



## Transition Metal complexes of 3-[3-(4-chloro-phenyl)-4-hydroxy-6-methyl-Pyran-2-one]- synthesis, Spectral, Thermal and Fungicidal Study

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### ABSTRACT

Transition metal complexes containing bidentate O,O donor ligand, i.e. 3-[3-(4-chlorophenyl)-4-hydroxy-6-methyl-pyran 2-one derived from 3-acetyl-6-methyl-pyran-2,4(3H)-dione (dehydroacetic acid) and p-chlorobenzaldehyde, have been synthesized and characterized by elemental analyses, conductometry, thermal analysis, magnetic, IR, UV-Vis and fungicidal study. From the analytical and thermal data, the stoichiometry of the complexes has been found to be 1:2 (metal : ligand). Octahedral geometries for all complexes are proposed except Pd(II), which is square planar. The Ligand and their metal complexes have been screened in vitro for their antifungal activities against *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum*.

**Key words:** Chalcones, dehydroacetic acid, transition metal complexes and antifungal study

### INTRODUCTION

Unsaturated ketones are gaining importance as reactive intermediates and are used to obtain the biologically important heterocycles. This class of compounds exhibits wide spectrum of pharmaceutical and biological properties<sup>1-3</sup>. It has been shown that the prime cause of these activities, is the presence of  $\alpha$ ,  $\beta$  unsaturated ketonic system<sup>4</sup>. The fungal and bacterial activities of such unsaturated ketones are also enhanced by the substitution of halogen groups<sup>5</sup>. It is well known from the literature that dehydroacetic acid (3-acetyl-6-methyl-2H-pyran 2,4(3H)-dione), a biologically

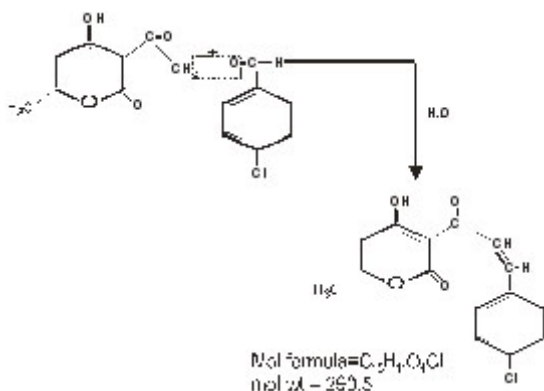
active compound has shown to have good antibiotic and antifungal effects, besides showing strong antiseptic properties<sup>6-8</sup>.

### EXPERIMENTAL

Dehydroacetic acid and p-chlorobenzaldehyde used for the preparation of ligand were from Merck and Aldrich respectively metal salts used for the complex preparation were from BDH. The carbon, hydrogen and sulphur content in each sample were measured on Perkin-Elmer (2400) CHNS analyzer. The UV-Vis Spectra of the complexes were recorded on a Shimadzu UV-1601

spectra photometer. Magnetic susceptibility measurements of complexes were carried out using a Gouy balance at room temperature and  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as calibrant. Molar conductivity was measured on an Elico CM180 conductivity meter with a dip-type cell using  $10^{-3}\text{M}$  solution of complexes in DMF.

IR spectra ( $\nu_{\text{max}}$ ,  $\text{cm}^{-1}$ ) were recorded on Shimadzu 820 IPC. FT-IR spectrophotometer in KBr discs. The solvents used were ethanol (distilled), methanol, benzene, chloroform, T.H.F, DMSO and DMF. All the solvents were of highest purity.



### Preparation of the Ligand

A solution of 3.4g (0.02mol) of dehydroacetic acid, 10 drops of piperidine and 2.8g (0.02mol) of p-chlorobenzaldehyde in 25ml chloroform was refluxed for 8-10h. 10ml of the chloroform water azeotrope mixture was separated by distillation. Crystals of product were separated on slow evaporation of the remaining chloroform and recrystallised from ethanol. The purity of the sample was checked by T.L.C.

## RESULTS AND DISCUSSION

The elemental analyses show 1:2 (metal : ligand) stoichiometry for all the complexes. The analytical data of the ligand and the complexes are given in Table 1. It corresponds well with the general formula  $[\text{ML}_2(\text{H}_2\text{O})_2]$ , where M = Ti(III), V(III), Mo(V),  $\text{MoO}_2$ (VI),  $\text{UO}_2$ (VI), Ru(III), Ru(II) and Pd(II). Except Pd(III) where nowaker molecule is present.

### I.R. Spectra

The IR spectrum of the ligands shows bands at 3112, 1715, 1676 and  $1232\text{ cm}^{-1}$  assignable to  $\nu_{\text{OH}}$  (intramolecular hydrogen bonded),  $\nu_{\text{C=O}}$  (lactone carbonyl),  $\nu_{\text{C=O}}$  (acetyl carbonyl) and  $\nu_{\text{C-O}}$  (phenolic) respectively<sup>9</sup>. In the IR spectra of all the metal chelates, no band is observed in the region  $3112\text{ cm}^{-1}$ , suggesting the cleavage of intramolecularly hydrogen bonded OH and participation of oxygen of phenolic group in coordination<sup>10</sup>.

