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TRANSITION METAL COMPLEXES OF 4-HYDROXY-6-METHYL-3-(3-PHENYL-ACRYLOYL)-PYRAN-2-ONE : SYNTHESIS, SPECTRAL, THERMAL AND FUNGICIDAL STUDY

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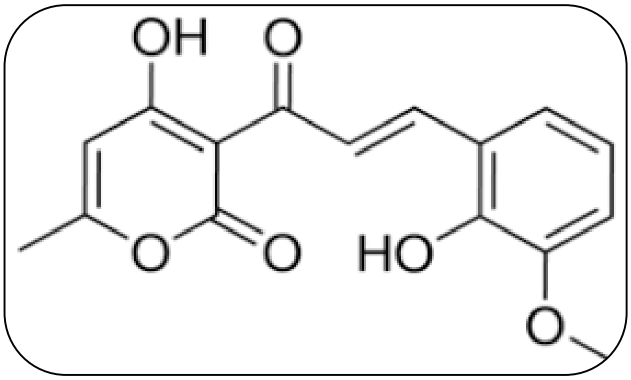
ABSTRACT:

Transition metal complexes containing bidentate O, O donor ligand, i.e., 4-Hydroxy -6-methyl-3-[3-(3-phenyl-acryloyl]-pyran-2-one (DHAC) derived from 3-acetyl-6-methyl pyran-2,4(3H)-dione (dehydroacetic acid) and bezaldehyde, have been synthesized and characterized by elemental analysis, conductometry, thermal analysis, magnetic, IR, NMR, UV-VIS, X-ray diffraction and fungicidal study. From the analytical and thermal data, the stoichiometry of the complexes has been found to be 1:2 (metal : ligand). The metal complexes have general formula $[ML_2(H_2O)_2]$*, where M = Mn(II), Co(II), Ni(II), Cu(II) and* $[ML_2(Cl)(H_2O)]$*, where M = Fe(III). Distorted octahedral geometry for Cu(II) complex and octahedral geometries for all other complexes are proposed. The Kinetic parameters, (n, E, A,* ΔS *and* ΔG*) from thermal analysis, have been estimated. The X-Ray diffraction suggest Monoclinic crystal system for Fe(III), Co(II), Ni(II) and Hexagonal crystal system for Mn(II) complexes. The ligand (DHAC) and its metal complexes have been screened in vitro for their antifungal activities against Aspergillus flavus, Curvularia lunata and Penicillium notatum.*



KEYWORDS: *Chalcone, Dehydroacetic acid, Transition metal complexes, Thermal analysis, Powder X-ray diffraction.*

INTRODUCTION

Dehydroacetic acid (3-acetyl-6-methyl-2H-pyran-2,4(3H)-dione), a biologically active compound has shown to have good antibiotic and antifungicidal effects,[1] besides showing strong antiseptic properties.[2] It has also been used to enhance vitamin 'C' stability in vegetable, food processing[3] and as a preservative.[4] Chalcones are associated with many biological activities due to the presence of α, β unsaturated system as evidenced from their bacteriostatic,[5] tuberculostatic,[6] insecticidal,[7] germicidal,[8] fungicidal[9] and carcinogenic[10] properties. It is well known from the literature that compounds containing unsaturated system and their metal complexes possess interesting biochemical properties.[11-13] Therefore, it was thought worthwhile to synthesize some metal complexes of dehydroacetic acid chalcone containing α, β unsaturated system and investigate their binding, thermal, spectral and fungicidal characteristics.

EXPERIMENTAL:

Dehydroacetic acid and bezaldehyde, used for the preparation of ligand, were from Merck and A.R.grade respectively. A.R.grade metal chlorides were used for the complex preparation. A.R.grade solvents were used for spectral measurements. The carbon, hydrogen and sulphur content in each sample were measured on Perkin Elmer (2400) CHNS analyzer. IR spectra (nujol) in the range of 4000-450 cm^{-1} were recorded on Perkin Elmer (C-75430) IR spectrometer. ^1H NMR spectra of the ligands were measured in $CDCl_3$. The AAS, TGA-DTA and XRD were recorded on Perkin Elmer PE-Analyist 300, TA/SDT-2960 and Philips 3701/Philips 1701 respectively. The UV-VIS spectra of the complexes were recorded on a Shimadzu UV-1601 spectrophotometer. Magnetic susceptibility measurements of the complexes were carried out using a Gouy balance at room temperature using $Hg[Co(SCN)_4]$ as calibrant. Molar conductivity was measured on an Elico CM180 conductivity meter with a dip-type cell using 10^{-3} M solution of complexes in DMF.

