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REVIEW OF RESEARCH



SYNTHESIS, SPECTRAL, THERMAL AND ANTIMICROBIAL STUDIES OF TRANSITION METAL COMPLEXES OF DEHYDROACETIC ACID CHALCONE



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ABSTRACT :

The solid complexes of Mn(II), Fe(III), Co(II), Ni(II), and Cu(II) with 4-Hydroxy-3-[3-(4-hydroxy-phenyl)acryloyl]-6-methyl-pyran-2-one have been synthesized and characterized by elemental analysis, conductometry, thermal analysis, magnetic, IR, PNMR, UV-VIS, X-ray diffraction and Antimicrobial study. From the analytical and spectral data, the stoichiometry of the complexes has been found to be 1:2 (metal : ligand). The physico-chemical data suggests distorted octahedral geometry for Cu(II) complexes and octahedral geometry for all other complexes. The X-Ray diffraction suggest Orthorhombic crystal system for Cu(II) complex and Monoclinic crystal system for Mn(II), Fe(III), Co(II) and Ni(II) complexes. The ligand and their metal complexes were screened for antibacterial activity against Staphylococcus aureus and Escherichia coli, and the fungicidal activity against Aspergillus flavus, Curvularia lunata and Penicillium notatum.

KEY WORDS - Chalcones, Dehydroacetic acid, Powder X-ray diffraction, Thermal analysis, Transition metal complexes.

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, besides showing strong antiseptic properties. It has also been used to enhance vitamin 'C' stability in vegetable, food processing and as a preservative [1]. In recent years a number of β -dicarbonyl compounds in which the carbonyl function(s) bonded to olefinic linkage(s) have gained considerable importance [2] mainly because of the fact that such compounds are structurally related to the active chemical constituents of several traditional medicinal plants. For instance, curcuminoids, the active chemical component present in Indian medicinal plant turmeric (curcuma longa, linn, zingiberacea family) contains three β -dicarbonyl moiety in which the diketo function is directly linked to C=C group [3]. Such unsaturated β -dicarbonyl compounds and their metal complexes possess interesting biochemical properties such as antitumour, antioxidant, antifungal, and antimicrobial activities [1-8]. Therefore, synthesis and characterisation of such unsaturated carbonyl system and their metal complexes have tremendous importance. In continuation to our work on dehydroacetic acid chalcones [9,10] containing β -dicarbonyl moieties and diketo group is directly linked to C=C group, the present paper reports the synthesis, spectral, thermal and biological studies.

EXPERIMENTAL

Dehydroacetic acid was purchased from Merck and was used as supplied. p-hydroxy benzaldehyde used for the preparation of ligand were A.R.grade. 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 determined 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 CDCl₃. The metal contents were determined by AAS on Perkin Elmer PE-Analyist 300. The TG-DTA and XRD were recorded on PerkinElmerTA/SDT-2960 and Philips 3701 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 (HL)

A solution of 0.01 mole of dehydroacetic acid, 10 drops of piperidine and 0.01 mole of p-hydroxy benzaldehyde in 25 ml chloroform were refluxed for 8 – 10 hrs. 10ml of the chloroform – water azeotrope mixture was separated by distillation. Crystals of product were separated on slow evaporation of the remaining chloroform. The resulting orange yellow crude precipitate was filtered, washed several times with ethyl alcohol and crystallized from chloroform.

Yield: 62 %. m.p: 235^oC, Anal. Calcd. for C₁₅H₁₂O₅: C, 63.57; H, 4.67. Found C, 63.01; H, 4.76 %. ¹HNMR (δ, CDCl₃): 2.27 (S, 3H, C₆-H); 5.39 (S, 1H, C₅-H); 6.33 (S, 1H, aromatic OH); 6.8-7.6 (m, 4H, aromatic ring); 7.9-8.19 (d, 2H, olefinic protons); 18.16 (S, 1H, C₄- phenolic hydrogen).

Preparation of Metal Complexes

To a DMF solution (30 ml) of the ligand (10 mmol), DMF solution (20 ml) of metal chloride (5 mmol) were added with constant stirring. It was then refluxed for 2 hours and poured on ice cold water. The resulting metal complex was filtered and washed with cold DMF, petroleum-ether and dried over calcium chloride in vacuum desiccator.

Synthesis of L-Copper II Complex

yield: 65 %. m.p: 283°C. Anal.Calcd. for C₃₆H₃₆N₂O₁₂Cu: C, 57.48; H, 4.82; N, 3.72, Cu, 8.44 %. Found C, 57.12; H, 4.21; N, 3.52; Cu, 8.31 %.

