub>13</sub> H <sub>15</sub> NO <sub>2</sub> Cu	260	55.52	5.69	4.98	56.26	5.32	4.82

H<sub>2</sub>PAP also indicate singlets at  $\delta$  5.594 and 5.216 ppm respectively due to =CH protons as expected.

The spectrophotometric studies of the reagent H<sub>2</sub>PAP in acetone indicates a band at 330 nm ( $\epsilon$  =12500), which could be due to intra ligand  $\pi$ - $\pi^*$  transition. Another band of weak intensity is observed at 400 nm ( $\epsilon$  =16), may be due to  $\pi$ - $\pi^*$  transition involving nonbonding electrons on azomethine nitrogen and  $\pi$  orbitals on aromatic phenyl ring. The absorption spectrum of H<sub>2</sub>F<sub>3</sub>PAP in acetone indicates bands at 380 nm ( $\epsilon$ =405) and 440 nm ( $\epsilon$  =78) as compared to H<sub>2</sub>PAP, which shows at 330 nm and 400 nm. It is therefore considered that a bathochromatic shift occurs in both the bands due to the substitution of electron withdrawing trifluoromethyl group in H<sub>2</sub>F<sub>3</sub>PAP. It may however be noted that the value of molar absorptivity ( $\epsilon$ ) at 380 nm ( $\epsilon$  = 405) in H<sub>2</sub>F<sub>3</sub>PAP is considerably lower than observed in the spectrum of H<sub>2</sub>PAP at 330 nm ( $\epsilon$  = 2400) in same solvent system.

The spectra of copper and nickel complexes of the ligands H<sub>2</sub>PAP and H<sub>2</sub>F<sub>3</sub>PASP indicate a weak absorption band between 650-530 nm (Table 2) with molar absorptivity in the range of 23-651 mol<sup>-1</sup> cm<sup>-1</sup> due to d-d transitions. The copper and

nickel complexes also indicate another band in the visible region between 365-410 nm, which is more sensitive with molar absorptivity in the range of 1400-8000 l.mole<sup>-1</sup> cm<sup>-1</sup>. Similarly iron(II) and cobalt(II) complexes of H<sub>2</sub>PAP and H<sub>2</sub>F<sub>3</sub>PAP indicate a reasonable molar absorptivity between 1.5-5.5103 l.mole<sup>-1</sup> cm<sup>-1</sup> for the possible use of the reagent for the spectrophotometric determination of metal ions. The reactions of the reagent H<sub>2</sub>AMP towards metal ions were investigated in methanol-water, but were observed less sensitivity (Table 2) spectrophotometrically.

Table 2: Quantitative Spectrophotometric Data of Reagent and Metal Chelates

Reagent	Metal Ion	Solvent	$\lambda_{max}$ . nm( $\epsilon$ l.mole <sup>-1</sup> cm <sup>-1</sup> )
H <sub>2</sub> PAP	-	Acetone	400(16), 330(12400)
	Cu(II)	Acetone	630(23), 365(8000)
	Ni(II)	Methanol	600(26), 402(1400)
	Fe(II)	Methanol	408(1520)
	Co(II)	Methanol	582(499), 410(5120)
	Cr(III)	Methanol	427(100)
H <sub>2</sub> F <sub>3</sub> PAP	-	Acetone	440(78), 380(404)
	Cu(II)	Acetone	650(65), 367(4650)
	Ni(II)	Methanol	530(53), 410(2380)
	Fe(II)	Methanol	400(893)
	Co(II)	Methanol	413(2070)
H <sub>2</sub> AMP	-	Methanol	415(64), 235(8200), 286(4200), 210(1540)
	Ni(II)	Methanol	500(341)
	Fe(II)	Methanol	425(870)
	Co(II)	Methanol	425(520)

### Experimental

*Preparation of isopropanoylacetone-2-imino phenol-(H<sub>2</sub>F<sub>3</sub>PAP), Trifluoroisopropanoylacetone-2-iminophenol-(H<sub>2</sub>F<sub>3</sub>PAP), Acetylmesityl oxide-2-iminophenol (H<sub>2</sub>AMP) and Trifluoroacetyl mesityl oxide-2-imino phenol (H<sub>2</sub>F<sub>3</sub>AMP)*

2-Aminophenol (0.01 M), 1.0 g dissolved in methanol (10 ml) was added to isopropanoylacetone, trifluoroisopropanoylacetone, acetylmesityl oxide or trifluoroacetylmesityl oxide in methanol (10 ml). The mixture was refluxed on water bath for half an hour. The product was cooled over night. The precipitates were filtered and recrystallized from methanol.

