Synthesis and spectrophotometric studies of Zn (II)-HMCPP complex and their use as an analytical reagent

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ABSTRACT

In the present investigation, 4-Hydroxy-8-methylcoumarin derivatives and metal complexes were synthesized and studies for chelate formulation with a metal ion Zn (II) using spectrophotometric method. 4-Hydroxy-8-methylcoumarin chalcones [1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-5-phenyl-2, 4-pentadiene-1-one] with Zn (II) complex was determined by mole ratio and job's method of continuous variation. The complexes of metal formed with coumarin derivative were compared with standard reagents.
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INTRODUCTION

The theory of metal based mixed valence complexes (MBMV) is well documented[1,2]. The synthesis of hydroxy coumarins[3] remains of great interest due to the wide application as chelating agents to metal ion. Hydroxy coumarin derivatives forms complex with V, Ti (IV), Zr (IV), Ca, Pr, Na, Sm, Gd, etc[4-8],.

The physico chemical studies of the coumarins with chelating groups at appropriate positions and their metal-complexes reveal that the ligands could be potential analytical reagents[9-13].

The present communication deals with synthesis of HMCPP [1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-5-phenyl-2, 4-pentadiene-1-one], HMCPP complex with metal ion, this may be used as an analytical reagent. It belongs to chalcone series[14]. Chalcones are the compounds which are obtained by the condensation of aromatic ketone with an aldehyde; this is reacting with Zn (II). The ligand is found to form complexes with above

metal ion in different pH ranges. The absorbtion spectra of the complex were recorded and the effects of pH on the absorbtion values were studied. The composition of complex was determined by Yoe and Jones mole ratio and job's method of continuous variation[15-16]. This has also been supported from thermo gravimetric analysis[17].

The structure of the synthesized compounds and complexes were assigned on the basis of ^{1}H NMR, IR spectra data and spectrophotometric study.

EXPERIMENTAL

All chemicals used throughout this work were of analytical grade. The absorbance measurements were done on a Shimadzu-UV-160-A Spectrophotometer. The pH of the solutions were measured on EQUIP TRONICS 614 pH meter and solutions of required pH were obtained using sodium-acetate-acetic acid, sodium acetate-HCl, NH_3-NH_4Cl or Borax-HCl buffer

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of suitable concentration. The stoichiometric ratios of metal to reagent in the complexes were determined by Job's method of continuous variation, Yoe and Jones mole ratio method and gravimetric method. The entire practical were done at room temperature.

Preparation of 4-hydroxy-8-methyl coumarin[18-28]

O-Cresol (10.8 g, 0.01mol) and malonic acid (10.4 g, 0.1mol) were added to a mixture of phosphorus oxychloride (40 ml) and anhydrous zinc chloride (30 g). The reaction mixture was heated on a waterbath at 70^0C for 18-20 hrs. The content was cooled and decomposed with ice-water giving solid, which was filtered and washed with water. It was then treated with sodium carbonate solution and filtered. The filtrate was acidified with dilute hydrochloric acid. The precipitate was washed with water and crystallized from methanol. Yield 75%, M.P. 225^0C.

Synthesis of 3-Acetyl-4-hydroxy-8-methyl coumarin[29-34]

4-Hydroxy-8-methyl coumarin (1.56 g, 0.01mol) was dissolved in mixture of acetic acid (5 ml) and phosphorus oxychloride (4 ml) and refluxed it on waterbath for half an hour. The reaction mixture was poured into ice-cold water; the product was isolated and crystallized from ethanol. Yield 85%, M.P. 110^0C.

Synthesis of 1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-5-phenyl-2, 4-pentadiene-1-one (HMCPP)

A mixture of 3-acetoacetyl-4-Hydroxy coumarin (1.98g, 0.01mol), cinnamaldehyde (1.06g, 0.01mol) and piperidine (1 ml) as a catalyst in chloroform (50 ml) was refluxed for 6 hrs on a water bath. The excess chloroform was distilled off and the residue was washed with methanol and crystallized from dioxane. Yield 68%, M.P.120^0C. ^1H-NMR ($CDCl_3$), δppm: 2.41(s, 3H, Ar-CH_3), 6.41-8.00 (m, 8H, Ar-H); IR (KBr, cm^{-1}): 3112, 3030, 2939, 2839, 1724, 1604, 1442, 1342, 1261, 1195, 760; Molecular Formula : $C_{21}H_{16}O_4$.