Synthesis of L-Nickel II Complex

yield: 67 %. m.p: >300°C. Anal.Calcd. for C₃₆H₃₆N₂O₁₂Ni: C, 57.85; H, 4.85; N, 3.74, Ni, 7.85 %. Found C: 58.01; H, 4.71; N, 3.82; Ni, 7.63 %.

Synthesis of L-Cobalt II Complex

yield: 67 %. m.p: >300°C. Anal.Calcd. for C₃₆H₃₆N₂O₁₂Co: C, 57.84; H, 4.85; N, 3.74, Ni, 7.88 %. Found C, 56.99; H, 4.52; N, 3.83; Co, 7.72 %.

Synthesis of L-Iron III Complex

yield: 62 %. m.p: >300°C. Anal.Calcd. for C₃₃H₂₉NO₁₁ClFe: C, 56.07; H, 4.13; N, 1.92; Cl, 5.02; Fe, 7.89 %. Found C, 56.12; H, 4.33; N, 1.82; Cl, 4.88; Fe, 7.62 %.

Synthesis of L-Manganese II Complex

yield: 67 %. m.p: 267°C. Anal.Calcd. for C₃₆H₃₆N₂O₁₂Mn: C, 58.15; H, 4.87; N, 3.76, Mn, 7.39 %. Found C, 58.42; H, 4.86; N, 3.66; Mn, 7.02 %.

RESULTS AND DISCUSSION

The elemental analysis show 1:2 (metal : ligand) stoichiometry for all the complexes. The analytical data of the ligand and there metal complexes corresponds well with the general formula $[M(L)_2(DMF)_2]$ where M = Mn(II), Co(II), Ni(II), Cu(II) and $[M(L)_2(DMF)(CI)]$ where M = Fe(III), L = C₁₅H₁₂O₅. The absence of chlorine except in the Fe(III) complexes were evident from volhard's test. The complexes are colored, stable in air, insoluble in water and partly soluble in common solvents except DMF and DMSO. The low conductance of the complexes in DMF solution supports the non-electrolytic nature of the metal complexes (Table 1).

IR Spectra:

Important spectral bands for the ligands and their metal complexes are presented in Table 1. The IR spectrum of the ligand show broad band in the region $3500 - 3000 \text{ cm}^{-1}$ assignable to vOH of intramolecular phenolic group and vOH aromatic ring. The other bands 1697, 1675 and 1223 cm⁻¹ assignable to vC=O (lactone carbonyl), vC=O (acetyl carbonyl) vC-O (phenolic) stretching mode respectively [11,12]. In the IR spectra of all the metal complexes of ligand the medium intensity broad band centered in the region 3500-3200 cm⁻¹ corresponds to aromatic vOH, the shifting of the band from 3500 – 3000 cm⁻¹ indicates deprotonation of the phenolic vOH of dehydroacetic acid moiety and involvement of the phenolic oxygen in bonding with metal ions. This is supported by an upward shift in vC-O (Phenolic) to the extent 40-60 cm⁻¹ [13]. The vC=O (acetyl carbonyl) in all the metal complexes is shifted to the lower energy with respect to the free ligands, to the extent 50-80 cm⁻¹, indicating participation of vC=O (acetyl carbonyl) in coordination [11,12]. Spectra of all metal complexes shows several medium intensity bands below 1600 cm⁻¹ due to various C=C and C-N stretching vibrations. IR spectra of all the compounds showed a prominent band at ~ 970 cm⁻¹ typical to trans –CH=CH- absorption [14]. The presence of new bands in the region 600 – 450 cm⁻¹ can be assigned to vM-O vibrations [15].

Compound	colour	Λ _m (Ω) ⁻¹	vOH (phenolic/ Aromatic)	vC=O (lactone)	vC=O (acetyl carbonyl)	νC-Ο-C	vC-O (phenolic)	vC=C (trans)	vC-N	νM-0
$C_{15}H_{12}O_5$	Yellowish	-	3500-	1697(m)	1675(m)	1377(s)	1223(m)	980(m)	-	-
	orange		3000(b)							
[Mn(C ₁₅ H ₂₂ O ₁₀) ₂ (DMF) ₂]	Light	15.1	3500-	1678(m)	1603(m)	1377(s)	1280(m)	975(m)	1157(m)	560(m)
	brown		3200(b)							462(m)
[Fe(C ₁₅ H ₂₂ O ₁₀) ₂ (DMF)(CI)]	Dark	15.3	3500-	1680(s)	1621(m)	1376(s)	1280(m)	975(m)	1166(w)	530(w)
	brown		3200(b)							488(m)
[Co(C ₁₅ H ₂₂ O ₁₀) ₂ (DMF) ₂]	Brown	22.7	3500-	1683(w)	1620(m)	1376(s)	1277(m)	970(m)	1161(w)	531(w)
	BIOWII		3200(b)							476(m)
[Ni(C ₁₅ H ₂₂ O ₁₀) ₂ (DMF) ₂]	Pale	9.8	3500-	1680(w)	1622(w)	1378(s)	1277(m)	988(m)	1163(w)	551(m)
	green		3200(b)							531(w)
[Cu(C ₁₅ H ₂₂ O ₁₀) ₂ (DMF) ₂]	Green	10.5	3500-	1686(m)	1628(m)	1377(s)	1280(m)	967(m)	1162(w)	560(w)
			3200(b)							480(m)

