

## Synthesis and characterization of Ti(III), V(III), VO (IV), MoO(V), Fe(II) & Fe (III) complexes of 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid) p-toluidine

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### ABSTRACT

The complexes of 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid) p-toluidine with Ti(III), V(III), VO (IV), MoO(V), Fe(II) & Fe (III) have synthesized and characterized by elemental analysis, magnetic measurement data, molar conductance, TGA, UV-Visible and I.R. spectra data. The complexes of Ti(III), V(III), Fe(II) & Fe (III) have octahedral geometry while those of VO (IV) & MoO (V) have been assigned distorted octahedral geometry with due to the presence of M=O moiety.

**Key words:** Schiff bases, synthesis, TGA spectroscopy.

### INTRODUCTION

3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid, DHA) a potential chelating agent<sup>1,2</sup> has been observed to possess several biological properties. The acetyl carbonyls of DHA reacts with different amines to give the corresponding Schiff bases<sup>3,4</sup>. Iguchi *et al.*,<sup>5</sup> have studied the condensation product of DHA with different amino acids and have noticed that carbonyls of C<sub>3</sub> acyl participates in the reaction. Literature survey reveals that the complexing behaviour of Schiff base derived from dehydro acetic acid and p-toluidine has not been investigated. In view of this work on the title complexes was undertaken and the results are reported herein.

Dehydro acetic acid was a Fluka reagent, all the other chemical was used of A.R. grade.

#### Preparation of metal complexes

The metal chelates were prepared by refluxing the ethanolic solutions of the respective

metal salts (0.01 mol) [except for Fe(II) Complex where aqueous ethanolic ferrous ammonium sulphate solution was adjusted to ~ 7 by dropwise addition of 10% sodium acetate solution. The precipitated metal chelates were filtered, washed repeatedly with ethanol followed by pet. ether (60-70) and dried in vacuo.

The I.R. spectra of the ligand and metal chelates were recorded in KBr phase in the range of 4000-400cm<sup>-1</sup> on a Perkin-Elmer I.R. spectrophotometer model no 377. Conductivity measurement were carried out using a digital direct reading conductivity meter 304 (Systronics). The electronic spectra of metal chelates were recorded on a DMR-21 UV-visible spectrophotometer in the range 13000-300 nm. in nujol at room temperature. Thermogravimetric analysis was carried out on a mutually operated thermobalance with a heating rate of 5°/min. Magnetic susceptibility of the complex were measured at room temperature on a Gouy-balance using CuSO<sub>4</sub>.5H<sub>2</sub>O as callibrant.

All the complexes are coloured, decomposed at high temperature and insoluble in common organic solvents.

The analytical data of the complexes indicate 1:2 (M:L) stoichiometry. Conductivities of their  $1 \times 10^{-3}$  M dilutions in DMF (8.2-22.00 mhos  $\text{cm}^2 \text{mol}^{-1}$ ) indicated their electrolytic nature.

## RESULTS AND DISCUSSION

The analytical data for the complexes suggested 1:2 (M:L) stoichiometry for all metal chelates (Table 1). The vast difference in the melting points of the ligand and the complexes indicated the formation of the adduct. At the room temperature the values of molar conductance suggested 1:1 electrolytic nature for Ti (III), V(III), Fe(III), MoO(V) and non-electrolytic nature for VO (IV) and Fe (II) complexes.

### Electronic spectra

#### Electronic spectrum of Ti(III)

Electronic spectra of the complex exhibits two bands one at  $16450 \text{ cm}^{-1}$  and the other at  $21,560 \text{ cm}^{-1}$  derived from  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  (P) and  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  transition, respectively. All these are typical for octahedral geometry of the complex<sup>6</sup>.

#### Electronic spectrum of V (III)

Electronic spectrum of the complex<sup>7</sup> showed only a band at  $19,650 \text{ cm}^{-1}$  which may be

derived from d-d transition  ${}^2T_{2g} \rightarrow {}^2E_g$  indicating an octahedral geometry for the complex<sup>8</sup>.

