

Studies on 2-Hydroxy-5-Methylacetophenoneanil as Analytical Reagent

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2-Hydroxy-5-methylacetophenoneanil has been found to be a chelating agent for copper, nickel and cobalt. It gives reddish brown precipitate of $\text{Cu}(\text{C}_{15}\text{H}_{14}\text{NO})_2$ at pH 10.5-10.8, red precipitate of $\text{Ni}(\text{C}_{15}\text{H}_{14}\text{NO})_2$ at pH 9.0-9.8 and green precipitate of $\text{Co}(\text{C}_{15}\text{H}_{14}\text{NO})_2$ at pH 10.0-11.0. The estimation of copper II was done gravimetrically with average error being less than one percent. The absorption spectra in ultra-violet and visible region was obtained for the reagent and the chelates. The magnetic properties of the chelates were studied.

2-HYDROXY-5 methylacetophenoneanil has the system $-\text{O}-\text{C}=\text{C}-\text{C}=\text{N}$. Similar to many precipitating agents used for a number of transition metal ions. The reagents having such a system have been investigated by several workers¹⁻³. The present work deals with the preparation of 2-Hydroxy-5 methylacetophenoneanil (HMAA) and its chelates with Cu^{2+} , Ni^{2+} and Co^{2+} . The reaction of the reagent with Cu^{2+} , gives a reddish brown precipitate at pH 10.5-10.8 and quantitative estimation of Cu^{2+} was done with the average error less than one percent. It also forms chelate with Ni^{2+} at pH 9.0-9.8 and with Co^{2+} at pH 10.5-11.0. The chelates of copper and cobalt were found to be paramagnetic whereas the nickel chelate was diamagnetic. Absorption spectra of the chelates were similar in nature with the spectra of the reagent.

Experimental

Preparation of 2-Hydroxy-5-methylacetophenoneanil: 2-Hydroxy-5-methylacetophenone was prepared by Fries migration of *p*-cresylacetate⁴ in presence of anhydrous aluminium chloride. The 2-Hydroxy-5-methylacetophenone (15.0 g; 0.1M) and aniline (11.2 g; 0.12M) were mixed and anhydrous zinc chloride (15 g) was added. The mixture was heated to 160° for half an hour and then the temperature was raised to 180°. After 5 min, it was cooled and the anil was extracted with chloroform. From chloroform extract the anil was isolated and recrystallised from alcohol as yellow plates, m. p. 109°. Found: C 79.9; H 6.4 and N 6.1%; Calc. for $(\text{C}_{15}\text{H}_{14}\text{NO})$: C 80.0; H 6.6; N 6.2%.

An alcoholic solution of the reagent was used for the preparation of the chelates.

Preparation of Copper chelate: Cupric chloride solution (10 ml, 0.1M) was diluted to 100 ml and warmed to 50°-60°. The pH was adjusted to 10.5-10.8 by adding ammonium hydroxide. A calculated amount of reagent solution (0.1M) was added with stirring followed with the addition of little excess of the reagent to ensure complete precipitation. The precipitates were digested on water-bath for 15 min. and then filtered

out, washed and dried at 100°-110° and weighed as $\text{Cu}(\text{C}_{15}\text{H}_{14}\text{NO})_2$. It can be crystallised from benzene.

For quantitative estimation, different amounts of Cu^{2+} was taken and precipitated as mentioned above at pH 10.5-10.8 at 60°. It shows that copper can be estimated from Cu^{2+} solution with the average error less than one percent.

The elemental analysis of the copper chelate is as follows:-

Found: C 70.34; H 5.40; N 5.46; Cu 12.38%
Calc. for $\text{Cu}(\text{C}_{15}\text{H}_{14}\text{NO})_2$: C 70.40; H 5.47; N 5.47;
Cu 12.43%

Preparation of Nickel chelate: Nickel chloride solution (10 ml, 0.1M) diluted with water and the pH was adjusted to 9.0-9.8 using ammonium hydroxide-ammonium acetate buffer. A calculated amount of alcoholic solution of the reagent (0.1M) with little excess was added to it and the mixture was refluxed on water bath for 30 min. The red precipitate of nickel complex so obtained was filtered out, washed, dried and crystallised from benzene.