SYNTHESIS OF LIGAND

A solution of 3.4 g (0.02 mole) of dehydroacetic acid, 10 drops of piperidine and 2.15ml (0.02 mole) of bezaldehyde in 25 ml chloroform was refluxed for 8-10 hours. 10 ml of the chloroform-water azeotrope mixture was separated by distillation. Crystals of product were separated on slow evaporation of the remaining chloroform and recrystalised from ethyl acetate.[14]

SYNTHESIS OF METAL COMPLEXES

To a chloroform solution (30ml) of the ligand (2mmol), methanolic solution (20ml) of metal chloride (1mmol) was added with constant stirring. The P^H of the reaction mixture was maintained around 7.5 by adding 10% methanolic solution of ammonia. It was then refluxed for 2 hours. The resulting metal complex was filtered in hot condition and washed with chloroform, methanol, pet-ether and dried over calcium chloride in vacuum desiccator.

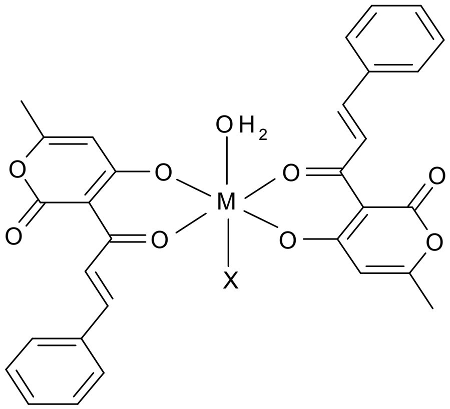
RESULTS AND DISCUSSION

The elemental analysis show 1:2 (metal : ligand) stoichiometry for all the complexes. The analytical data of the ligand and the complexes are given in Table I. It corresponds well with the general formula $[ML_2(H_2O)_2]$ where M = Mn(II),Co(II), Ni(II), Cu(II) and $[ML_2(Cl)(H_2O)]$ where M = Fe(III), L = $C_{15}H_{11}O_4$. The presence of water of crystallization is confirmed by TGA-DTA analysis. The low conductance of the chelate solution supports the non electrolyte nature of the metal complexes.

Table I: Physical characterization, analytical and molar conductance data of the Compounds

Compound	Color	Found (Calculated) %				Mol.Wt.	M.P/ Decom position Temp. °C	λm Mho cm^2mol^{-1}
		C	H	Cl	M			
Ligand $C_{15}H_{12}O_4$	yellow	70.21 (70.31)	4.63 (4.72)	-	-	256.3	131	-
$[C_{30}H_{26}O_{10}Mn]$	Yellowish brown	60.21 (59.95)	4.426 (4.356)	-	8.926 (9.134)	601.5	192	13.1
$[C_{30}H_{24}O_9ClFe]$	red	59.01 (58.13)	4.02 (3.903)	5.626 (5.727)	9.124 (9.002)	619.8	195	12.2
$[C_{30}H_{26}O_{10}Co]$	Light brown	60.12 (59.51)	4.213 (4.328)	-	9.526 (9.733)	605.5	265	17.7
$[C_{30}H_{26}O_{10}Ni]$	Pale green	60.15 (59.53)	4.296 (4.329)	-	9.499 (9.697)	605.2	249	12.1
$[C_{30}H_{26}O_{10}Cu]$	green	59.12 (59.06)	4.320 (4.295)	-	10.23 (10.41)	610.1	273	15.1

Fig 1: The proposed structure of the complexes



X = H_2O; When M = Mn(II), Co(II), Ni(II), and Cu(II)
X = Cl; When M = Fe(III)

IR Spectra

Important spectral bands for the ligands and their metal complexes are presented in Table II. The IR spectrum of the ligand shows bands at 3162,1713,1659 and 1253 cm^{-1} assignable to νOH (hydrogen bonded), νC=O (lactone carbonyl), νC=O (acetyl carbonyl) and νC-O (phenolic) respectively.[15] In the IR spectra of all the metal chelates, no band is observed in the region 3162 cm^{-1}, instead in its place broad band characteristic of νOH of coordination water is observed in the region 3500-3200 cm^{-1}.The presence of coordinated water is further confirmed by the appearance of non-ligand band in the region 830-840 cm^{-1}, assignable to the rocking mode of water.[16] Besides, it is also established and supported by TG and DT analysis. The absence of νOH (phenolic) at 3162 cm^{-1} suggests subsequent deprotonation of the phenolic group and subsequent coordination of phenolic oxygen to the metal ion. This is supported by an upward shift in νC-O (phenolic) to the extent 30 – 50 cm^{-1}(ref 17).The νC=O (acetyl carbonyl) is shifted to the lower energy with respect to the free ligand, suggesting the participation of νC=O (acetyl carbonyl) in coordination.[15] The presence of new bands in the region 600– 450 cm^{-1} can be assigned to νM-O vibrations.[18]

