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## Preparation of Some (Transition Metal-Flavylium Salt-Substitutes Chalcon) Complexes

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### Abstract

Three ligands were prepared and spectroscopic method and elemental analysis verified their structures. Two of the ligands L1 and L2 are flavylium salts and the third L3 is a chalcone. Reaction between transition metal salts and the ligands have synthesized two groups of new metal complexes. One group contains L1, L3 and the metal. The other group contains L2, L3 and the metal. These complexes have been identified by available spectroscopic tools (UV-visible ,IR and <sup>1</sup>HNMR), the C.H.N results confirmed the proposed structures. The experimental data disclosed that the complexes were coordinated by 6- the coordinate with mono-and bidentate ligands forming octahedral structure, in which L3 acts as monodentate and L1, L2 as bidentate ligands. The metal linked with L1 and L2 through the oxygen in ortho position in ring B, were as the linkage of the metal with L3 takes place through the oxygen of the carbonyl group.

**Keywords:** Flavylium salt , metal complexes, Synthesis, Chalcone.

### Introduction

In this research similar complexes prepared from different types of Flavylium salts than that used by Takeda et al (1). And chalcone instead Flavone. These newly prepared complexes similar to naturally occurring commelinin may have partial applications as trace elements enriching food additives, metals carrier drugs. The complexes may be also considered as food colorants synthesized from natural like

complexes, which are stable in wide pH-range. The discovery of commelinin justified the theory of Shibata et al (2). regarding the existence that the blue color of commelinin very stable in wide pH range and can be obtained by attacked molecular complexes between awobanin and Flavo commelinin without the intervention of Mg Hayashi and Takeda (3) reported at the ratio of (1:2:2) the experimental (molecular weight) obtained for the complex agree approximately with the theoretical value to Osawa and et al(4).

Hayashi and et al (5) extracted a blue anthocyanin (commelinin) from the petals and found it to contain Mg. Flavone like substance and awobanin (delphinidin 3-p-6-commaroyl glucoside-s-glucoside) Abathochromic shift have been observed in the UV spectrum by Asem (6) when Aluminum chloride was added which indicates the formation of Aluminum-cyanodin complexes. Many metal complexes with different type of anthocyanins have been prepared later by other workers (7,8). The structure of metal complexes depends upon the ratio of ligands to metal and to the Oxidation State of the metal ion. Evidence of the structure and bonding state of the commelinin metal was provided by ESR studies of Mg complexes, electrophoreses and IR spectra (9-11).

Goto (12) showed that the blue color of the commelinin is very stable in wide pH range on contrary to free anthocyanins, which is sensitive to pH variation.

In the present work commelinin like complexes have been prepared from different transition metal using Flavylium salts and chalcone instead of Flavone.

### **Materials and Methods:**

#### **Experimental**

#### **Instrumentation and Chemical:**

IR spectra were recorded Pye Unicam Sp. 3100 spectrophotometer, solid samples were measured as KBr disc. For UV measurement absolute methanol and ethanol were used as solvents. Atomic absorption spectra on Shimadzu AA-680. Rotary evaporator RE-120 Buchi. Gallenkamp (hot stage) determined M.P. Perkin Elmer B-240 was used for the metal analysis. BDH chemicals Ltd.-England, Fluka AG Buchs-Swaziland and Riedel Du Haen Germany supplied chemicals.

#### **General procedure for the Preparation of ligands:**

The flavylium chloride 2-(3,4-dihydroxyphenyl)chromenylium (L1) and (L2) were prepared as described in the literature (13).

**3-acetoxy-2-(3,4-dihydroxyphenyl)chromenylium (L1):**

Brownish red powder, m.p. 115-116 °C, yield 84%, IR (KBr disc) shows absorption at 3400  $\text{cm}^{-1}$  (OH), 1680  $\text{cm}^{-1}$  (C=O). UV-Vis shows max (EtOH) 494 nm, 274 nm.  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 5.13 (m, 6H, Ar-H) ppm; 9.31 (s, 1H, OH), 4.3 (s, 3H, OAC); C. H. N. analysis; C=68.5 (cal. 68.4), H=4.2 (cal. 3.9).

