



Synthesis and Structural Studies of Transition Metal Complexes with Bidentate Schiff Base Derived from 3-Acetyl-6-methyl-(2*H*)-pyran-2,4(3*H*)-dione

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Abstract: The solid complexes of Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) with Schiff base ligands derived from heterocyclic compounds 3-acetyl-6-methyl-(2*H*)-pyran-2,4(3*H*)-dione (Dehydroacetic acid) and *o*-chloroaniline were synthesized and characterized by elemental analysis, conductance, magnetic, thermal, UV-Vis and ¹H-NMR spectroscopy. The ligand field parameters have been evaluated for Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) complexes which suggest an octahedral geometry for each of them. The magnetic moment and spectral data suggest the dimeric nature of Mn(II) complexes with octahedral geometry. The fungicidal activities of the ligands and their metal complexes have been screened *in vitro* against *Aspergillus niger* and the percentage inhibition of the metal complexes is found to be increased considerably then that of their corresponding ligands and the order is Cu>Ni>Fe>Mn>Co.

Keywords: Dehydroacetic acid, Schiff base, Transition metal complexes, Ligand field parameters, Kinetic calculations, Fungicidal activity

Introduction

Schiff bases are one of the most widely used as chelating ligands in coordination chemistry¹⁻². Literature survey reveals that though some work has been done on the metal complexes of Schiff base derived from dehydroacetic acid with aliphatic amines, hydrazides, thiosemicarbazides have been prepared and studied intensively³⁻⁴. However, much less attention has been focused on the metal complexes of Schiff bases derived from dehydroacetic acid and aromatic amines. In the view of the above fact, we report here the

synthesis and characterization of the Schiff bases derived from biologically active dehydroacetic acid and *o*-chloroaniline (L^1). The structure of the complexes has been established using analytical, magnetic, IR, electronic spectral data and thermal analysis. The results obtained are in good agreement with the ligand field splitting energy $10Dq$.

Experimental

Dehydroacetic acid for synthesis was obtained from E-Merk, Germany. *o*-chloroaniline of AR Grade are obtained from Lancaster are used for the synthesis of Schiff Base. The AR Grade metal chlorides from E-Merck and qualigens were used for the synthesis of metal complexes. C, H and N analysis were determined on Perkin Elmer CHN Analyzer (2400). The metal contents were determined by atomic absorption spectra on Perkin Elmer atomic absorption spectrophotometer (2380). The molar conductance measurements were made using Systronics conductivity meter with a dip type cell (cell constant = 0.1 cm^{-1}) using approximately 10^{-4} M solutions of the complexes in DMSO. Magnetic measurements were carried out by using Gouy's balance at room temperature using $\text{HgCo}(\text{CNS})_4$ as calibrant. The IR spectra of the ligands and their metal complexes were recorded as KBr pellets on a Perkin Elmer (1430) FTIR spectrophotometer in the range $4000\text{-}400 \text{ cm}^{-1}$. The electronic spectral measurements were made on Shimadzu UV-Visible spectrophotometer uv-160. The TG and DT analysis were carried out in $25\text{-}650 \text{ }^\circ\text{C}$ range using thermal analysis with a heating rate 10^0 min^{-1} using alumina as a standard. The NMR spectra of the ligands were recorded on Bruker FT 200 mhz NMR spectrophotometer in CDCl_3 solvent using TMS as a reference sample. The fungicidal activity tested from Department of Botany, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad.

Synthesis of Schiff base

The Schiff base ligand 3-(1-(2-chlorophenylimino) ethyl)-6-methyl-3*H*-pyran-2,4-dione were synthesized by refluxing equimolar solution of dehydroacetic acid and corresponding aromatic amine in 50 mL ethanol on 1 RML Rotamantale for about 4-5 h. The thus formed Schiff base was cooled at room temperature and collected by filtration, followed by recrystallisation in ethanol. The purity of the ligands was checked by TLC technique and elemental analysis.

Synthesis of metal complexes

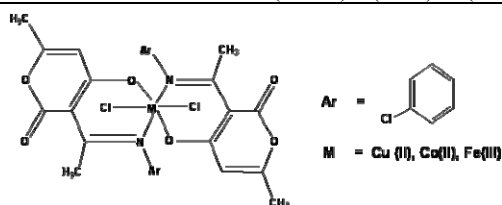
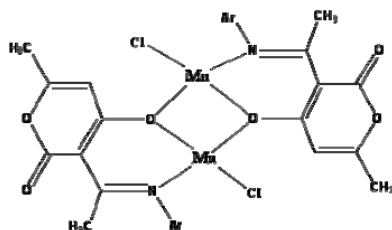
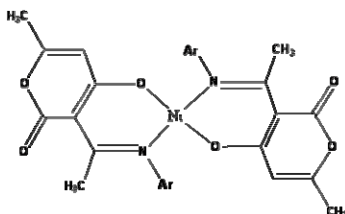
To a hot methanolic solution (25 mL) containing 2.0 mmol of the ligand, a methanolic solution (25 mL) of a metal chloride (1.0 mmol) was added drop wise with constant stirring. The pH of the reaction mixture was maintained around 7.5 by adding 10% alcoholic ammonia solution and refluxed for about 2 h. The precipitated solid metal complex was filtered off under hot conditions and washed with hot methanol, petroleum ether ($40\text{-}60 \text{ }^\circ\text{C}$) and dried over anhydrous CaCl_2 in vacuum desiccators.