Found: C 70.96; H 5.50; N 5.51; Ni 11.54%
Calc. for $\text{Ni}(\text{C}_{15}\text{H}_{14}\text{NO})_2$: C 71.04; H 5.53; N 5.53;
Ni 11.59%

Preparation of Cobalt chelate: Cobalt chloride solution (10 ml, 0.1M) diluted with water and the pH was adjusted to 10.8-11.0 by adding excess of ammonium hydroxide. A calculated amount of reagent solution (0.1M) with little excess was added to it and the mixture was refluxed on water bath for half an hour. The green precipitate of cobalt chelate so obtained were filtered out, washed, dried and crystallised from benzene.

Found: C 70.90; H 5.50; N 5.1; Co 11.45%
Calc for $\text{Co}(\text{C}_{15}\text{H}_{14}\text{NO})_2$: C 71.01, H 5.52
N 5.2; Co 11.62%

The percentage of copper and nickel in the complex was determined by oxide method whereas of cobalt was determined by anthranilate method. The molecular

weights of the chelates of Cu^{2+} , Ni^{2+} and Co^{2+} , determined cryoscopically agrees with the empirical formula weights suggest that all these chelates are monomers.

The magnetic susceptibility of the chelates was determined by Gouy balance method. The copper and cobalt chelates were found to be paramagnetic having one unpaired electron whereas nickel chelate was diamagnetic as shown in table II. From magnetic properties it can be said that the nickel and cobalt chelates have square planar configurations with dsp^2 hybridization.

TABLE I—GRAVIMETRIC ESTIMATION OF Cu^{2+} at pH 10.5–10.8

Sr. No.	Cu^{2+} taken in mg	Complex in mg	Cu^{2+} found in mg.	Error in mg.
1.	50.5	402.0	50.7	+0.2
2.	62.5	502.0	62.4	-0.1
3.	75.0	606.0	75.3	+0.3
4.	153.75	1238.0	153.35	-0.4

TABLE II—MAGNETIC SUSCEPTIBILITY OF THE CHELATES

Complex	Current — Amount 'm' in g	4 amp. Force of magnetic fields f' in mg.	T = 309°K		
			$\chi \times 10^{-6}$ C.G.S	$\chi_M \times 10^{-6}$ C.G.S	μ_{eff} B.M.
$\text{Cu}(\text{C}_{15}\text{H}_{14}\text{NO})_2$	0.62554	1.54	1.88650	965.04	1.76
$\text{Ni}(\text{C}_{15}\text{H}_{14}\text{NO})_2$	1.12151	-1.01	-0.61631	—	—
$\text{Co}(\text{C}_{15}\text{H}_{14}\text{NO})_2$	0.55579	1.26	1.7540	889.54	1.71

A known amount of the crystallised chelate was dissolved in chloroform and made upto 250 ml. The absorption spectras were recorded for these solutions using Unicam Sp 500 spectrophotometer. The absorption spectra of the reagent solution was also recorded.

Three absorption maximas were observed for the reagent Ni^{2+} and Cu^{2+} chelates but only two maximas were clearly seen in the spectra of cobalt chelate.

The nature of the absorption curves of Cu^{2+} , Ni^{2+} and Co^{2+} is similar to the absorption curve of reagent but the position of maximas are different. The results are presented in table III. The absorption spectra of metal chelates do not show any characteristic absorption maxima expected in the visible region. The tail of the charge transfer spectrum goes much into the visible region.

TABLE III—ABSORPTION SPECTRA OF THE ANIL AND METAL CHELATES

Chelate		Ist	IInd	IIIrd
$\text{Cu}(\text{C}_{15}\text{H}_{14}\text{NO})_2$	λ_{max}	335 $\text{m}\mu$	257 $\text{m}\mu$	226 $\text{m}\mu$
	Log ϵ	4.0863	4.4863	4.7859
$\text{Ni}(\text{C}_{15}\text{H}_{14}\text{NO})_2$	λ_{max}	408 $\text{m}\mu$	322 $\text{m}\mu$	248 $\text{m}\mu$
	Log ϵ	4.3625	4.7041	5.2169
$\text{Co}(\text{C}_{15}\text{H}_{14}\text{NO})_2$	λ_{max}	370 $\text{m}\mu$	249 $\text{m}\mu$...
	Log ϵ	4.1251	5.4299	...
Reagent $\text{C}_{15}\text{H}_{15}\text{NO}$	λ_{max}	335 $\text{m}\mu$	260 $\text{m}\mu$	226 $\text{m}\mu$
	Log ϵ	4.2969	4.6029	4.9563

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