**3-chloro-2-(3,4-dihydroxyphenyl)chromenylium (L2):**

orange red powder. m.p. 125-126 °C, yield 82 %, IR (KBr disc) show adsorption at 3380  $\text{cm}^{-1}$  (-OH). UV-Vis shows max (EtOH) 482 nm, 259 nm and 224 nm.  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 5.11 (m, 6H, Ar-H) ppm; 9.22 (s, 1H, OH), C. H. N. analysis; C=58.18 (cal. 58.3), H=3.2 (cal. 2.6).

**The substituted chalcone (L3)** was prepared as described in the literature (14).

**(E)-3-(3-hydroxy-4-methoxyphenyl)-1-(4-hydroxyphenyl)prop-2-en-1-one(L3):**

yellow, m.p. 79 °C. yield 75%, IR (KBr disc) show at 1680  $\text{cm}^{-1}$  C=O), 1660 (C=O). UV-Vis show  $\lambda_{\text{max}}$  (EtOH) 323 nm, 351 nm and 328 nm ,  $^1\text{H}$  NMR (100 MHz,  $\text{CDCl}_3$ ): 6.35 (m, 6H, Ar-H) ppm; 9.3 (s, 1H, OH), 3.67 (ss, 1H,  $\text{OCH}_3$ ), C. H. N. analysis: C=84.0 (cal. 85.2), H=5.7 (cal 5.7).

**General procedure for the preparation of the complexes:**

0.2 mmoles from L1 ( $\text{C}_{16}\text{H}_{18}\text{O}_5$ ) or L2 ( $\text{C}_{15}\text{H}_{10}\text{O}_3$ ) was dissolved in MeOH (30 ml) then 0.1 mmole metal chlorides was added. The mixture refluxed for 20 min during this time the solution became dark. A solution of L3 ( $\text{C}_{16}\text{H}_{14}\text{O}_4$ ) in methanol (0.2 mmole) was poured to the dark solution. The resulting mixture was refluxed for 30 min. and the volume of the final mixture was reduced under vacuum. The crude products were purified by recrystallization from MeOH to give a powder, yield 82%. The complexes are listed in Tables (1,2).

**Results and discussion:**

The flavylium chlorides L1 and L2 have been synthesized according to the method devised by Robinson et al (13) through the condensation of O-hydroxy benzaldehyde with substituted acetophenone followed by ring closure with anhydrous hydrogen chloride. Claisen Schmidt condensation was chosen for the synthesis of chalcone (L3). The reaction partners are acetophenone and benzaldehyde, which condense in the presence of base in aqueous alcoholic solution

(14). All prepared ligands have been characterized by spectroscopic methods (UV-Vis, IR) and C. H. N. analysis.

#### **IR spectra:**

The IR spectra exhibit the expected absorption bands of the Flavylum chlorides (L1&L2) and chalcone (L3). In the case of the complexes, in which L3 is involved, the carbonyl stretching frequency decreases to the range ( $1650-1630\text{ cm}^{-1}$ ), due to the electron transfer from the ligand to the metal (9). The evidence for the linkage of the metal to ring B in the flavylum complexes depends on the observation that an intensive band at  $1620-1610\text{ cm}^{-1}$  was observed. This band is due to the conjugation between the C=C and C=O which occur during the chelation (9). The flavylum-metal complexes characteristic peak at  $1265\text{ cm}^{-1}$  for C-O (phenol). The -OH stretching band at  $3400\text{ cm}^{-1}$  appear broad with dimensioned intensity with, which is indicative for complex information (15). This finding has lead us to the conclusion that the metal was linked to ring B in each of the to flavylum ligands Table (2) .

#### **UV-Vis spectra:**

The UV-vis spectra of the complexes expected differences in the position of the absorption bands between the ligands and the related complexes, which are due to the coordination between the ligands and the transition metals. Appearance of new absorption maxima is considered as a hint for the formation of complexes. The bathochromic shift in band I upon coordination is due to the electronic transition ( $n \rightarrow \pi^*$ ) of the lone pair of electrons of the hydroxyl group in the complex Table (2). Band III, which caused by the transition ( $\pi \rightarrow \pi^*$ ) of the aromatic ring, exhibit absorption maxima at 285 nm. This measured wavelength reflect the effect of substitution by auxochromes (hydroxyl and methoxyl group). Replacement of chloride in L1 by acetate group caused a bathochromic shift in bands I, II, and III of the complexes (16).