Preparation of standard solution of Zn (II)

Stock solution of Zn (II) (0.05 M) was prepared by dissolving 3.208 g of $ZnSO_4.5H_2O$ in distilled water and hydrochloric acid and diluting it to 250 ml. This solution was standardized volumetrically using EDTA. Experimental solutions of required concentration were prepared by appropriate dilution of the above stock solution.

Reaction of HMCPP with Zn (II)

1.0 % solution of the reagent in dioxane was used in all detection and gravimetric determination. IR (KBr, cm^{-1}): 3049, 3028, 2924, 2852, 1732, 1593, 1442, 1339, 1261, 1203, 773.

Reaction of HMCPP with Zn (II) at different pH values

5 ml HMCPP solution was added to 2 ml of standard 0.05 M Zn (II) solution at different pH. The results are tabulated in TABLE 1.

Stability of chelate

The buff colour Zn (II) chelate is insoluble in water and ethanol, while it is soluble in chloroform, dioxane, DMF, ethyl acetate. The solution of the chelate was stable and could be kept for long time without any decomposition.

Gravimetric determination of Zn (II) with HMCPP

A 1.0 % solution of the reagent in dioxane was used. Zinc sulphate solution (0.05 M, 10 ml) taken in a clean beaker was diluted to about 100 ml with distilled water and pH of the solution was adjusted to 3.0 to 4.0 by using sodium acetate – hydrochloric acid buffer. The solution was warmed at 60^0C and small excess of reagent HMCPP was added (1%, 25 ml). A light green precipitate obtained was digested on water bath for 60 minutes at 60^0C. The precipitate was filtered through a previously weighed sintered glass crucible (G4) and washed with warm water, followed by dioxane to remove excess of the reagent which might have precipitated on dilution. The chelate was dried to constant weight at 110-115^0C in hot air oven, cooled and

TABLE 1: Reaction with Zn (II) at deferent pH values

pH	Buffer	Observation
2.0	$HCl + CH_3COOH$	Colouration
2.5	$HCl + CH_3COOH$	Buff precipitate
3.0	$HCl + CH_3COOH$	Buff precipitate
4.0	$CH_3COOH + CH_3COONa$	Buff precipitate
5.0	$CH_3COOH + CH_3COONa$	Buff precipitate
6.0	$CH_3COOH + CH_3COONa$	Buff precipitate
7.0	$CH_3COOH + CH_3COONa$	Buff precipitate
8.0	$NH_3 + NH_4Cl$	Buff precipitate
9.0	$NH_3 + NH_4Cl$	Buff precipitate
10.0	$NH_3 + NH_4Cl$	Buff precipitate

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TABLE 2 : Gravimetric estimation of Zn (II) using HMCPP ligand (Cu: 0.03200 g)

pH	Zn (II) complex in (g)	Zn (II) found in (g)	Error In(g)	%
2.5	0.1595	0.3129	-0.0071	-2.21
2.5	0.1604	0.3147	-0.0053	-1.65
3.0	0.1612	0.3162	-0.0038	-1.18
3.0	0.1619	0.3176	-0.0024	-0.75
3.5	0.1626	0.3190	-0.0010	-0.31
3.5	0.1632	0.3203	+0.0003	-0.09
4.0	0.1641	0.3219	+0.0019	+0.59
4.0	0.1648	0.3233	+0.0033	+1.03
4.5	0.1657	0.3251	+0.0051	+1.59
4.5	0.1666	0.3268	+0.0068	+2.12
5.0	0.1674	0.3284	+0.0084	+2.62
5.0	0.1684	0.3300	+0.0100	+3.12

TABLE 3: Verification of Beer's law at 410 nm

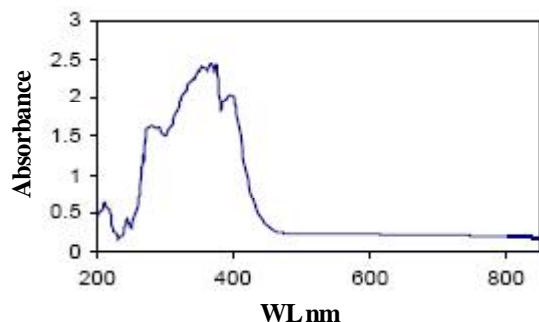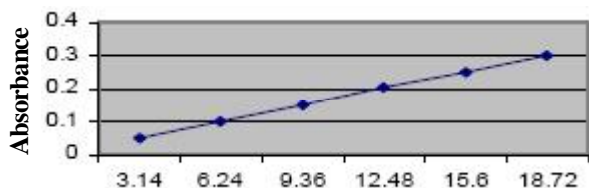| Zn (II) solution taken in ppm.	Zn (II) on taken in ppm.	Absorbance
0.3	3.14	0.051
0.6	6.24	0.102
0.9	9.36	0.151
1.2	12.48	0.203
1.5	15.60	0.250
1.8	18.72	0.300

