

Formation Constants of the Complexes of Some Bivalent Metal Ions with a New Tridentate Schiff Base, 7-Hydroxy-8-[(2-mercaptophenyl)iminomethyl]-4-methyl-2H-1-benzopyran-2-one

(Mrs) S V KALAVATHI & K L OMPRAKASH*

Department of Chemistry, P.G. College (Osmania University),
Secunderabad 500 003

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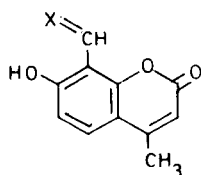
K JAGANNADHA CHARYULU, A V CHANDRA PAL
& M L N REDDY*

Department of Chemistry, Osmania University,
Hyderabad 500 007

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A new tridentate schiff base, 7-hydroxy-8-[(2-mercaptophenyl)iminomethyl]-4-methyl-2H-1-benzopyran-2-one (HMMB), derived from 8-formyl-7-hydroxy-4-methyl-2H-1-benzopyran-2-one and 2-mercaptoaniline has been synthesised and characterised by analytical and spectral data. Proton-ligand formation constants of the schiff base and metal-ligand formation constants of its chelates with Cu(II), Co(II), Ni(II), Fe(II), Mn(II), Zn(II), Cd(II), Hg(II) and Pb(II) have been determined pH-metrically in 70% (v/v) aq. dioxane medium at 20, 25, 32 and 45° and $I = 0.05 M$ (NaClO₄). The $\bar{n}$ and pL values reveal the formation of only 1:1 chelates with this tridentate ligand. The order of chelate stabilities is found to be almost in conformity with Irving-Williams order. Thermodynamic parameters, ΔG , ΔH , and ΔS , associated with the complex formation reactions, have been evaluated. The schiff base HMMB is suggested as suitable acid-base indicator for the titration of HCO₃⁻, HPO₄²⁻ and CH₃COO⁻ against a strong mineral acid.

Metal complexes of coumarins and schiff bases are reported to be potential biochemical and analytical reagents. This prompted us to study the synergistic effect of these two moieties on the complexing tendencies of the ligands containing them with metal ions. In the present investigation the schiff base 7-hydroxy-8-[(2-mercaptophenyl)iminomethyl]-4-methyl-2H-1-benzopyran-2-one (HMMB) has been synthesised by condensing 8-formyl-7-hydroxy-4-methyl-2H-1-benzopyran-2-one (FHMB) with 2-mercaptoaniline. The interaction of HMMB with bivalent transition metal ions has been studied pH-



1 X = O, FHMB;
X = 2-SH-Ph-N₂-HMMB

metrically in 70% (v/v) aq. dioxane at 20, 25, 32 and 45° and $I = 0.05 M$ (NaClO₄).

All the chemicals used were of AR/GR grade. Equimolar quantities of FHMB¹ and 2-mercaptoaniline were refluxed (1 hr) in methanol. The resultant schiff base, HMMB, was repeatedly crystallised from methanol to get TLC-pure sample; m.p. 167°; IR(KBr): 3100-3250br(vOH), 1720(vC=O lactonic), 1620(vC=N) and 2550 cm⁻¹(vSH); PMR: δ 60 MHz (CDCl₃; TMS internal ref): 2.06 (3H, t, 4-CH₃), 6.0 (1H, s, 3-H), 6.8-7.8 (6H, m, Ar-H), (1H, s, S-H, D₂O exchangeable), 9.25 (1H, s, CH=N) and 14.8 (1H, s, OH, D₂O exchangeable); Mass: M⁺ 311 (23%) [Found: C, 65.8; H, 4.1; N, 4.4; S, 10.1, C₁₇H₁₃O₃NS requires: C, 65.6; H, 4.2; N, 4.5; S, 10.3%]. Based on the above analytical and spectral data, structure (I) has been assigned to the schiff base HMMB.