#### *Preparation of copper complex*

Copper(II) acetate (0.001M) dissolved in methanol (10 ml) was added to the warm of solution H<sub>2</sub>PAP, H<sub>2</sub>F<sub>3</sub>PAP, H<sub>2</sub>AMP or H<sub>2</sub>F<sub>3</sub>AMP (0.001M) in methanol (10 ml). The mixture was refluxed for 15 min. and was concentrated to half the volume. The mixture was cooled overnight. The precipitates were filtered, recrystallized from methanol and dried at 105°C.

#### *Spectrophotometric studies*

The spectrophotometric studies of reagents and their copper chelates were recorded in acetone or methanol containing 0.4 mg/ml or after its appropriate dilution in the same solvent. The absorption spectra were recorded against solvent.

The spectrophotometric studies for nickel (II), cobalt(II), iron(II) and chromium(III) were carried out as under:

The solution (1 ml) containing 0.5-5 mg of nickel(II), cobalt(II), iron(II), or chromium (III) was added reagent solution (5 ml, 0.3% W/V) in methanol and sodium acetate buffer (1 M) pH 7 (2 ml). The mixture was warmed at water bath for 5 min. and volume was adjusted to 25 ml with methanol. The absorption spectra of the solutions were recorded against reagent blank in the same solvent.

The β-diketone were prepared by Claisen condensation as reported [11,13]. The elemental micro-analytes were carried out by Elemental Micro-Analysis Ltd. Deven, U.K. <sup>1</sup>H-NMR of the reagents were recorded at HEJ Research Institute of Chemistry, University of Karachi, in CDCl<sub>3</sub> in the range δ 0-13 ppm. The IR spectra in KBr were recorded on Perkin Elmer 1430 IR spectrophotometer. The spectrophotometric studies were carried out on Hitachi 220 spectrophotometer.

### References

1. M.Y. Khuhawar and Altaf I. Soomro, *Anal. Chim. Acta*, **26B**, 49 (1992).
2. M.Y. Khuhawar and Altaf I. Soomro, *Talanta*, **39**, 609 (1992).
3. E.E. Nifantev, A.T. Taleshev and M.P. Koroteev, *Zh. Oshykh. Khim.* **53**(7), 1640 (1983).
4. E. Hohaus, *Monatsh Chem.*, **111**(4), 863 (1980).
5. K.P. Sharma, R.V. Singh and J.P. Tandon, *Synth. React. Inorg. Met. Org. Chem.*, **10**(3), 221 (1980).
6. T.N. Srivastana, A.K.S. Chanhan and G. K. Mehrotra, *Indian J. Chem. Sect. A*, **22A**(8), 712 (1983).
7. S.A. Kudryavtsev, L.A. Movchan, and I.A. Savich, *Zh. Fiz. Kim.*, **45**(4), 968 (1971).
8. H. Imai, K. Ikendi, T. Shiraiwa and M. Oiwa, *Nippon Kagaku Kaishi*, (3), 451 (1976).
9. S.R. Gupta and J.P. Tandon, *Z. Naturforsch B*, **25**(11), 1231 (1970).
10. J.P. Tandon, S.R. Gupta and R.N. Prasad, *Synth. React. Inorg. Met. Org. Chem.*, **5**(3), 215 (1975).
11. R. Belcher, J. R. Major, W.I. Stephen, I.J. Thomson and P.C. Uden, *Anal. Chim. Acta*, **50**, 423 (1970).
12. M.Y. Khuhawar and A.K. Talpur, *J. Chem. Soc. Pak.*, **10**, 373 (1988).
13. M.Y. Khuhawar and A.K. Talpur, *Pak. J. Sci. Ind. Res.*, **11**, 185 (1989).