### Electronic spectrum of VO (IV)

Electronic spectrum of the complex shows four bands at  $17,695 \text{ cm}^{-1}$ ,  $22,875 \text{ cm}^{-1}$ ,  $31,645$  and  $38,650 \text{ cm}^{-1}$ . The first two bands corresponds to  ${}^2B_2 \rightarrow {}^2B_1$  and  ${}^2B_2 \rightarrow {}^2A_1$  transitions and the later two bands corresponds to charge-transfer bands. All these are typical for octahedral oxovanadium complex<sup>9</sup>.

### Electronic spectrum of MoO(IV)

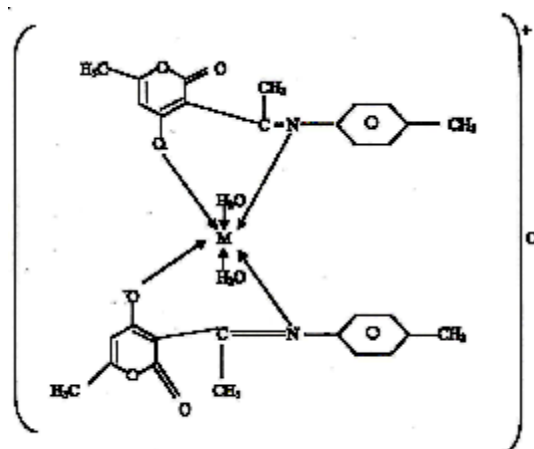
The electronic spectrum of the complex exhibited three distinct bands. The peak at long wavelength region ( $13,100 \text{ cm}^{-1}$ ) transition  ${}^2B_2 \rightarrow {}^2E$  ( $d_{xy} \rightarrow d_{xz}, d_{yz}$ ). The second transition was observed at  $19,200 \text{ cm}^{-1}$  due to  ${}^2B_2 \rightarrow {}^2B_1$ . The third peak was observed at  $26,200 \text{ cm}^{-1}$  due to transition ( $d_{xy} \rightarrow d_{xz2}$ ) at these transition suggested octahedral geometry with a strong tetragonal distortion resulting from Mo=O band<sup>10</sup>.

### Electronic spectrum of Fe (II)

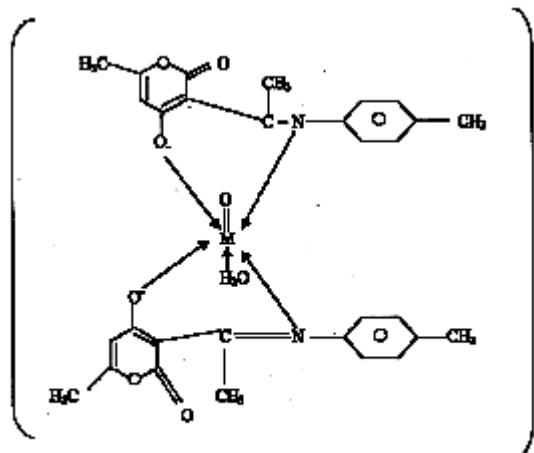
The electronic spectrum of Fe (II) complex was recorded in nujol at room-temperature. The spectrum displays two absorption bands at  $10,200 \text{ cm}^{-1}$  and  $19,800 \text{ cm}^{-1}$  which are assigned to  ${}^5T_g \rightarrow {}^5E_g$  transition and charge-transfer, respectively, which is the characterisation of the octahedral geometry.