Table II: Characteristic IR frequencies of the ligand and its metal complexes (cm^{-1})

Compound	νOH	νC=O (lactone)	νC=O (acetyl carbonyl)	νC-O (phenolic)	νM-O
ligand	3162 (b)	1712 (m)	1659 (m)	1253 (s)	-
Mn(II) Complex	3374 (b)	1710 (m)	1625 (m)	1281 (m)	526 (m) 568 (m)
Fe(III) Complex	3374 (b)	1719 (m)	1622 (s)	1273 (m)	493 (m) 533 (m) 582 (m)
Co(II) Complex	3357 (b)	1708 (m)	1626 (s)	1263 (m)	493 (m) 530 (m) 578 (m)
Ni(II) Complex	3348 (b)	1709 (m)	1626 (m)	1280 (m)	485 (m) 498 (m) 531(m)
Cu(II) Complex	3377 (b)	1713 (m)	1645 (m)	1271 (m)	541 (m) 619 (m)

^{1}H-NMR spectrum

The ^{1}H-NMR spectrum of the ligand was recorded in $CDCl_3$. The spectrum shows sharp peaks at δ = 2.27(S, 3H, C_6-CH_3), 6.03(S, 1H, C_5-H) for dehydroacetic acid moiety,

δ = 7.2 - 8.32(m, 7H) for aromatic and olefinic protons and δ = 16.3(S, 1H, C_4-OH) phenolic hydrogen.

MAGNETIC MOMENT AND ELECTRONIC ABSORPTION SPECTRA

The magnetic and electronic spectral data is shown in Table III. The data is in relevance to the proposed structure of the complexes (fig 1). The observed magnetic moment value for the Cu (II) complexes is 1.98 BM. The electronic spectral data[19] coupled with magnetic moment value suggest a distorted octahedral geometry for the Cu (II) complexes.[20] The observed electronic spectral data and magnetic moment values for Mn(II), Fe(III), Co(II) and Ni(II) are consistent with high spin octahedral geometry.[20-23] The reduction of Racah parameters (B) and Nephelauxetic effect (β) from the free ion value suggest appreciable amount of covalent character in the metal ligand bonds.[22] The relative strength of the ligand and geometry of the complexes can be illustrated by calculating ligand field parameters like ligand field splitting energy (10Dq), interelectronic repulsion parameter (B), covalent factor (β) and ligand field stabilization energy (LFSE). These values have been calculated using standard equations[22] and are compiled in Table III. The values of LFSE (10Dq) determine the stability of the complexes and follows the order in terms of metal ion Cu(II)>Ni(II)>Co(II). This stability order is in fair agreement with the order reported.[17]

Table III: Magnetic and electronic spectral data of complexes and Ligand field parameters

Complex	μeff BM	Band Position Cm^{-1}	Assignment	10 Dq cm^{-1}	B cm^{-1}	β	ν_2/ν_1	LFSE Kcal mole^{-1}
$[C_{30}H_{26}O_{10}Mn]$	5.84	17513 19685 33557	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) charge transfer	-	-	-	-	-
$[C_{30}H_{24}O_9ClFe]$	6.0	14706 21008 24876	$^6A_{1g} \rightarrow {}^4T_{1g}(G)$ $^6A_{1g} \rightarrow {}^4T_{2g}$ (G) $^6A_{1g} \rightarrow {}^4E_g$ (G)	-	-	-	-	-
$[C_{30}H_{26}O_{10}Co]$	4.53	9794 18622 23753	$^4T_{1g}(F) \rightarrow {}^4T_{2g}$ (F) $^4T_{1g}(F) \rightarrow {}^4A_{2g}$ (F) $^4T_{1g}(F) \rightarrow {}^4T_{1g}$ (P)	8828	866.8	0.89	1.90	25.22
$[C_{30}H_{26}O_{10}Ni]$	2.95	9708 15384 24937	$^3A_{2g} \rightarrow {}^3T_{2g}$ (F) $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) $^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	9708	746.5	0.71	1.58	27.73
$[C_{30}H_{26}O_{10}Cu]$	1.98	15128 25380	$^2Eg \rightarrow {}^2T_{2g}$ charge transfer	1513	-	-	-	42.80