Proton-ligand and metal-ligand formation constants have been determined using Irving-Rossotti pH-titration technique² in 70% (v/v) aq. dioxane ($I = 0.05 M$ NaClO₄) at 20, 25, 32 and 45°. The experimental details are similar to those described earlier³. The pH-meter readings (B) in 70% (v/v) aq. dioxane were corrected by the method of Van Uitert and Hass⁴. The titration curve of HMMB showed the liberation of two protons per ligand molecule, corresponding to the -OH and -SH groups. From the proton-ligand formation curve log K_1^H and log K_2^H values have been obtained by various computational methods². As the hydroxyl group is more acidic (due to high electronegativity of oxygen) than mercapto group, log K_1^H and log K_2^H are designated as log K_{SH} and log K_{OH} , respectively.

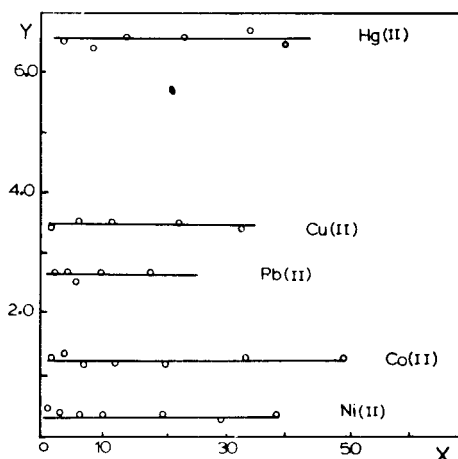


Fig. 1—X-Y plots for M(II)-HMMB systems [Cu, Hg, ($X \times 10^{20}$, $Y \times 10^{-19}$); Co ($X \times 10^{19}$, $Y \times 10^{-19}$); Pb ($X \times 10^{15}$, $Y \times 10^{-15}$) and Ni ($X \times 10^{17}$, $Y \times 10^{-16}$)]

Table 1—Formation Constants and Thermodynamic Parameters Associated with M(II)-HMMB Chelate Systems
[Medium: 70% (v/v) aq. dioxane; $I = 0.05\text{ M}$]

	log K_1				$-\Delta G$ (kJ mol ⁻¹)	$-\Delta H$ (kJ mol ⁻¹)	$-\Delta S$ (J mol ⁻¹ K ⁻¹)
	20	25	32	45°C			
Log K_{SH}	11.73	11.33	11.04	10.33	..	..	..
Log K_{OH}	10.45	10.19	9.85	9.24	..	..	..
Hg(II)	22.40	21.27	19.76	17.25	115.4	382.4	875.8
Cu(II)	22.15	20.98	19.48	16.68	113.8	386.6	895.1
Co(II)	21.70	20.56	19.06	16.32	111.3	382.0	888.1
Ni(II)	18.85	17.81	16.46	14.01	96.1	343.5	811.4
Pb(II)	17.22	16.43	15.42	13.59	90.1	257.3	548.6
Fe(II)	15.37	14.97	14.45	13.48	84.4	133.5	161.3
Zn(II)	14.90	14.52	14.05	13.22	82.2	118.0	117.7
Cd(II)	14.25	14.02	13.66	13.02	79.8	88.7	29.5
Mn(II)	10.83	10.50	10.05	9.22	58.7	114.6	183.5

The metal-ligand titration curves were well below the metal-ion hydrolysis curves. The low concentrations of metal ions ($4 \times 10^{-4}\text{ M}$) used are likely to prevent the formation of polynuclear complexes. The maximum $\bar{n}$ values calculated for each metal-ligand system have been found to be around 1.0 indicating the formation of only 1:1 complexes. An attempt has been made to check whether only 1:1 chelate⁵⁻⁷ is formed by constructing X-Y plots of the Eq. 1 (Fig. 1),

$$\frac{\bar{n}}{(1-\bar{n})[L]} = \beta_1 + \beta_2 \frac{(2-\bar{n})[L]}{(1-\bar{n})} \quad \dots (1)$$

In the present investigation all the M(II)-HMMB systems gave plots parallel to the abscissa confirming the formation of only 1:1 complex. The ligand is expected to act as a tridentate chelating agent coordinating through the phenolic oxygen, mercapto sulphur and azomethine nitrogen. Therefore, the stereochemistry of the ligand molecule may hinder the formation of a 1:2 complex. The metal-ligand formation constants (log K_1) have been evaluated by various computation techniques². The values obtained by different methods are in agreement with each other. The average log K_1 values are presented in Table 1. The standard deviations are in the range ± 0.03 .

