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Preparation of Some (Transition Metal-Flavylium Salt-Flavon) Complexes

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Abstract. Three ligands were prepared, spectroscopic method and elemental analysis verified their structures. The L₁ and L₂ ligands are flavylium salts while the third one L₃ is a Flavon. The reactions between transition metal salts and the ligands have synthesized two groups of new metal complexes, one group contains L₁, L₃ coordinated with the metal ion. The other group contains L₂, L₃ and the metal. These complexes have been identified by available spectroscopic tools (UV-Visible and IR), the C.H.N results confirmed the proposed structures. The experimental data disclosed that the complexes were coordinated by 6th 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 the linkage of the metal with L₃ takes place through the oxygen of the carbonyl group.

Keywords: Flavylium salt, metal complexes, Synthesis, Flavon.

Introduction

The magnesium commelinin complexes was synthesized by Osawa (1) et al. while Takeda (2) et al prepared these complexes from their compounds Anthocyanin, Flavone and Magnesium. In the present work similar complexes were prepared from different type of Flavylium salt than that used Takeda.

Hayashi (3) and Mitsui et al (4) extracted a blue anthocyanin (commelinin) from the petals and found it to contain Mg, Flavone like substance and awobanin (delphindin 3-p-6-commaroyl glucoside-s-glucoside).

Takeda and Hayashi (5) reported that anthocyanin and Flavone give stable metal complexes with bivalent and trivalent metal ions under suitable conditions. The structure of the metal complexes depends on the ratio of ligand and or Oxidation State of metal ion the bivalent or trivalent character of the metal ion. Hayashi and Mitsui et al (6) 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 (7) 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 (8, 9). 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 (10, 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 Flavone.

Materials and Methods:

Experimental

Instrumentation and Chemical:

Conductivity was determined with conductivity meter type Jeneway 4070 with cell constant 0.1 while pH was determined with ORION model SA720. 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. Flavone (Kampferol) (L_3) was supplied from 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 (L_1) and (L_2) were prepared according to the procedure described in the literature (13).

3-acetoxy-2-(3,4-dihydroxyphenyl)chromenylium (L_1):

Brownish red powder, m.p. 115-116 °C, yield 84%, IR (KBr disc) shows absorption at 3400 cm^{-1} (OH), 1680 cm^{-1} (C=O). UV-Vis shows max (EtOH) at 494 and 274 nm. ^1H NMR (100 MHz, CDCl_3): 5.13 (m, 6H, Ar-H), 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 (L_2):

orange red powder. m.p. 125-126 °C, yield 82 %, IR (KBr disc) shows adsorption at 3380 cm^{-1} (-OH). UV-Vis shows max (EtOH) at 482, 259 and 224 nm. ^1H NMR (100 MHz, CDCl_3): 5.11 (m, 6H, Ar-H), 9.22 (s, 1H, OH); C. H. N. analysis; C=58.18 (cal. 58.3), H=3.2 (cal. 2.6).

2-(3,4-dimethoxyphenyl)-3,7-dimethoxy-4H-chromen-4-one (L_2):

Yellow powder. m. p. 140 °C, yield 82 %, IR (KBr disc) show adsorption at 1670 cm^{-1} (-C=O). UV-Vis shows max (EtOH) at 328, 351 and 381 nm, C. H. N. analysis; C=66.63 (cal. 66.66), H=5.25 (cal. 5.30).

General procedure for the preparation of the complexes:

0.1 mmole metal chloride was added to 0.2 mmoles from L₁ (C₁₆H₁₈O₅) or L₂ (C₁₅H₁₀O₃) in MeOH (30 ml). The mixture was refluxed for 20 min, during this time the solution became dark. A solution of L₃ (C₁₆H₁₄O₄) in methanol (0.2 mmole) was poured to the mixture of reaction. The resulting mixture was refluxed for 30 min. The volume of the final mixture was reduced under vacuum. The crude products were purified by recrystallization from methanol 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 prepared according to the general method devised by Robinson *et al* (13) by 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.