THERMAL ANALYSIS

Thermogravimetric analysis shows a weight loss equivalent to two moles of coordinated water, per mole of the complexes of Mn(II), Co(II), Ni(II), Cu(II) while in case of Fe(III), the loss is equivalent to one mole of water per mole of the complex. The Co(II) and Cu(II) complexes of ligand DHAC are chosen for determining the kinetic parameters i.e. n (order of reaction), E (energy of activation), Z (pre-exponential factor), ΔS (entropy) and ΔG (free energy change). The different decomposition stages of the complexes with percentage losses are represented in Table IV. The TG curve of the Co(II) complex shows three stage decomposition. The first stage involves loss of three lattice water molecules at 135.95°C and the second stage involves loss of two coordinated water at 199.26°C. This is supported by DT curve having one sharp endothermic peak. The third stage decomposition is in the range of 250-675°C, may be attributed to oxidative degradation of ligand. The mass of the final residue correspond to stable metal oxide.

In case of Cu(II) complex, the TG curve shows two stage decomposition. The first stage involves loss of two coordinated water at 235.98°C. This is supported by DT curve having one sharp endothermic peak. The second stage decomposition is rapid and in the range of 250-325°C, may be attributed to oxidative degradation of ligand. The mass of the final residue correspond to stable metal oxide.

In order to calculate the kinetic parameters, three methods have been used namely Coats-Redfern, MacCallum-Tanner and Horowitz-Metzger.

Coats-Redfern method[24]:

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)T^2}\right] = \log\frac{ZR}{Eq}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303R}\cdot\frac{1}{T} \qquad (1)$$

MacCallum-Tanner method[25] :

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \log\frac{ZE}{Rq} - 0.485E^{0.435} - \frac{0.449+0.217\,E}{T}\cdot 10^3 \qquad (2)$$

Horowitz-Metzger method[26] :

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{(1-n)}\right] = \log\frac{ZRT_s^2}{Eq} - \frac{E}{2.303RT_s} + \frac{E\theta}{2.303RT_s^2} \qquad (3)$$

Where α = fraction decomposed, T = absolute temperature, Ts = Temperature at half weight loss, $\theta = T - Ts$, R = gas constant, q = heating rate ($10^{o}Cmin^{-1}$). The left-hand side of equs. (1) and (2) was plotted against 1/T and against θ = (T – Ts) for eqn. (3). By using different values of order of reaction, straight line was fitted by regression. The highest value of r (correlation coefficient) gave the correct value of 'n'. From the slope and intercept, Ea and A values were calculated.[27] Using E and A values, the values of ΔS and ΔG were determined[27] (Table IV). The value of E is sufficiently high and is comparable with other observations.[28] The negative values of ΔS show that the complexes are more ordered in the activated state than the reactants and the positive value suggest that the activated complex has less ordered configuration than the reactants.[29]

Table IV: Calculation of Kinetic parameters by Coats-Redfern (C.R), MacCallum-Tanner (M.T) and Horowitz-Metzger (H.M) methods.

Complex	Step	ΔT °C	Mass loss(%) Exp(Calc)	Probable Species	method	n	Ea KJmole^{-1}	A S^{-1}	ΔS JK^{-1} mole^{-1}	ΔG KJ mole^{-1}
[$C_{30}H_{26}O_{10}Co$]	1	50-140	7.5 (8.6)	three molecules of lattice water		-	-	-	-	-
	2	150-210	6.0 (5.9)	two coordinated H_2O	C.R M.T H.M	0.97 0.99 0.99	29.15 28.33 36.54	3.42x10^{7} 7.45x10^{2} 2.83x10^{4}	-104.2 -193.5 -163.2	34.83 38.87 45.44
	3	250-675	79.5 (81.7)	ligand moiety	C.R M.T H.M	1.21 1.20 0.81	16.46 19.25 28.93	2.85x10^{9} 11.63 7.604	-71.57 -232.2 -235.2	22.89 40.14 50.14
[$C_{30}H_{26}O_{10}Cu$]	1	200-240	6.0 (5.9)	two coordinated H_2O	C.R M.T H.M	1.1 1.1 1.07	150.9 151.7 167.7	2.68x10^{14} 1.83x10^{16} 1.04x10^{18}	26.87 65.59 95.61	149.3 147.6 161.8
	2	250-340	84.0 (83.6)	ligand moiety	C.R M.T H.M	0.65 0.65 0.82	13.5 114.9 157.0	1.23x10^{10} 8.72x10^{11} 1.29x10^{14}	-57.69 -22.25 -19.28	117.8 116.5 155.6