**Table 1: Analytical data of the complexes of 3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydro aceticadi DGA) p-toluidine**

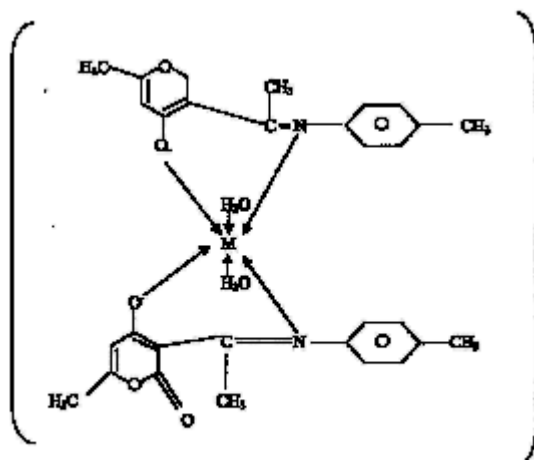
Complexes (Mol. Formulae)	Calculated (found) percentage					Magnetic moment $\mu_{\text{eff}}$ (B.M.)
	Metal	C	H	N		
[TiCl <sub>3</sub> (C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	6.81(6.75)	51.25 (50.80)	4.55 (4.48)	3.98 (3.68)	1.68	
[VCl <sub>3</sub> (C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	7.22 (7.00)	51.03 (50.06)	4.53 (4.50)	3.96 (3.90)	1.58	
[VOSO <sub>4</sub> (C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	7.35 (7.11)	51.95 (51.60)	4.32 (4.20)	4.04 (4.00)	1.72	
[MoOCl <sub>3</sub> (C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	16.90 (16.70)	63.42 (63.24)	5.28 (5.20)	4.93 (4.69)	1.68	
[FeCl <sub>2</sub> (C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	8.27 (8.00)	53.34 (52.98)	4.74 (4.70)	4.14 (4.00)	5.73	
[FeCl <sub>3</sub> (C <sub>15</sub> H <sub>14</sub> NO <sub>3</sub> ) <sub>2</sub> · 2H <sub>2</sub> O]	7.86 ( 7.50)	50.67 ( 50.60)	4.50 (4.25)	3.04 (3.78)	5.68	



M= Ti(III), V(III), Fe(III)



M= V, Mo



M= Fe (II)

### Electronic spectrum of Fe(III)

Electronic spectrum of the complex exhibits two bands one at  $16,400\text{ cm}^{-1}$  and the other at  $21,800\text{ cm}^{-1}$  derived from  ${}^3T_{1g} \rightarrow {}^3T_{2g}$  (P) &  $T_{1g} \rightarrow {}^3T_{2g}$ .

The observed spin-only value of magnetic moment for the complexes of paramagnetic character and octahedral geometry for all the complexes<sup>11-15</sup>.

The I.R. spectra of the ligand and the complexes were compared for taking information regarding coordination sites. The I.R. spectrum of the ligand shows a broad band at  $3400\text{ cm}^{-1}$  which has been assigned to  $\nu(\text{OH})$  group<sup>16</sup>. The bands observed at  $1720\text{ cm}^{-1}$  and  $1655\text{ cm}^{-1}$  has been assigned to  $\nu(\text{C}=\text{O})$  of lactone carbonyls and  $\nu(\text{C}=\text{N})$  of azomethine group respectively<sup>17</sup>. The  $\nu(\text{C}-\text{O})$  (phenolic) and  $\nu(\text{C}-\text{O}-\text{C})$  vibrations are displayed at  $1245\text{ cm}^{-1}$  and  $1025\text{ cm}^{-1}$ (18), respectively.

In the I.R. spectra of the complexes the band around  $3300\text{ cm}^{-1}$  in all complexes which may be assigned to  $\nu(\text{OH})$  of coordinated water which is further confirmed by the appearance of non-ligand bands in the range of  $820-880\text{ cm}^{-1}$  assignable to wagging mode of coordinated water molecule. The presence of coordinated water molecules is further confirmed by TGA which shows the loss of water molecules in the range of  $150-180^\circ\text{C}$ .

On the basis of above mentioned physico-chemical evidences octahedral geometry has been suggested for all the complexes with slight distortion in case of MoO & VO complexes where  $\text{M}=\text{O}$  may have caused some distortion.

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