Ft-IR spectra:

IR spectra show the expected absorption bands of the Flavylium 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 cm⁻¹) and this because of the electron transfer from the ligand to the metal (9). The evidence for the linkage of the metal to ring B in the flavylium complexes depends on the observation that an intensive band at 1620-1610 cm⁻¹ was detected. This band is observed due to the conjugation between the C=C and C=O band which occur through the chelation (9). The flavylium-metal complexes characteristic peak at 1265 cm⁻¹ for C-O (phenol). The -OH stretching band at 3400 cm⁻¹ appear broad with dimensioned intensity with, which is indicative for complex information (15). This finding has led us to the assumption that the metal was linked to ring B in each of the flavylium ligands Table (2).

UV-Vis spectra:

UV-Vis spectra of the complexes expected differences in the position of the absorption bands between the ligands and the related complexes, and this due to the coordination between the ligands and the transition metals. The presence of the new absorption maxima is considered as a clue of the formation of complexes. The bathochromic shift in band I upon coordination is due to the electronic transition (n → *) of the lone pair of electrons of the hydroxyl group in the complex Table (3).

Band III, which caused by the transition (→ *) of the aromatic ring, exhibit absorption maxima at 285 nm. These wavelengths 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).

Conductivity Measurements

Molar electrical conductivity of the complexes in methanol measurement are shown in Table (1). These results obviously show the values for the molar conductivity of the complexes of bivalent metals of (Mn, Zn and Cd) show low values for the molar conductivity meaning that these complexes are non-electrolyte. (17-18).

pH Effect Study

Buffer solution was added to the complex mixture in methanol, a hypsochromic shift was observed in case of decreasing pH as shown in Fig. (1). below pH=2 (strong acidic medium) the complexes are unstable, nevertheless a stable complex has been observed in higher pH-values (pH=8). (19). In opposing the anthocyanin (free ligand) is very sensitive to high pH-values. It degrades at pH above (6).

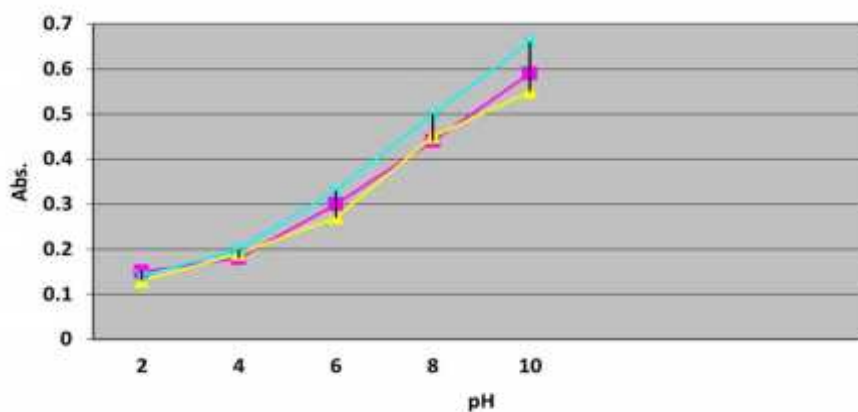
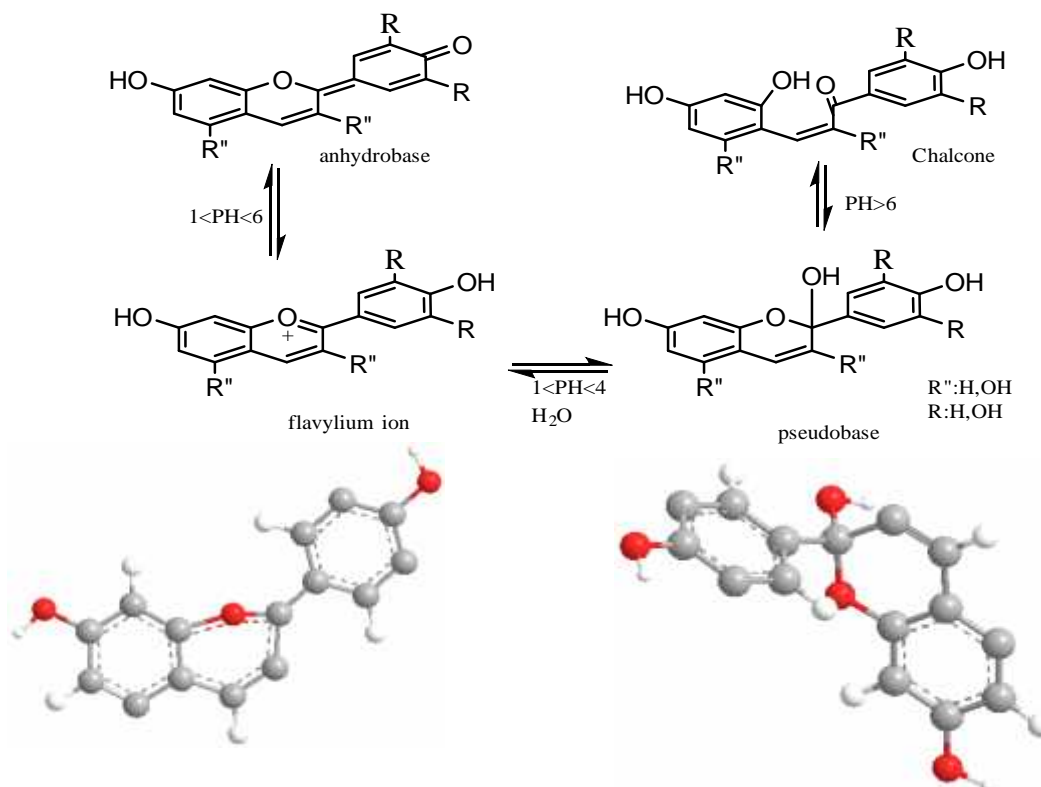