Powder X-Ray Diffraction

The diffractogram of [$C_{30}H_{26}O_{10}Mn$] complex records fourteen reflections between 5 to 80^{o}(2θ) with maxima at 2θ = 7.13^{o} corresponding to d value 12.3905A^{o}. The diffractogram of [$C_{30}H_{24}O_9ClFe$] complex records thirteen reflections with maxima at 2θ = 6.598^{o} corresponding to d value 13.4008A^{o}, The diffractogram of [$C_{30}H_{26}O_{10}Co$] complex records eight reflections with maxima at 2θ = 26.26^{o} corresponding to d value 3.3902A^{o}, where as [$C_{30}H_{26}O_{10}Ni$] complex records seven reflections with maxima at 2θ = 26.199^{o} corresponding to d value 3.3984^{o}. The X-Ray diffraction patterns of [$C_{30}H_{26}O_{10}Mn$], [$C_{30}H_{24}O_9ClFe$], [$C_{30}H_{26}O_{10}Co$] and [$C_{30}H_{26}O_{10}Ni$] with respect to prominent peaks having relative intensity greater than 10% have been indexed by using computer software.[30] The above indexed method also yielded miller indices (hkl), unit cell parameters, volume of unit cell and space group. The experimental density values of the complexes were determined by using specific gravity method.[31] By using this value of density, molecular weight of the complexes, Avogadro's number and volume of unit cell, the number of molecules (n) per unit cell were calculated by using equation ρ = nm/NV and was found to be 1 for [$C_{30}H_{26}O_{10}Co$] and [$C_{30}H_{26}O_{10}Ni$] complexes, and 4 for [$C_{30}H_{26}O_{10}Mn$] and [$C_{30}H_{24}O_9ClFe$] complexes. With this value, theoretical density has been computed. The other parameters such as porosity and particle size[32] were also calculated (Table V).

Table V: X- ray parameters of Fe(III), Co(II), Ni(II) and Cu(II) complexes.

Parameters	Fe(III) complex	Mn(II) complex	Co(II) complex	Ni(II) complex
Structure	Monoclinic	Hexagonal	Monoclinic	Monoclinic
Space group	P	P	P	P
Point group	2/m	6/mmm	2/m	2/m
Symmetry of lattice	simple	simple	simple	Simple
Lattice parameters				
a A^o	15.6753	14.3453	7.6287	8.6865
b A^o	10.6659	14.3453	9.5124	3.9778
c A^o	13.4251	11.3021	4.5040	8.1819
Bond angle	$\alpha = \gamma = 90º$ $\beta = 94.3487^o$	$\alpha = \beta = 90º$ $\gamma = 120.0^o$	$\alpha = \gamma = 90º$ $\beta = 107.9075^o$	$\alpha = \gamma = 90º$ $\beta = 101.9365^o$
Vol.unit cell (V) A^{o3}	2238.10	2014.24	311.01	276.60
Density ρ g cm^{-3}				
Experimental	1.6286	1.7854	2.904	2.904
Theoritical	1.8394	1.9835	3.233	3.633
Partical size A^o	184.4	71.81	63.66	84.59
Porosity %	11.46	9.98	10.18	20.08

FUNGICIDAL ACTIVITY

To evaluate fungicidal activity of the ligands and their corresponding metal complexes, their effect on the growth of Aspergillus flavus, Curvularia lunata and Penicillium notatum was studied. The ligand DHAC and their corresponding metal chelates in DMF were screened by mycelia dry weight method[17] in vitro for their fungicidal activity in glucose nitrate media. The ligand exhibited 20-35 % inhibition. Due to synergistic combination of the coordinated metal ions with the ligands, the inhibition by metal complexes has been increased by 30 – 65% and 40 – 70 % for 125 and 250 ppm concentration respectively. The order of inhibition with respect to metal ions is Cu>Ni>Co>Mn>Fe. The results obtained are shown in Table VI. The antifungal data reveals that the metal complexes are superior to the free ligands and the inhibition increased as the concentration increased.

Table VI: Yield of Mycelial dry weight in mg (% inhibition)

compound	Aspergillus flavus		Curvularia lunata		Penicillium notatum	
	125 ppm	250 ppm	125 ppm	250 ppm	125 ppm	250 ppm
control	97	98	71	69	86	86
Ligand DHAC	77(21)	64(35)	58(18)	47(32)	68(21)	55(36)
Fe(III) Complex	65(33)	55(44)	50(30)	40(42)	57(34)	50(42)
Mn(II) Complex	60(38)	47(52)	46(35)	38(45)	54(37)	41(52)
Co(II) Complex	57(41)	39(60)	42(41)	31(55)	50(42)	36(58)
Ni(II) Complex	52(46)	34(65)	39(45)	27(61)	47(45)	32(63)
Cu(II) Complex	44(55)	30(69)	35(51)	24(65)	41(52)	27(69)

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