Tables (2) show that the complexes of Cr, Mo, and W are deeper in color and exhibit  $\lambda_{\text{max}}$  at considerable longer wavelength , this observation due to the occurrence of charge transfer phenomena in trivalent metal complexes.

**$^1\text{H}$  NMR Spectra:** The  $^1\text{H}$  NMR spectral data of ligands (L1,L2 and L3) are provided in the experimental part. The  $^1\text{H}$ NMR spectra of the ligands (L1 and L2), show signals between  $\delta$  6.5-7.0 due to aromatic ring .

## Conductivity Measurements

The measurements of the molar electrical conductivity of the complexes in methanol are indicated in Tables (1). These results clearly show values for the molar conductivity of the complexes of trivalent metals of group VIB namely (Cr, Mo, W) show high values for the molar conductivity meaning that these complexes are electrolyte (i.e. ionic).

Molar conductivity (high and low) of complexes are commonly observed depending upon the properties of the metal and the ligands and can also be effected by the presence of unpaired electron in the  $t_{2g}$  eg orbitals of an octahedrally coordinated elements.

In high spin configuration of a high  $\Delta M$  value are obtained, while in case of ( $t_{2g}^6$ ,  $eg^4$ ) a low complexes (Cr, Mo, W) ( $3d^3$ ,  $4d^3$ ,  $5d^2$ ) ( $t_{2g} eg^0$ ,  $t_{2g}^3 eg^0$ ,  $t_{2g}^2 eg^0$ ),  $\Delta M$  increased periodically due to complexation through d orbital (3d).

## pH Effect Study

The complex was dissolved in methanol and buffer solution was added, a hypsochromic shift was noticed in case of decreasing pH as shown in Fig.(1). Below pH2 (strong acidic medium) the complexes are unstable, but a stable complex has been observed in higher pH-values (pH=8). In contrary the anthocynin (free ligand) is very sensitive to high pH-values. It degraded at pH above (6).

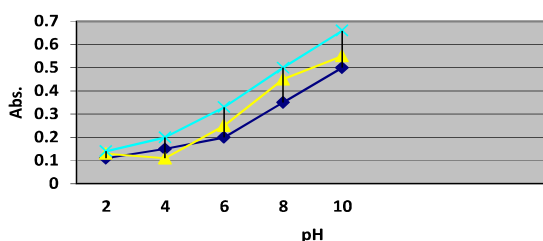
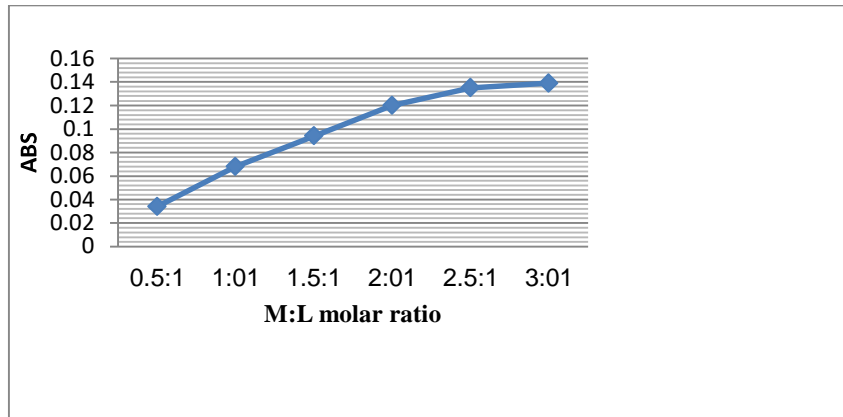


Fig. 1: UV-Vis. Spectra of complexes at different pH values.

