Copper(II) & Dioxouranium(VI) Complexes with Biologically Active Ligands: Part I— Complexes with Schiff Bases Derived from γ-Chromone

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Copper(II) and dioxouranium(VI) complexes of some schiff bases derived from vesnagin[1] and some amines have been prepared. These complexes have been characterised on the bases of elemental analysis, UV, visible, infrared spectra and molar conductance data. It is concluded that the anions of the schiff bases are coordinated to the metal ions as bidentate ligands.

Though, a large number of papers have appeared on metal complexes with schiff bases, no work has been reported on the schiff bases derived from 6-formyl-7-hydroxy-5-methoxy-2-methylchromone (I). This prompted us to undertake the study on metal complexes of

(I)
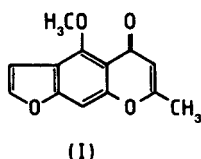
γ-chromone schiff bases and in the present note we report the copper(II) and dioxouranium(VI) complexes of some schiff bases derived from 6-formyl-7-hydroxy-5-methoxy-2-methylchromone and some amines. The complexes have been characterised on the basis of elemental analyses, UV, visible and IR spectra as well as conductance studies. The schiff bases used in the present study are (II a-d)

(II)
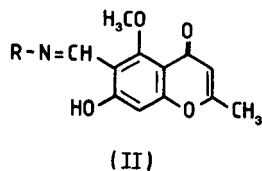
a; R = C_6H_4.COOH(p)   (L$_1$)
b; R = C_6H_5 (L$_2$)
c; R = C_6H_4.CH$_3$(p)   (L$_3$)
d; R = C_6H_{11}(cyclohexyl)   (L$_4$)

Synthesis of the schiff bases

6-Formyl-7-hydroxy-5-methoxy-2-methyl-

chromone (I) was obtained from vesnagin by oxidation of its furan ring with chromic acid[1].

The desired schiff bases (II a-d) were obtained when (I) was condensed with the appropriate amine in acetic acid. The structures of these compounds were confirmed by elemental analyses, UV and infrared spectra. The structures assigned to the schiff bases are confirmed by their PMR spectra. PMR spectrum of a representative sample (II C) is summerised below:

(II; L$_3$) exhibits signals (δ,ppm) at 1.1 [s,3H,CH$_3$ (a)], 2.15[s,3H,CH$_3$(b)], 3.9[s,3H,CH$_3$ (d)], 5.1 [s,1H, −CH =(e)], 6.0[s,1H,−CH= (f)], 6.8[s,1H,Ar-H(g)], 7.7[q,4H,(AB)], and 9.2[s,1H,OH(h)].

(II C; L$_3$)
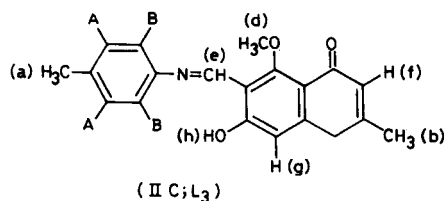
Preparation of 1:1 complexes

The complexes were synthesised by mixing equimolar amounts of CuCl$_2$.2H$_2$O or UO$_2$(NO$_3$)$_2$.6H$_2$O and schiff base in ethanol and refluxing the reaction mixture on a water bath for ~ 0.5-3 hr. The solid complexes which separated out were filtered, washed with ethanol and dried in vacuo. The solid complexes were analyzed for carbon, hydrogen and metal contents. The analytical data are given in Table 1.

The electronic spectra were measured with PYE UNICAM SP 8-100 spectrophotometer using 1 cm matched silica cells. The infrared spectra of the schiff bases and their complexes were recorded on a PERKIN ELMER 559 infrared spectrophotometer using KBr pellets of the samples. Conductance measurements were made with a PYE conductance bridge 25°C ± 1°C.