Table 1: Conductance and characteristic IR frequencies of the ligand and its metal complexes (cm⁻¹).



Magnetic moment and Electronic absorption spectra

The electronic spectra of Mn(II) complex exhibit three bands at 18345, 19763 and 32154 cm⁻¹, which are assigned to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}(G)$, ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (G) and ${}^{6}A_{1g} \rightarrow {}^{4}A_{1g}$, indicating an octahedral configuration [16,17] around Mn(II). The octahedral geometry of Mn(II) is further confirmed by the value of magnetic moment (5.84 B.M).

Three electronic transitions are observed at 14472, 21322 and 24272 cm⁻¹ for Fe(III) complex, which are assigned to ${}^{6}A_{1g} \rightarrow {}^{4}T_{1g}$ (G), ${}^{6}A_{1g} \rightarrow {}^{4}T_{2g}$ (G) and ${}^{6}A_{1g} \rightarrow {}^{4}E_{g}$ (G). These bands are consistent with an octahedral complex of Fe(III) and confirmed by the value of magnetic moment (5.93 B.M.)[17].

The electronic spectra of Co(II) complex exhibit three bands at 9487, 18656 and 21551 cm⁻¹, which are assigned to ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{2g}(F)$, ${}^{4}T_{1g}(F) \rightarrow {}^{4}A_{2g}(F)$ and ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)$ respectively, indicating octahedral configuration around Co(II) ion. The magnetic moment of Co(II) complex is 4.54 B.M. The calculated spectral parameters v_2/v_1 , 10Dq, B, β and ligand field stabilizing energy (LFSE) have values 1.96, 9169 cm⁻¹, 783.1 cm⁻¹, 0.81 and 26.20 Kcal mole⁻¹ respectively, which are in good agreement with the reported values of octahedral Co(II) complex [17]. The electronic spectra of Ni(II) exhibit three bands at 9345, 15698 and 22471 cm⁻¹, which are assigned to ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$ (F), ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (F) and ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$ (P) respectively. The ligand field parameters v_2/v_1 , 10Dq, B, β and LFSE have values 1.68, 9345 cm⁻¹, 675.6 cm⁻¹, 0.65 and 26.69 Kcal mole⁻¹. These values as well as the magnetic moment value (3.13 B.M.) support the octahedral geometry of Ni(II) complex [17].

The Cu(II) complex consists of a broad band at 14225 cm⁻¹ assigned to ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ character of distorted octahedral stereochemistry with D_{4h} geometry [18]. Beside, the above band, the band observed at 25316cm⁻¹ may be assigned due to charge transfer. The LFSE of Cu(II) complex is 42.64 KCalmol⁻¹. The obtained value of LFSE determines the stability of the complexes and follows the order in terms of metal ions Cu(II)>Ni(II)>Co(II).

Thermal Analysis

The Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes were chosen for thermal study. The TG curve of all the complexes shows same pattern of two steps decomposition. All the complexes shows high thermal stability and decomposes from > 250°C indicating absence of any lattice or coordinated water molecules. The TG curve of Mn(II) complex shows rapid first step decomposition in between 220 - 350°C with 48% mass loss (calcd. 48.14 %), an exotherm in DTA (Δ Tmax = 247.38 °C) indicates loss of two coordinated DMF and non-coordinating part of the complex i.e, aromatic ring with beta carbon (scheme 1). The complex does not

