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NOTES

SPECTROPHOTOMETRIC STUDIES ON COBALT (II) COMPLEX OF 4-METHYL DIBENZOYLMETHANE

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4-Methyl dibenzoylmethane forms 1 : 1 (M : R) yellow complex with Co(II) at pH 8.0 to 8.9 Working wavelength used for spectrophotometric study of the complex is 390 nm. Values of λ-maxima, molar absorptivity 'ε', sandell's sensitivity, stability constant (log *K*) and free energy of formation (ΔF) were found to be 385 nm, 8000 $cm^{-1}mol^{-1}$, 0.0073 μg cm^{-2}, 4.675 and –6.376 k.cals per mole respectively. Beer's law is obeyed in concentration range of 1×10^{-5}–6×10^{-5} *M*.

Some of the reagents recently used for the spectrophotometric determination of Co(II) are indane-1,2,3-trione trioxime[1]; eriochrome azurol B, 4,4′-bipyridyl and hexadecyl trimethyl ammonium bromide combination[2]; 4,5-dibromophenyl fluorone and hexadecyl pyridinium bromide[3]; 1-(2-quinolylazo)- 2,4,5-trihydroxy benzene [5-(2-quinolinylazo) benzene-1,2,4-triol][4] and 3-hydroxy-2-methyl-1,4-naphthaquinone-4-oxime[5].

4-Methyl dibenzoylmethane (4-Me DBM) was obtained by following the general method reported in organic syntheses[6] as pink coloured crystals, m.pt. 85°C. m.f.: $C_{16}H_{14}O_2$; elemental analysis: C% found 80.67, calc. 80.64; H% found 5.90 calc. 5.92; (yield *ca.* 80%).

4-Me DBM solution (1×10^{-2} *M*) was always freshly prepared by dissolving the requisite quantity of pure compound in ethanol. Weaker solutions were prepared by appropriate dilution with ethanol. A stock solution of 1×10^{-2} *M* Co(II) was prepared by dissolving the requisite quantity of $Co(NH_3)_2{\cdot}6\,H_2O$ (A.R. Merck) in double distilled water. The solution was standardised by titrating it against standard EDTA solution using xylenol orange as indicator[7]. Weaker solutions were prepared by appropriate dilution with ethanol.

Spectrophotometric studies on Co(II) complex with 4-Me DBM were made at working wavelength 390 nm in ethanol solvent and full colour development was obtained at pH 8.0 to 8.9. For determination of λ-maxima and working wavelength of the complex Co(II) to reagent ratio was kept 1 : 10.

Job's[8], mole ratio[9] and slope ratio[10] methods were used to determine the composition of the complex and was found to be Co(II) : R = 1 : 1. Beer's law is obeyed for Co(II) concentration of $1\times10^{-5}M$. The molar absorptivity 'ε' of the complex was found as 8000 $cm^{-1}mol^{-1}$ and Sandell's sensitivity as 0.0073 μg cm^{-2}. The stability constant was determined by using Harvey and Manning's method[11] and free energy of formation was calculated as –6.376 k.cals. per mole at 25°C by using the relationship:

$$\Delta F = -2.303\, RT \log K \text{ (stab.)}.$$

The standard deviation σ was obtained as .038 ppm (0.64%) by measuring the absorbance of ten solutions containing 5.9 ppm of Co(II).

For the sake of comparison the values of sandell's sensitivity and working wavelength for some of the reagents used for Co(II) are given in Table 1, alongwith the values of dibenzoylmethanes studied so far.

TABLE 1

S.No.	Reagents	Sandell's sensitivity in μg cm^{-2}	Wavelength used in nm
1	5-Chloro-8-hydroxy-7-iodoquinoline[12]	0.0063	430
2	2-pyridyl-2-thienyl-β-ketoxime[13]	0.0295	412
3	Sod. alizarino-sulphonate[14]	0.009	600
4	3', 5'-dichloro-2'-hydroxy acetophenone oxime[15]	0.046	420
5	5-(3, 5-dibromo-2-pyridylazo) toluene-2, 4-diamine[16]	0.0005	580
6	N-phenyl cinnamohydroxamic acid[17]	0.032	625
7	2-(3, 5-dibromo-2-pyridylazo)-5-diethylaminobenzoic acid[18]	0.00038	673
8	O-hydroxy quinolphthalein and H_2O_2[19]	0.00015	530
9	Thiocyanate[20]	0.033	628
10	4-Methoxy dibenzoylmethane[21]	0.0173	405
11.	3-nitro-α-methyl dibenzoylmethane[21]	0.015	410
12.	α-methyl dibenzoylmethane[21]	0.035	420
13.	4-Methyl dibenzoylmethane	0.0073	390

A persual of the Table 1, reveals that 4-Me DBM is the most sensitive reagent among the four dibenzoylmethanes; 2-pyridyl-2-thineyl-β-ketoxime; sodium alizarino sulphonate; 3',5'-dichloro-2'-hydroxy acetophenone oxime; N-phenyl cinnamohydroxamic acid and thiocyanate. Thus, 4-Me DBM is a good addition to the reagents used for spectrophotometric determination of Co(II).

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