The electronic absorption spectra of the schiff bases are characterized by three absorption bands in the region 260-370 nm. The longest wavelength band is assigned to the intramolecular charge - transfer. The medium wavelength band is attributed to n-π^* transition of the carbonyl group; while the shorter wavelength band is due to π-π^* transition of the C = N moiety[2,3]. It is presumed that the γ-chromone moiety is the donor centre of the CT and the aniline ring is the acceptor one. Generally, the electronic spectra of schiff bases under investigation do not resemble those of their mixtures with Cu(II) in 1:1 molar ratio. This can

Table 1—Characterisation Data of the Schiff Bases and Their Complexes

Compd.	Found (Calc.),%			Dec. Temp. (°C)
	C	H	M	
L_1	64.32 (64.59)	4.32 (4.25)	—	>300
$[Cu\,L_1]Cl$	50.24 (50.55)	3.40 (3.32)	15.35 (14.08)	>300
$[UO_2L_1]\,NO_3$	33.20 (33.28)	2.25 (2.19)	34.98 (34.74)	>300
L_2	69.96 (69.90)	4.81 (4.85)	—	175
$[Cu\,L_2]\,Cl$	53.82 (53.07)	3.55 (3.68)	15.24 (15.60)	>300
$[UO_2\,L_2]\,NO_3$	34.82 (33.75)	2.24 (2.34)	36.83 (37.19)	>300
L_3	70.73 (70.59)	5.30 (5.26)	—	300
$[CuL_3]\,Cl$	53.63 (54.18)	4.14 (4.04)	14.26 (15.08)	>300
$[UO_2L_3]\,NO_3$	34.82 (34.86)	2.52 (2.60)	36.44 (36.39)	>300
L_4	68.34 (68.57)	6.62 (6.66)	—	185
$[CuL_4]\,Cl$	52.76 (52.30)	5.15 (5.08)	52.85 (15.37)	>300

be considered as an evidence for the complex formation. The longest wavelength band of the schiff bases undergoes a red shift on complexation which can be explained on the basis of an easier intramolecular charge-transfer in the complexed ligand.

Stoichiometry of the complexes

The stoichiometry of the Cu(II) complexes with schiff bases L_1, L_2, L_3 and L_4 was ascertained by using the mole ratio and continuous variation methods[4,5]. The results revealed formation of two types of complexes of stoichiometries 1:1 and 1:2 for L_1, L_2 and L_3 but only 1:1 type for L_4 which may be attributed to steric factors.

Apparent formation constant

The apparent formation constants (K_f) of 1:2 complexes of L_1, L_2 and L_3 as well as 1:1 complexes of L_4 formed with Cu (II) were determined by the continuous variation method[6].

The K_f values for L_1-L_4 were 6.68×10^8, 27.10×10^8, 56.90×10^8 and 4.88×10^5 respectively. This indicates that the stability of Cu(II) complex depends largely on the molecular structure of the ligand used. The stability order is : $L_3 > L_2 > L_1 > L_4$.

This is in agreement with the complex forming tendency of these ligands since the basicity of nitrogen azomethine decreases as the electron donor character of the substituent R decreases. However, the unexpected low complex forming tendency of $L_4(C_6H_{11}$-cyclo) may be attributed to steric factors.

The molar conductance values of the isolated complexes (1:1 ratio) of L_1, L_2, L_3 and L_4 with Cu(II) in DMF have been found to be in the range 71-78 ohm^{-1} cm^2 mol^{-1} suggesting that these complexes behave as 1:1 electrolytes[7].

The tentative assignments of some of the important IR bands of the schiff bases under investigation and their metal complexes are presented here.

A sharp band at 3500 in the spectrum of the schiff base L_1 may be assigned to the stretching vibrations of free hydroxyl group of γ-chromone moiety. This band disappears on complex formation.

Two strong bands are observed at 2900 and 2500 for the schiff base L_1 and its complex can be attributed to H-bonded O-H of carboxyl group.

The broad band at 2900 in the schiff bases L_2, L_3 and L_4 can be assigned to the stretching vibrations of intramolecular hydrogen bonded $-OH$ existing in the molecule. This band disappeared in the IR spectra of the metal complexes[8]. A band at 1258-1260 in the spectra of the ligands may be ascribed to the phenolic C-O stretching vibration[9]. These bands are found in the region 1265-1280 in the spectra of the metal complexes. The $\nu(C=N)$ bands of the complexes occur at lower frequencies compared to the free ligand positions. This behaviour suggests that the ligands are coordinated to the central metal ions through the central azomethine nitrogen atom[10].

In conclusion, The schiff bases derived from γ-chromone are bonded to the metal ions as bidentate ligands. The two bonding sites are the oxygen of the deprotonated hydroxyl group of the γ-chromone moiety of azomethine nitrogen leading to a stable six-membered chelating ring.

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