The order of stability constants of M(II)-HMMB is: Hg(II) > Cu(II) > Co(II) > Ni(II) > Pb(II) > Fe(II) > Zn(II) > Cd(II) > Mn(II) which is almost in accordance with Irving-Williams natural order of stabilities except for Co(II) > Ni(II) and Fe(II) > Zn(II). The higher values for Co(II) and Fe(II) chelates may be due to the resonance stabilisation in these systems. Further, it has been found that Hg(II) and Pb(II) form more stable chelates compared with those of Zn(II) and Cd(II). Hg(II) and Pb(II) being relatively soft acids (due to their larger size) compared to Zn(II) and Cd(II), such an observation is not unexpected.

The thermodynamic parameters associated with the chelation reactions of M(II)-HMMB systems have

been evaluated from the pH-metric data at different temperatures and are presented in Table 1. The negative free energy change (ΔG) for M(II)-HMMB reaction in each case indicates that the chelation is spontaneous. Further, ΔG becomes more positive with an increase in temperature suggesting a decrease in the extent of complex formation at higher temperatures. The negative values of enthalpy change (ΔH) indicate exothermic nature of chelation and their magnitudes suggest strong metal-ligand bond. The negative entropy change (ΔS) can be attributed to the extensive solvation⁸ of metal chelates in an aquo-organic medium. This may be due to the exposure of the polar oxygen, nitrogen, sulphur and the metal ions of the chelate to solvent molecules⁹.

HMMB as an acid-base indicator

The ligand (H_2L) is colourless in the acid medium. In the pH-metric titration of the ligand HMMB with the alkali, an intense red colour was observed at the equivalence point. The formation of red colour may be due to the deprotonated form (HL^-) of the ligand. The presence of chromophoric centers like phenolic, mercapto, azomethine and lactonic groups coupled with highly extended conjugation in the ring system may be responsible for the intense red colour of the reagent. Keeping this in view, it was thought worthwhile to examine the suitability of this ligand as an acid-base indicator. It was found that with the aqueous sodium salt solutions of HCO_3^- , HPO_4^{2-} , and CH_3COO^- , the ligand formed intense red colouration instantaneously, whereas no colouration was noted with solutions of HSO_4^- , SO_4^{2-} , ClO_4^- , Cl^- , $H_2PO_4^-$, and NO_3^- . The colour formation reaction of the ligand with HCO_3^- , HPO_4^{2-} and CH_3COO^- was followed spectrophotometrically using a Systronics digital spectrophotometer type 106 with 1 cm quartz cells. Maximum absorption of the colour occurred at 500 nm. Reverse S-shaped curve (absorption vs volume of

HCl) was obtained when 20 ml of 0.05 *M* solution of HCO_3^- , HPO_4^{2-} or CH_3COO^- was titrated against 0.075 *M* standard HCl solution confirming the sharp colour change at the stoichiometric end point. The *pH* range of the colour change interval (as revealed by *A* vs *pH* plateaus) has been noted to be 4.9-7.1.

To have an insight as to why the reagent gives red colour with the aqueous solutions of HCO_3^- , HPO_4^{2-} and CH_3COO^- only, the proton-ligand stability of the ligand was determined in aqueous medium by extrapolating the plot of $\log K_{\text{OH}}$ versus mole fraction of dioxane or acetone to zero mole fraction. The value of $\log K_{\text{OH}}$ of the ligand in aqueous medium was found to be 6.5. This is consistent with the *pH* range of the colour change interval of the reagent.

Standard solutions of NaHCO_3 , Na_2HPO_4 or CH_3COONa (0.1 *M* to 0.001 *M*) were successfully titrated with standard mineral acids in the presence of

this ligand, end point being from dark red to colourless solution. Two drops of 0.1% ligand solution prepared in acetone were added. The titration error was found to be within 0.5-1.5%.

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