## The Molar – Ratio Study

The mole-ratio (4) is one of the most common spectrophotometric techniques employed in complex studies. It is an available tool for elucidating the composition of complex in solution. Molar-ratio (2:1) of Falvylum ligand ( $L_1$ ) to the metal (Cr)

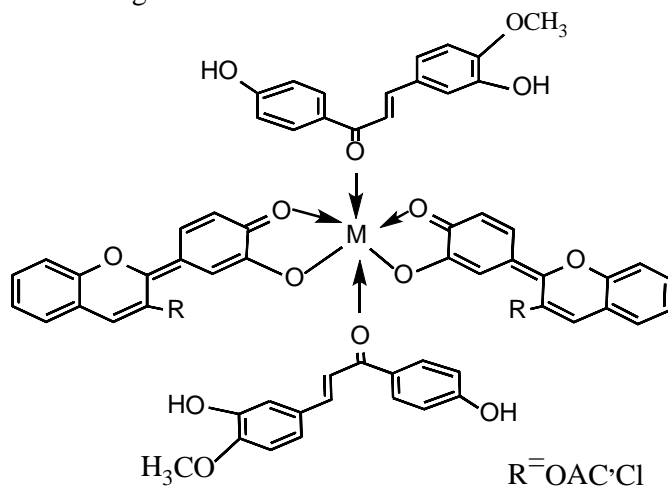
is effected by the absorption due to change in coordinate ion of the ligand complexes. Another molar-ratios (2:2:1, L<sub>3</sub>-L<sub>1</sub>-M) was also obtained, when chalcone L<sub>3</sub> was added to the above mixture as shown in Table (3) .



**Fig. 2: Plot of the Cr(III) complex formation**

**The proposed structure :**

According to the results obtained from (IR, UV/visible, <sup>1</sup>HNMR, molar ratio, molar conductivity, atomic absorption) measurements for the prepared complexes, the proposed molecular structure of the complexes has an octahedral structure as shown in Fig.3 .



**Fig.3: The proposed structure of complexes where M= Cr(III), Mo(V) and W(VI).**

**Table(1): Physical characterization ,analytical and Molar Conductance data of the compounds**

Compound	Yield%	Colour	$\Delta M/Scm^2 mol^{-1}$ In DMSO	m.p °C	Metal analysis (% found) % cal
[Cr(L1) <sub>2</sub> (L3) <sub>2</sub> ]Cl	81	Purple-red	98	185-187	(4.36) 4.39
[Mo(L1) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>3</sub>	83	Purple-blue	226	170-172	(7.80) 7.82
[W(L1) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>4</sub>	85	Purple-blue	284	165-167	(13.94) 13.98
[Cr(L2) <sub>2</sub> (L3) <sub>2</sub> ]Cl	80	Purple-violet	115	220-222	(4.56) 4.58
[Mo(L2) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>3</sub>	82	Purple	244	180-182	(8.12) 8.13
[W(L2) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>4</sub>	85	brown	366	183-185	(14.47) 14.50

**Table(2): Infrared and UV-Visible Spectra data of the prepared compounds**

Compound	UV-Visible Spectra ( nm)	IR Spectra (Cm <sup>-1</sup> )		
		$\nu^{(C=O)}$	$\nu^{(C-O)}$	$\nu^{(M-O)}$
[Cr(L1) <sub>2</sub> (L3) <sub>2</sub> ]Cl	302,444,526	1650	1210	533 m
[Mo(L1) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>3</sub>	301,423,549	1635	1220	530 w
[W(L1) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>4</sub>	306,425,522	1645	1235	535 m
[Cr(L2) <sub>2</sub> (L3) <sub>2</sub> ]Cl	297,303,558	1640	1230	540 m
[Mo(L2) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>3</sub>	299,545	1625	1220	525 m
[W(L2) <sub>2</sub> (L3) <sub>2</sub> ]Cl <sub>4</sub>	297,518	1630	1260	545 w

**Table(3): Molar-Ratio of (L1) to (Cr) with UV-Visible Spectra data.**

Molar-Ratio of (L1) to (Cr)	Max (nm)	$\epsilon Mol^{-1} cm^2$	Color solution
0.5:1	562	0.034	Purple-Blue
1:1	569	0.068	=
1.5:1	565	0.094	=
2:1	563	0.120	=
2.5:1	562	0.135	=
3:1	562	0.139	=



## Conclusion

The available experimental data suggest that the prepared L1 and L2 possesses two coordinating sites and L3 as monodentate ligand. Physical and spectroscopic characterization of the complexes revealed that the OH group of the flavylum and carbonyl group of chalcone were involved in the coordination and that the Cr(III) , Mo(V) and W(VI) had octahedral geometry.

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