This is supported by an upward shift in  $\nu_{\text{C-O}}$  (phenolic)<sup>10</sup> to the extent  $30\text{-}60\text{ cm}^{-1}$ . The  $\nu_{\text{C=O}}$  (acetyl carbonyl) is shifted to the lower energy with respect to the free ligand, suggesting the participation of  $\nu_{\text{C=O}}$  (acetyl-carbonyl) in coordination<sup>11</sup>. In the IR spectra of the chelates a broad trough appeared around  $3500\text{-}3200\text{ cm}^{-1}$  which is due to OH of coordinated water. This is supported by the presence of non ligand band<sup>12</sup> around  $820\text{-}840\text{ cm}^{-1}$ . The presence of new bands in the region  $600\text{-}450\text{ cm}^{-1}$  can be assigned to M-O vibrations<sup>13</sup>.

A very strong band found at  $950\text{ cm}^{-1}$  in the spectra of Mo(V) complexes corresponds to Mo=O stretching frequency. The strong bands exhibited by the dioxomolybdenum(VI) complexes in the region  $950\text{-}970$  and  $910\text{ cm}^{-1}$  are attributed to  $\nu_{\text{sym}}(\text{O}=\text{Mo}=\text{O})$  and  $\nu_{\text{asym}}(\text{O}=\text{Mo}=\text{O})$ , respectively of cis- $\text{MoO}_2$  configuration due to the maximum utilization of the available  $\pi$  orbitals for bonding with the oxogroups<sup>14</sup>. The complex trans- $[\text{UO}_2]$  shows a strong IR band at  $920\text{ cm}^{-1}$  assigned to as( $\text{UO}_2$ ) of the trans-O-U-O group<sup>15</sup>.

### Magnetic Moment and Electronic Absorption Spectra

The Ti(III) complex shows magnetic moment of 1.96 B.M. for one unpaired electron. The higher value may be due to the orbital contribution. The electronic spectra of the chelate shows a single broad band has been observed at  $19230\text{ cm}^{-1}$ , for Ti(III) complex derived from the transition  ${}^2T_{2g} \rightarrow {}^2E_g$  for an octahedral symmetry<sup>16</sup>. This band is unsymmetrical in shape and is indeed made up to two closely shaped bands. The second band appears as a hump and which is due to the presence of Jahn Teller distortion in the complex.

Table 1: Characterisation of ligand & metal chelates prepared  
The molar conductance and characteristic IR frequencies of the ligand and its metal complexes.

S.NO.	FORMULA OF THE LIGAND & COMPLEX & Molecular wt.	COLOUR	Decom temp (°C)	Elemental Analysis				IR frequencies (in cm <sup>-1</sup> )						Electrolytetype
				%C	%H	%Cl	%M	vOH	vC=O (lactone)	vC=O (acetylcarbonyl)	vC-O (phenolic)	vM-O / vM-N		
1	C <sub>15</sub> H <sub>10</sub> O <sub>4</sub> Cl Mol.Wt.=290.5	Light Orange	161	61.90 (61.96)	3.41 (3.44)	12.01 (12.22)	—	3112(b)	1715(m)	1676(m)	1232(s)	—	—	
2	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> Ti]Cl Mol. Wt.=698.367	Yellow	201	51.14 (51.54)	3.27 (3.43)	15.13 (15.24)	6.49 (6.85)	3378(b)	1714(m)	1645(m)	1282(m)	530 425	1:1	
3	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> V]Cl Mol.Wt.=701.441	Light yellow	203	51.11 (51.32)	3.23 (3.42)	15.01 (15.18)	7.05 (7.26)	3372(b)	1715(m)	1648(m)	1283(m)	535 410	1:1	
4	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> MoO]Cl Mol. Wt.=762.44	Yellow	269	47.10 (47.21)	3.10 (3.14)	13.32 (13.96)	12.14 (12.58)	3375(b)	1713(m)	1646(m)	1285(m)	540 430	1:1	
5	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> MoO <sub>2</sub> ] Mol. Wt.=742.94	Cream	278	48.19 (48.45)	3.12 (3.23)	9.25 (9.55)	12.41 (12.91)	3373(b)	1714(m)	1640(m)	1284(m)	530 410	Non electrolyte	
6	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> UO <sub>2</sub> ] Mol. Wt.=885.03	White	281	40.51 (40.67)	2.37 (2.71)	7.89 (8.02)	26.18 (26.89)	3377(b)	1715(m)	1642(m)	1285(m)	540 425	Non electrolyte	
7	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> Ru(III)]Cl Mol. Wt.=751.57	Green	261	47.39 (47.89)	3.01 (3.19)	14.03 (14.17)	13.13 (13.44)	3374(b)	1715(m)	1645(m)	1282(m)	535 415	1:1	
8	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> Ru(II)] Mol. Wt.=716.07	Light green	256	50.17 (50.27)	3.15 (3.35)	9.41 (9.91)	14.07 (14.11)	3371(b)	1714(m)	1641(m)	1282(m)	535 410	Non electrolyte	
9	[C <sub>30</sub> H <sub>24</sub> O <sub>10</sub> Cl <sub>2</sub> Pd] Mol. Wt.=721.42	White	238	49.64 (49.90)	3.17 (3.32)	9.53 (9.84)	14.21 (14.75)	3376(b)	1715(m)	1642(m)	1285(m)	540 425	Non electrolyte	

Figures in parenthesis are calculated values.