remain stable at higher temperature and shows slow second step decomposition in the temperature range 360 - 950 °C with mass loss 42% (calcd. 42.22%). A broad endotherm for this step in DTA corresponds to oxidative degradation of coordinated part of the ligand. The decomposition is completed at ~ 950 °C leading to the formation of stable metal oxide MnO (obs. 10%, calcd. 9.54%). The thermal study of Fe(III) complex shows stability upto 325 °C. The first step shows rapid decomposition and is in between 340 - 400 °C with 45% mass loss (calcd. 45.3%). A broad exotherm is observed in DTA (Δ Tmax = 366.1 °C). This step may be attributed to the removal of one coordinated DMF, one chloride and non-coordinated part of the ligand (scheme 2). The complex continues slow decomposition of the remaining part of the ligand with mass loss 44% (calcd. 44.42%) in the temperature range 400 - 900 °C. A broad endotherm is observed for this step in DTA. The mass of the final residue corresponds to stable FeO (obs. 11%, calcd. 10.2%). The Co(II) complex decomposes in two successive steps in the temperature range of 300 - 850 $^\circ$ C. The two coordinated DMF and non-coordinated part is removed in first step at 300 - 400 °C with a mass loss 47.5% (calcd. 47.88). A broad exotherm is observed in between 200 - 400 °C (Δ Tmax = 338.12 °C). The complex finally decomposes to CoO with removing coordinated part of ligand (obs. 42%, calcd. 42%) in the temperature range 400 - 850 °C (scheme 1). Ni(II) complex also decomposes in two step at the temperature range 300 - 900°C. The first step 300 - 400 °C in TG corresponds to elimination of two coordinated DMF molecules and non-coordinated part of ligand with mass loss 47.5% (calcd. 47.89%). A broad exotherm in the temperature range 200 - 400 °C is observed (Δ Tmax = 332.51 °C). The second step decomposition is observed at the temperature range 400 – 900°C with a mass loss 42.5% (calcd. 42.01%). A broad exotherm in DTA could be assigned to the removal of coordinated part of the ligand. The final weight 10% (calcd. 9.99%) corresponds to NiO (scheme 1). The TG curve of Cu(II) complex shows first step decomposition in the temperature range 260 - 350 °C with a mass loss 45.5% (calcd. 47.60%), an exotherm in DTA between 200 - 330 °C with (ΔTmax = 300.21 °C), corresponds to removal of two coordinated DMF and non-coordinated part of ligand. The second step decomposition in the temperature range 350 - 875°C with a mass loss 43.0% (calcd. 41.74%). A broad endotherm in DTA corresponds to removal of coordinated part of the ligand. The final residue 11.5% (calcd. 10.56%) corresponds to CuO (scheme 1).

 $[M(C_{15}H_{11}O_{5})_{2}(C_{3}H_{7}NO)_{2}] \xrightarrow{220 - 400 \circ C} -2C_{3}H_{7}NO \qquad [M(C_{8}H_{5}O_{4})_{2}] \xrightarrow{400 - 950 \circ C} -C_{16}H_{10}O_{7} \qquad MO$ metal oxide

Where M = Mn(II), Co(II), Ni(II), Cu(II)

Scheme 1

 $\begin{bmatrix} M(C_{15}H_{11}O_{5})_{2}(C_{3}H_{7}NO)(CI) \end{bmatrix} \xrightarrow{325 - 400^{\circ}C} \begin{bmatrix} M(C_{8}H_{5}O_{4})_{2} \end{bmatrix} \xrightarrow{400 - 900^{\circ}C} -C_{16}H_{10}O_{7} \qquad MO$ metal oxide -CI -CI₁₄H₁₂O₂

Where M = Fe(III)

Scheme 2

Powder X-Ray diffraction

The diffractogram of Cu(II) complex records seven reflections between 20 to $80^{\circ}(2\theta)$ with maxima at $2\theta = 27.14^{\circ}$ corresponding to d value 3.283 Å. The diffractogram of Ni(II) complex records eight reflections between 05 to $80^{\circ}(2\theta)$ with maxima at $2\theta = 6.28^{\circ}$ corresponding to d value 14.064 Å, where as Co(II)