Figure. 1: UV-Vis. Spectra of complexes at different pH values.



Scheme 1: structure change of anthocyanin with different pH values.
Molar – Ratio Study

The mole-ratio (4) is one of the most common spectrophotometric techniques used in complex studies. It is an accessible tool for explaining the composition of complex in solution. Molar-ratio (2:1) of Falvylium ligand (L_1) to the metal (Mn) is effected by the absorption due to change in coordinate ion of the ligand complexes. Another molar-ratios (2:2:1, L_3-L_1-M) was also attained, when Flavon L_3 was added to the mixture above as shown in Figure .(2).

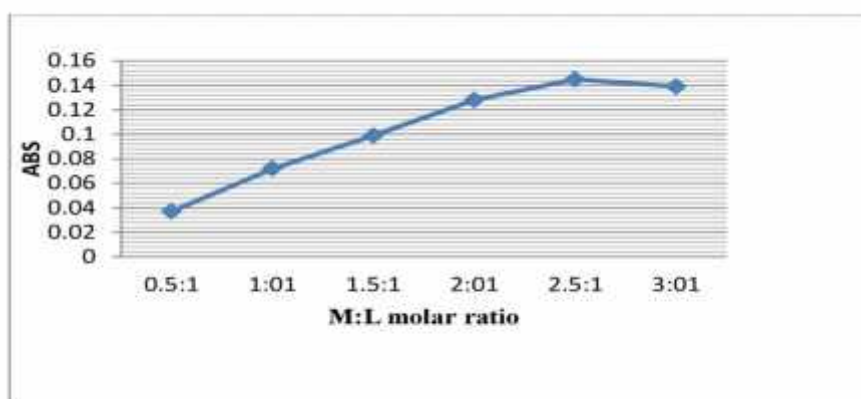


Figure. 2: Scheme of the Mn(II) complex

Proposed structure:

Proposed molecular structure of the complexes has an octahedral structure as shown in Figure..3,Table 3., this assumption has been reached according to the results obtained from (IR, UV/visible, molar ratio, molar conductivity, atomic absorption) measurements for the prepared complexes.