Figure 1: Absorption spectra of Zn (II)-HMCPP complex

Verification of Beer's Law : Zn (II) - HMCPP Complex

Figure 2: Verification of Beer's law

weighed.

The experiment was repeated at different pH of solution. The experiment was also repeated with different aliquots keeping the optimum pH to evaluate its applicability. The results are given in TABLE 2.

Spectrophotometric study of Zn (II) complex

The Zn (II) - HMCPP chelate has been found to be soluble in chloroform, dioxane, benzene, carbon tetrachloride, DMF, ethyl acetate. This enabled to verify the Beer's law and its application for spectrophotometric determination.

Absorption spectra

To record the absorption spectra, 5 mg of chelate was dissolved in 25 ml of dioxane and absorbance of this solution was measured at different wave length in the range of 350-600 nm.

The absorbance was plotted against wave length to get absorption spectra. It was observed that the absorbance of the coloured solution of chelate increases continuously towards the shorter wave length. A shoulder is observed at 410 nm and hence all the measurements were carried out at 410 nm. Absorption Spectra of Zn (II)-HMCPP complex is shown on figure 1.

Verification of Beer's law

To 5 ml of solution (0.01 M) of the reagent HMCPP, varying amounts of the metal ion solution (0.005 M) were added and the pH was adjusted to 5.0 using $CH_3COONa + CH_3COOH$ buffer. The insoluble complex precipitated was extracted in chloroform using three 5 ml portions of chloroform and final volume of the chloroform extract was adjusted to 25 ml. The absorbance of these solutions were measured at 410 nm against chloroform as the blank. Absorbance values were plotted against the metal concentration expressed in ppm. A straight line passing through the origin, indicating the obeyance of Beer's law as was obtained up to 30.22 ppm of Zn (II). The standard graph thus obtained may be used for the determination of Zinc in an unknown solution using HMCPP reagent. The results are tabulated in TABLE 3. The graph is shown on figure 2.

Molar absorptivity calculated from Beer's law plot was found to be 10.01×10^2 lit $mol^{-1}cm^{-1}$ for Zn (II)-HMCPP reagent at 410 nm.

Composition of chelate

The composition of Zn (II) chelate with the reagent HMCPP has been determined on the basis of Job's method of continuous variation and Yoe and Jones mole ratio method.

Full Paper

TABLE 4: Data obtained from Job's method of continuous verification

Metal ion solution ml	Ligand solution ml	Cm/Cm +CL	Absorbance
1.	11	0.08	0.350
2.	10	0.17	0.371
3.	9	0.25	0.388
4.	8	0.33	0.410
5.	7	0.42	0.490
6.	6	0.50	0.432
7.	5	0.58	0.408
8.	4	0.66	0.397
9.	3	0.75	0.382
10.	2	0.83	0.361
11.	1	0.91	0.338

TABLE 5: Data obtained from Yoe and Jones mole ratio method

Metal ion solution ml.	Ligand solution ml.	Cm +CL	Absorbance
1.	6	0.17	0.225
2.	6	0.33	0.234
3.	6	0.50	0.260
4.	6	0.66	0.265
5.	6	0.83	0.265
6.	6	1.00	0.265
7.	6	1.16	0.265
8.	6	1.33	0.265

Composition of Zn (II)-HMCPP complex by Job's method of continuous variation

A 0.005 M solution of Zn (II) was prepared by suitable dilution of the standard solution. The solution of reagent (0.005 M) was prepared in dioxane. The solution of metal salt and the reagent were mixed in varying proportions as under:

Metal ion solution :   0, 1, 2, 3, - - - - 11, 12 ml
Reagent solution   :   12, 11, 10, 9, - - - - 1, 0 ml

pH of the solution was adjusted to 5.0. The precipitated complex was extracted with three 5 ml portions of chloroform and final volume of chloroform extract was adjusted to 25 ml. The absorbance of chloroform extracts were measured at 410 nm. The results are tabulated in TABLE 4.

