

COMPLEXES OF 3-ACETYL-6-METHYL-2H PYRAN-2,4-(3H)- DIONE

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INTRODUCTION

All the complexes of ligand 3-acetyl-6-methyl-2H-pyran-2,4-(3H) –dione with metal (II) ions (Cr^{2+} , Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) are anhydrous as also supported from analytical and spectral studies. All these complexes are stable upto 150°C . The complexes are generally soluble in water and ethanol but sparingly soluble in DMSO and DMF and insoluble in benzene, ether and acetone.

All these complexes with Cr^{2+} , Mn^{2+} and Fe^{2+} were found to be non-electrolytic in nature. The molar conductance of these complexes have been recorded in nitrobenzene in digital systonic conductivity meter-304 and are given in following table.

Complexes	Colour	M.Pt. ($^\circ\text{C}$)	Soluble	μ_{eff}	Conductance ($\Omega\text{-1cm}^2\text{mol}^{-1}$)
$[\text{CrL}(\text{H}_2\text{O})_2]$	Red	158	In benzene and ethanol	3.48	4.02
$[\text{MnL}(\text{H}_2\text{O})_2]$	Light yellow	172	In benzene and ethanol	3.60	4.50
$[\text{FeL}(\text{H}_2\text{O})_2]$	Brick red	198	In benzene and ethanol	1.61	3.91
$[\text{Co}(\text{L})]$	Orange	182	In benzene and ethanol	1.71	2.21
$[\text{Ni}(\text{L})]$	Green	216	In benzene and ethanol	Diamagnetic	3.78
$[\text{Cu}(\text{L})]$	Light Green	160	In benzene and ethanol	1.73	3.94
$[\text{Zn}(\text{L})]$	Colourless	140	In benzene and ethanol	Diamagnetic	4.01

EXPLANATION :

The IR spectral data and assignment of bands of transition metal (II) complexes are given in following table.

Compound	$\nu_{(\text{CO})}$ lactone	$\nu_{(\text{C}=\text{N})}$	$\nu_{(\text{CO})}$ α , β - unsatura- ted	$\nu_{(\text{CO})}$	$\nu_{(\text{NH})}$	$\nu_{(\text{MO})}$	$\nu_{(\text{MN})}$	$\nu_{(\text{H}_2\text{O})}$
AMPD	1780	1600	1685	1620	3250	---	---	770
[CrL(H ₂ O) ₂]	1778	1590	1640	1625	3248	454	605	780
[MnL(H ₂ O) ₂]	1775	1585	1665	1615	3245	430	550	750
[FeL(H ₂ O) ₂]	1780	1540	1630	1618	3245	425	590	810
[Co(L)]	1775	1560	1650	1620	3253	450	565	835
[Ni(L)]	1775	1565	1660	1620	3250	455	575	870
[Cu(L)]	1777	1550	1645	1615	3250	445	580	845
[Zn(L)]	1778	1545	1665	1615	3248	440	585	860

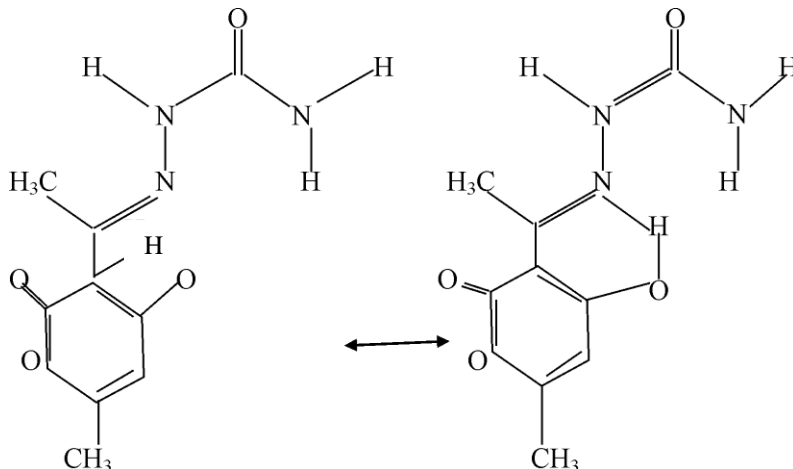
The ligand 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione has many donor sites such as α , β unsaturated carbonyl group, $-\text{NH}$ group, $\text{C}=\text{N}$ group, carbonyl amide group and carbonyl group. However, the infrared frequencies in the ligand 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione associated with the α , β unsaturated carbonyl group and $\text{C}=\text{N}$ group have been influenced on complex formation with Metal (II) ions.