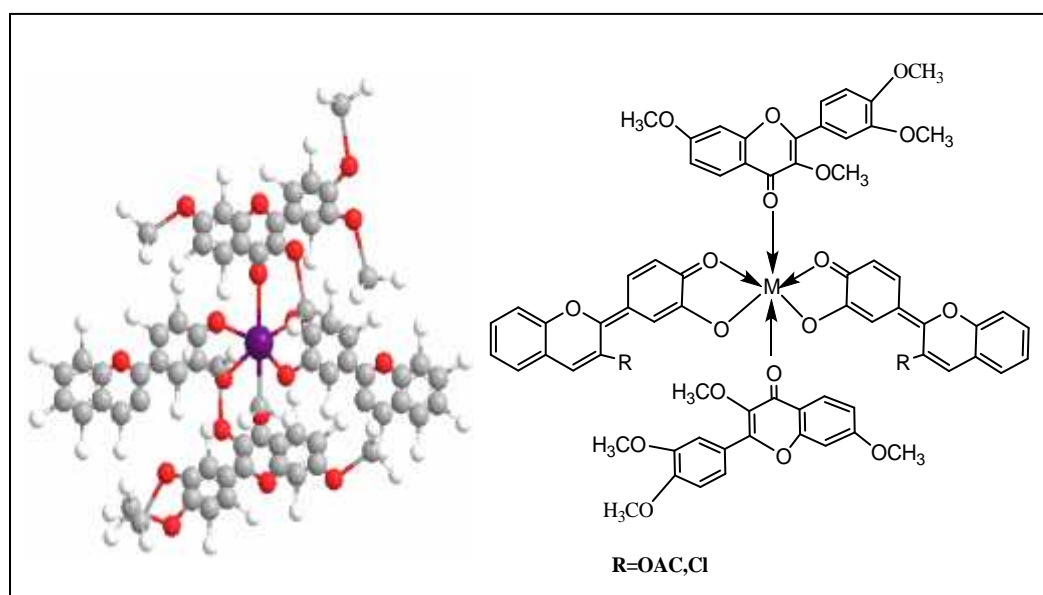


Figure.3: The proposed structure of complexes where $M= Mn(II), Zn(II)$ and $Cd(II)$.

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

Compound	Yield%	Colour	M/Scm ² mol ⁻¹ In DMSO	m.p C	Metal analysis (% found) % cal
[Mn(L1) ₂ (L3) ₂]	79	brown	9	160-162	(4.10) 4.13
[Zn(L1) ₂ (L3) ₂]	85	Pale-red	7	150-152	(4.84) 4.88
[Cd(L1) ₂ (L3) ₂]	80	Pale-red	11	140-142	(8.07) 8.10
[Mn(L2) ₂ (L3) ₂]	82	brown	10	125-127	(4.26) 4.28
[Zn(L2) ₂ (L3) ₂]	72	Pale-brown	8	135-137	(5.02) 5.06
[Cd(L2) ₂ (L3) ₂]	77	Pale-brown	12	183-185	(8.34) 8.39

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

Compound	IR Spectra (Cm ⁻¹)		
	(C=O)	(C-O)	(M-O)
[Mn(L1) ₂ (L3) ₂]	1655	1230	525 m
[Zn(L1) ₂ (L3) ₂]	1645	1240	535 w
[Cd(L1) ₂ (L3) ₂]	1640	1245	530 m
[Mn(L2) ₂ (L3) ₂]	1630	1220	545 m
[Zn(L2) ₂ (L3) ₂]	1645	1190	540 m
[Cd(L2) ₂ (L3) ₂]	1620	1215	520 w

Table 3: Electronic Spectral data, of the mixed ligands complexes

Compound	max (nm)	(cm ⁻¹)	Assignments
[Mn(L1) ₂ (L3) ₂]	329	30395	Charge transfer ⁶ A _{1g} (^S) ⁴ T _{1g} (3) ⁶ A _{1g} (^S) ⁴ T _{2g} (2)
	404	24752	
	523	19120	
[Zn(L1) ₂ (L3) ₂]	283	35335	Charge transfer
	308	32467	Charge transfer
	429	23310	π→π*
[Cd(L1) ₂ (L3) ₂]	285	35087	Charge transfer
	300	33333	Charge transfer
	522	19157	π→π*
[Mn(L2) ₂ (L3) ₂]	297	33670	Charge transfer ⁶ A _{1g} (^S) ⁴ T _{1g} (3) ⁶ A _{1g} (^S) ⁴ T _{2g} (2)
	304	32894	
	515	19417	
[Zn (L2) ₂ (L3) ₂]	286	34965	Charge transfer
	330	30303	Charge transfer
	520	19230	π→π*
[Cd(L2) ₂ (L3) ₂]	287	34843	Charge transfer
	305	32786	Charge transfer
	535	18691	π→π*

Table (4.4b). Molar Absorbency of Prepared Complex to Determined Molar Ratio.

-	(1) Mn : L1
M	2
L	0.25
1	0.088
2	0.149
3	0.162
4	0.169
5	0.181

Conclusion

The presented experimental data recommend that the prepared L₁ and L₂ possess 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 flavon were involved in the coordination and that the Mn (II), Co (II) and Ni (II) had octahedral geometry.

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