From the graph is shown on figure 6, it has been found that maximum occurs at 0.4 ratio of metal ion concentration to the total metal and ligand concentration indicating the formation of 1:2 (M : L) complex.

Yoe and Jones mole ratio method

In this method, equimolar solutions of the Zinc (II) and the reagent (0.005 M) were used. A series of solutions were prepared, keeping the reagent solution (6.0
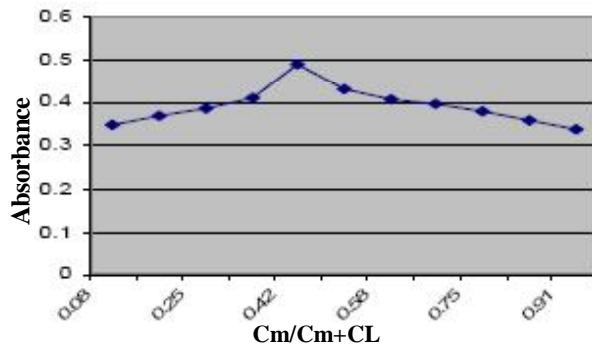

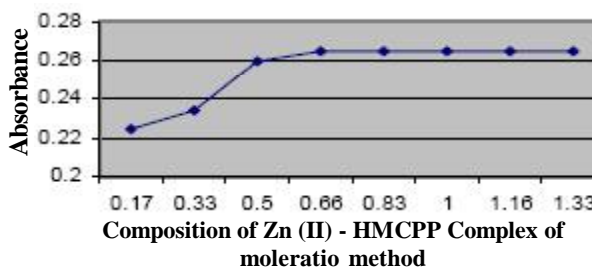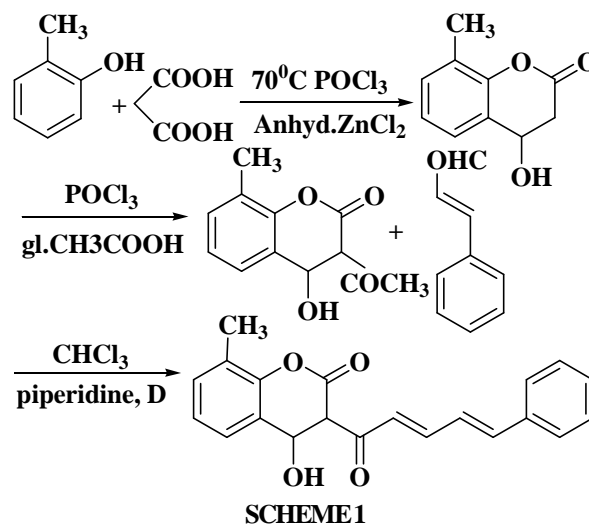**Figure 3: Result of Job's method of continuous verification**

Figure 4: Result of Yoe and Jones mole ratio method

SCHEME 1

ml) constant while varying the amount (from 1 to 7.0 ml) of 0.005 M metal solution.

pH of the solutions were adjusted to 5.0. The resulting precipitate was extracted in chloroform and final volume of chloroform extract was adjusted to 25 ml. Absorbance were recorded at 410 nm and plotted against the ratio of concentration of metal ion to reagent. The results are tabulated in Table-V and Graph shown on figure 3.

It is evident from the graph that absorbance gradu-

ally increases up to molar composition of metal to the reagent and after that it becomes constant indicating 1:2 stoichiometry of the complex.

RESULT AND DISCUSSION

In the current paper, 4-Hydroxy-8-methylcoumarin was synthesized by the condensation of o-cresol with malonic acid. 4-Hydroxy-8-methylcoumarin was acetylated and subjected to fries migration to give 3-acetoacetyl-4-hydroxy-8-methylcoumarin. The acetyl coumarin was condensed with o-nitro benzaldehyde to yielded compound 1-(4'-hydroxy-8'-methyl coumarin-3'-yl)-5-phenyl-2, 4-pentadiene-1-one.

In the present study the reagent HMCPP form complexes with Zn (II) in the various range of pH.

The composition of complexes determined by mole ratio and job's method of continuous variation, was found to be 1:2 (M: L), this has also supported by gravimetric analysis. The synthesized reagents are quite stable at room temperature for long time without showing any sign of decomposition. The reagents are well suited as gravimetric reagents.