The infrared spectra of complexes of ligand 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione with Metal (II) ions and the ligand 3-acetyl-6-methyl-2H-pyran-2, 4-(3H)-dione were recorded in the range of 400 – 4000 cm^{-1} . The highest frequency of the bands of the ligand at $\sim 1600 \text{ cm}^{-1}$ can be assigned to the ν_{CN} vibration. This band is shifted to lower frequency 1590 – 1540 cm^{-1} on complexation indicating the involvement of $-\text{C}=\text{N}$ group in complex formation. The shift of ν_{CO} of α , β unsaturated carbonyl group to lower frequency from 1685 to 1665 – 1630 cm^{-1} on complexation suggests coordination through $-\text{C}=\text{N}$ group. The absence of a band at 2885 cm^{-1} characteristics of 3° hydrogen in all complexes, suggest that 6, 7-enolization takes place before coordination with metal ions. The occurrence of bands at 605 – 550 cm^{-1} (M–N) and 455 – 430 cm^{-1} (M–O) proves the bonding of nitrogen and oxygen to the metal ions. The spectra of the complexes exhibited a broad band about 3600 – 3400 cm^{-1} which may be due to water molecules. The presence of a band in the range of 870 – 750 cm^{-1} indicates the coordinated water molecules in the complexes.

Thus on account of infrared spectral properties we can say that 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione acts as quadridentate ligand.

In the spectra of the Cr^{2+} , Mn^{2+} and Fe^{2+} complex there are an additional band observed at $\sim 720 - 705 \text{ cm}^{-1}$. These bands can be assigned to the coordinated chloride ion.

The singlet peak at $\delta = 4.70$ ppm of 3° hydrogen of the lactone ring is disappeared in all complexes of M^{2+} ions with ligand 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione. It may be due to the enolization of the carbonyl group before the complexation as :



The spectral data for the solution of transition metal (M^{2+}) ion complexes with ligand 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione investigated in acetonitrile are presented in the following table.

CONCLUSION :

TABLE : Electronic spectral data of 3-acetyl-6-methyl-2H-pyran-2,4-(3H)-dione with M^{2+} ions in cm^{-1} .

M^{2+} complexes	Spectral bands (in cm^{-1})	Transitions
$[\text{CrL}(\text{H}_2\text{O})_2]$	14,000	${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$
$[\text{MnL}(\text{H}_2\text{O})_2]$	18590, 22800, 24850, 24910, 25250, 27850, 29550, and 32550	${}^6\text{E}_{1g} \rightarrow {}^4\text{T}_{1g}, {}^4\text{T}_{2g}$ (G) ${}^4\text{E}_g, {}^4\text{A}_{1g}$ and ${}^4\text{T}_{2g}$ (D)
$[\text{FeL}(\text{H}_2\text{O})_2]$	10,000	${}^5\text{T}_{2g} \rightarrow {}^5\text{E}_g$
$[\text{Co}(\text{L})]$	8000, 19,600 and 21,600	${}^4\text{T}_{1g} \rightarrow {}^4\text{T}_{2g}, {}^4\text{T}_{1g}$ and ${}^4\text{A}_{2g}$
$[\text{Ni}(\text{L})]$	8,700, 14,500 and 25,300	${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}, {}^3\text{T}_{1g}$ (F) and ${}^3\text{T}_{1g}$ (P)
$[\text{Cu}(\text{L})]$	12,000	${}^2\text{E}_{2g} \rightarrow {}^2\text{T}_{2g}$

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