The magnetic moment of the Vanadium(III) complex is 2.94 B.M. which is nearly equal to the calculated value for d2 system like V(III). The electronic spectrum of V(III) complex exhibited a band at 16000cm<sup>-1</sup> with a shoulder at 20500cm<sup>-1</sup>. The low energy band has been assigned to  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  and the high energy band to  ${}^2T_{1g} \rightarrow {}^3T_{1g}(p)$  transitions respectively. These bands are characteristic of octahedral geometry<sup>17</sup>.

The electronic spectrum of oxomolybdenum (V) complex suggested that the complex may be considered as octahedral with a strong tetragonal distortion resulting from Mo=O bond<sup>18</sup>. The spectrum exhibited three distinct absorption bands in the ligand field region. The low intensity band at 13000cm<sup>-1</sup> in the long wavelength region is possibly due to first crystal field transition  ${}^2B_2 \rightarrow {}^2E$  ( $d_{xy}, d_{yz}, d_{zx}$ ). The second crystal field transition at 19000 cm<sup>-1</sup> is assignable to  ${}^2B_2 \rightarrow B_1$  ( $d_{xy} \rightarrow dx^2-y^2$ ). The third peak was observed at 30000 assignable to  ${}^2B_2 \rightarrow {}^2A_1$  ( $d_{xy}-dz^2$ ).

The electronic spectrum of MoO<sub>2</sub>(VI) complex has a single band due to charge transfer transition.

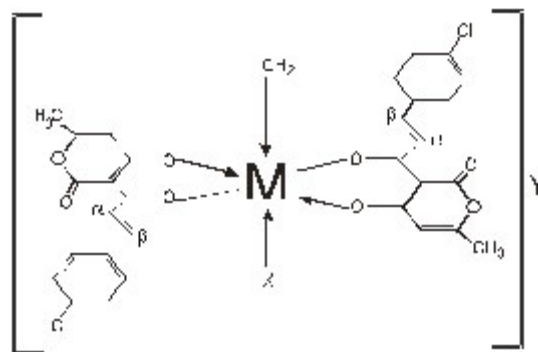
The UO<sub>2</sub>(VI) complex does not exhibit any characteristic transition except the charge transfer bands.

The magnetic moment for the complex is 2.10 B.M. which is nearly the same as reported for other Ru(III) complexes<sup>19</sup>. Three transitions are observed, the first two bands are assigned to  ${}^2T_{2g} \rightarrow {}^4T_{1g}$  and  ${}^2T_{2g} \rightarrow {}^4T_{2g}$  transitions and the third one to  ${}^2T_{2g} \rightarrow {}^2A_{2g}, {}^2T_{1g}$  levels respectively<sup>19</sup>. These are characteristic of octahedral symmetry.

The Ru(II) complex is diamagnetic in nature. The electronic spectrum of the complex in CH<sub>2</sub>Cl<sub>2</sub> shows a band assigned to the charge transfer transition arising from the excitation of an electron from the metal  $t_{2g}$  level to the unfilled molecular orbitals derived from the  $\pi^*$  level of the ligand in accordance with the assignments made for other similar octahedral ruthenium(II) complex<sup>20-22</sup>.

The Pd(II) complexes show three peaks around 14000, 16600 and 25000 cm<sup>-1</sup> that could be assigned, in the increasing order of frequency, to the transitions  ${}^1A_{1g} \rightarrow {}^1A_{2g}, {}^1A_{1g} \rightarrow {}^1B_{1g}$  and  ${}^1A_{1g} \rightarrow {}^1E_g$  of square planar geometry<sup>23</sup>.

Based on the studies performed an octahedral geometry has been proposed for all the complexes except Pd(II) which is square planer.



#### Fungicidal activity

To evaluate fungicidal activity of the ligand and its corresponding metal complexes, their effect on the growth of *Aspergillus flavus*, *Curvularia lunata* and *Penicillium notatum* was studied. The ligand and its corresponding metal chelates in DMF were screened by mycelia dry weight method<sup>24</sup> in vitro for their fungicidal activity in glucose nitrate media. The ligand exhibited 20-25 and 30-35% inhibition for 125 and 250 ppm concentration respectively. It is observed that the metal complexes show enhanced antifungal activity as compared to the ligand. This is because of chelation, which reduces the polarity of metal ion due to partial sharing of its positive charge with donor groups and also due to delocalization of pi electrons over whole chelate ring. Thus chelation increase lipophilic character in the complexes and results in the enhancement of activity<sup>24</sup>. The inhibition by metal complexes has been increased by 30-65% and 40-70% for 125 and 250ppm concentration respectively. The order of inhibition with respect to metal ions is Mo(V)>V>Ti>Pd>Ru.

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