CONCLUSION

From the finding, we are concluded that, coumarin derivatives as an analytical reagent has found extensively used in analytical determination of various metal ions.

ACKNOWLEDGMENTS

REFERENCES

[1] N.S.Hush; Prog.Inorg.Chem., **8**, 391 **(1967)**.
[2] T.J.Meyer; Acc.Chem.Res., **11**, 94 **(1978)**; C.Creutz; Prog.Inorg.Chem., **30**, 1 **(1980)**.
[3] R.Anschtz; Chem.Ber., **36**, 465 **(1903)**.
[4] H.B.Singh; Ph.D.Thesis, Delhi University, **(1966)**.
[5] M.Katyal, H.B.Singh; Talanta, **15**, 1054 **(1968)**.
[6] G.S.Manku; Ph.D.Thesis, Delhi University, **(1970)**.
[7] A.K.Kalara; Ph.D.Thesis, Delhi University, **(1972)**.
[8] N.Kohli; Ph.D.Thesis, Delhi University, **(1974)**.
[9] K.Jagnadha, K.L.Omprakash; J.Indian Chemical Soc., **L12**, **(1985)**.
[10] A.K.Kalra, R.P.Singh; J.I.C.S., **1**, 49 **(1972)**.
[11] H.B.Singh; J.Inst.Chemists, India, **54**, **(1982)**.
[12] G.P.Pokhariyal; J.Indian.Chem.Soc., **74**, **(1997)**.
[13] K.B.Gudasi, T.R.Goudar; J.I.C.S., **74**, **(1997)**.
[14] K.H.Popat, K.S.Nimavat, S.L.Vasoya, H.S.Joshi; Indian Journal of Chemistry, **42B**, 1497-1501 **(2003)**.
[15] R.S.Bakry, O.A.Razak, A.F.Walily, S.F.Belal; J. Pharma Biomed Anaal., **17(1)**, 95-101 **(1998)**.
[16] A.K.Malik, K.N.Kaul, B.S.Lark, W.Faubel, A.L.J. Rao; Turk J.Chem., **25**, 99-105 **(2001)**.
[17] S.R.Mwelase, J.Bariyanga; Journal of Molecular Structure, **60(2-3)**, 235-244 **(2002)**.
[18] **(a)** R.Anschutz; Ann., **367**, 169 **(1909)**.
    (b) I.M.Helborn, D.W.Hill; J.Chem.Soc., 1704 **(1927)**.
    (c) K.C.Ghosh; J.Ind.Chem., **24**, 321 **(1947)**.
[19] H.Kneyuki; Bull.Chem.Soc., Japan, **35**, 579 **(1962)**.
[20] A.Sonn; Ber., **50**, 129 **(1917)**.
[21] K.G.Baner, F.Scholder; Arch.Pharma., **53**, 259 **(1929)**.
[22] K.Howsch; Ber., **48**, 1122 **(1915)**.
[23] **(a)** S.Iguchi; J.Pharma.Soc.Japan, **72**, 122 **(1952)**.
    (b) S.Iguchi; N.Utshugi; J.Pharma.Soc.Japan, **73**, 1290 **(1953)**.
[24] J.F.Garden.N.F.Hafes, R.H.Thomson; J.Chem. Soc., 3315 **(1956)**.
[25] E.Ziegler, H.Junkek; Montch, **86**, 29 **(1955)**; C.A., **50**, 256 **(1956)**.
[26] K.Ziegler, H.Junkek; Montch, **87**, 212 **(1956)**; C.A., **51**, 7365 **(1957)**.
[27] V.R.Shah, J.L.Bose, R.C.Shah; J.Org.Chem., **25**, 677 **(1960)**.
[28] F.Dallaeker, P.Kratzer, M.Lip; Ann., **643**, 97-109 **(1961)**.
[29] V.N.Dholakia, M.G.Parekh, K.N.Trivedi; Aust.J.Chem., **21**, 2345-7 **(1968)**.
[30] H.R.Eisenhaur, K.P.Link; J.Am.Chem.Soc., **75**, 2044 **(1953)**.
[31] R.Anschtz; Ber., **36**, 465 **(1903)**.
[32] H.Pauly, K.Lockmann; ibdi., **48**, 28 **(1915)**.
[33] A.Sonn; ibdi., **50**, 1292 **(1917)**.
[34] M.A.Stahmenn, I.Wolff, K.P.Link; J.Am.Chem. Soc., **65**, 2285 **(1943)**.