complex records twelve reflections with maxima at $2\theta = 13.39^{\circ}$ corresponding to d value 6.603 Å. The diffractogram of Mn(II) complex records fourteen reflections between 05 to $80^{\circ}(2\theta)$ with maxima at 2θ = 23.69° corresponding to d value 3.753 Å. The diffractogram of Fe(III) complex records nine reflections between 05 to $80^{\circ}(2\theta)$ with maxima at $2\theta = 23.11^{\circ}$ corresponding to d value 3.846 Å. The X-Ray diffraction pattern of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes with respect to prominent peaks having relative intensity greater than 10% have been indexed by using computer software [19]. The above indexed method also yielded miller indices (hkl), unit cell parameters and volume of unit cell. The experimental density values of the complexes were determined by using specific gravity method [20]. 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 $\rho = nm/NV$ and was found to be 1 for Fe(III), Co(II), Ni(II) and Cu(II) complexes and 2 for Mn(II) complex. With this value, theoretical densities have been computed. The experimental density values of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes are 1.132, 1.246, 1.385, 2.351 and 1.385 g cm⁻³ respectively. The theoretical density values of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes are 1.1846, 1.259, 1.387, 2.372 and 1.405 g cm⁻³ respectively. When experimental density value of the complexes compared with the theoretical density value, it is found that there is good agreement within the limits of experimental errors. The particle size [21] of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes were found to be 140.65, 112.68, 450.77, 194.21 and 141.59 Å respectively. The unit cell of the Mn(II) complex yielded values for lattice constant a = 14.1774 Å, b = 13.2463 Å, c = 11.5175 Å and unit cell volume V = 2084.87 Å³. The unit cell of the Fe(III) complex yielded values for lattice constant a = 23.3054 Å, b = 4.1073 Å, c = 10.9423 Å and unit cell volume V = 931.79 Å³. The unit cell of the Co(II) complex yielded values for lattice constant a = 15.4831 Å, b = 4.5785 Å, c = 13.2868 Å and unit cell volume V = 894.73 Å³. The unit cell of the Ni(II) complex yielded values for lattice constant a = 7.6539 Å, b = 14.0594 Å, c = 5.4805 Å and unit cell volume V = 523.25 Å³ and the unit cell of the Cu(II) complex yielded values for lattice constant a = 14.6515 Å, b = 13.67657 Å, c = 4.4358 Å and unit cell volume V = 888.75 Å³. In conjunction with these evaluated cell parameters, the condition such as $a \neq b \neq c$ and $\alpha = \delta = 90^{\circ} \neq \beta$ required for the samples to be Monoclinic for of Mn(II), Fe(III), Co(II), Ni(II) and $a \neq b \neq c$ and $\alpha = \delta = \beta = 90^{\circ}$ required to be Orthorhombic for Cu(II) were tested and found to be satisfactory. The prominent lines in the X-ray powder diffraction pattern of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes are given in Table 2 (Fig 2).

Mn(II) complex	Fe(III) complex	Co(II) complex	Ni(II) complex	Cu(II) complex							
d(Å)	d(Å)	d(Å)	d(Å)	d(Å)							
13.355	7.597	8.3717	14.064	4.353							
11.071	5.462	7.352	6.797	4.055							
10.016	4.864	6.603	5.269	3.795							
7.998	3.845	4.381	4.688	3.657							
5.941	3.355	4.279	3.5755	3.537							
5.36	3.097	4.016	3.302	3.335							
5.238	2.849	3.754	2.986	3.283							
5.005	2.301	3.346	2.812								
4.670	1.671	3.121									
4.041		2.907									
3.753		2.659									
3.456		2.472									
3.339											
3.251											

Table 2: Prominent lines in the X-ray powder diffraction pattern of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes.

X = DMF; When $M = Mn^{"}$, Co["], Ni["], and Cu["]

X = CI; When M = Fe^{III}



Fig 2: X-ray powder pattern of Mn(II), Fe(III), Co(II), Ni(II) and Cu(II) complexes.

ANTIMICROBIAL SCREENING

The ligand and its metal complexes have been screened against antibacterial and antifungal activities in vitro.

Antibacterial activity

The ligand and there metal complexes were screened for antibacterial activity against gram positive bacteria, i.e., *Staphylococcus aureus* and gram negative bacteria, i.e. *Escherichia coli* by paper disc plate method [22]. The compounds were tested at the concentration of 500 and 1000 ppm in DMF and compared with known antibiotics viz Ampicillin and Ciproflaxin at the same concentration. It was observed that ligand show weak antibacterial activity and their complexes show moderate activity against both the bacteria's.

Antifungal Activity

To evaluate fungicidal activity of the ligand and their corresponding metal complexes, their effect on the growth of *Aspergillus flavus, Curvularia lunata* and *Penicillium notatum* was studied. The ligand and their corresponding metal chelates in DMF were screened by mycelia dry weight method [23] in vitro for their fungicidal activity in glucose nitrate media. The ligand exhibited 25-38 % inhibition for all the three fungi. Due to synergistic combination of the coordinated metal ions with the ligand, the inhibition by metal complexes has been increased by 30 - 68% and 49 - 87% for 125 and 250 ppm concentration respectively for all the three fungi. The order of inhibition with respect to metal ions is Cu>Co>Ni>Mn>Fe. The antifungal data reveals that the metal complexes are superior to the free ligand and the inhibition increased as the concentration increased.

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