Results and Discussion

All the metal complexes are colored solids, stable to air and nonhygroscopic. They are insoluble in water but soluble in DMF, DMSO. The physical characteristics, analytical and molar conductance data of the ligands and metal complexes are given in Table 1. The molar conductance values of all the metal complexes in DMSO at the concentration of 10^{-4} M are very low indicating their non electrolytic nature. The analytical data indicate 1:2 metal: ligand stoichiometry for the Cu(II), Ni(II), Co(II), Fe(III) and 1:1 stoichiometry for the Mn(II) complexes are given in Figure 2.

Table 1. Physical characterization, analytical and molar conductance data of the compounds

Compound.	F.W.	M.P °C	Colour	Found (Calculated) %				Λ_m Scm ² mol ⁻¹
				C	H	N	M	
HL ¹ C ₁₄ H ₁₂ O ₃ NCl	277	165	White	60.48 (60.49)	4.28 (4.32)	5.02 (5.04)	-	
Cu(C ₂₈ H ₂₄ O ₆ N ₂ Cl)Cl ₂	689	252	Pinkish	48.73 (48.74)	3.47 (3.48)	4.06 (4.06)	9.20 (9.21)	16.9
Ni(C ₂₈ H ₂₄ O ₆ N ₂ Cl)Cl ₂	684	300	Brown	49.07 (49.08)	3.50 (3.50)	4.08 (4.09)	8.56 (8.57)	15.1
Co(C ₂₈ H ₂₄ O ₆ N ₂ Cl)Cl ₂	684	300	Blue	49.05 (49.07)	3.50 (3.50)	4.05 (4.08)	8.59 (8.60)	13.5
Mn ₂ (C ₂₈ H ₂₄ O ₆ N ₂ Cl)Cl ₂	734	300	Brown	45.74 (45.77)	3.24 (3.26)	3.79 (3.81)	14.95 (14.96)	10.6
Fe(C ₂₈ H ₂₄ O ₆ N ₂ Cl)Cl ₂	681	260	Brown	49.28 (49.29)	3.51 (3.52)	4.08 (4.10)	8.17 (8.19)	11.1


Figure 1. The proposed geometry of Cu(II), Co(II), Fe(III) Complexes

Figure 2. The proposed geometry of Mn(II) complexes

Figure 3. The proposed square planar geometry of Ni(II) complex of ligand L¹

¹H-NMR spectrum of the Schiff base

The ¹H-NMR spectra of the free ligands in CDCl₃ at room temperature showed the following signals at δ(ppm): for Ligand L¹ 2.15(3H,s,C₆-CH₃), 15.80(1H,s, C₃-H), 5.80(1H,s, C₅-H), for DHA moiety, 2.55(3H,s,N=CH₃) methyl hydrogen bonded to carbon azomethine, 7.20-7.60 (4H,m) for phenyl moiety.

IR spectra

The characteristic IR frequencies (cm^{-1}) of the ligands and their complexes are shown in Table 2. The IR spectrum of the free ligands show a broad weak band $\sim 2600\text{-}2400\text{ cm}^{-1}$ attributed to intramolecular bonding $\nu(\text{OH})$. The bands 1697 cm^{-1} are assigned to $\nu(\text{C}=\text{O})$ (Lactone carbonyl), $\nu(\text{C}=\text{N})$ (azomethine), $\nu(\text{C}-\text{N})$ (aryl azomethine) and $\nu(\text{C}-\text{O})$ (enolic) stretching modes, respectively. The disappearance of IR band at 2600 cm^{-1} (intramolecular hydrogen bonding) in the spectra of all the complexes indicates deprotonation of enolic oxygen and azomethine nitrogen in coordination to the metal ion⁵. It is further supported by an upward shift in $\nu(\text{C}-\text{O})$ by $20\text{-}30\text{ cm}^{-1}$ in all complexes. A downward shift in $\nu(\text{C}=\text{N})$ by $15\text{-}20\text{ cm}^{-1}$ indicates participation of azomethine nitrogen in complex formation. The IR spectra of the metal complexes showed new bands in the $527\text{-}648\text{ cm}^{-1}$ and $437\text{-}582\text{ cm}^{-1}$ region, which can be assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ vibrations respectively⁶.

Table 2. Characteristic IR frequencies (cm^{-1}) of the ligands and their complexes

Comp.	$\nu(\text{C}=\text{O})$	$\nu(\text{C}=\text{C})$	$\nu(\text{C}=\text{N})$	$\nu(\text{C}-\text{N})$	$\nu(\text{C}-\text{O})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$
$\text{HL}^{15}_{15}\text{C}^{15}\text{H}^{15}\text{O}^{15}\text{N}^{15}$	1697	1563	1662	1364	1233	-	-
$\text{Cu}(\text{L}^3)_2\text{Cl}_2$	1697	1565	1648	1375	1267	530	450
$\text{Ni}(\text{L}^3)_2\text{Cl}_2$	1697	1560	1642	1367	1260	566	437
$\text{Co}(\text{L}^3)_2\text{Cl}_2$	1697	1560	1645	1381	1252	648	582
$\text{Mn}_2(\text{L}^3)_2\text{Cl}_2$	1697	1557	1646	1676	1252	527	455
$\text{Fe}(\text{L}^3)_2\text{Cl}_2$	1697	1563	1348	1373	1250	536	480

Magnetic measurements and electronic absorption spectra

The magnetic and electronic spectral data are given in Table 3. The data is of relevance for the proposed structure of the complexes. The electronic spectra of the Cu(II) complexes in DMSO shows the bands at $12048\text{-}16163\text{ cm}^{-1}$ for ligand HL^1 assignable to ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$ transition which is characteristic of distorted octahedral geometry⁷. This is further supported by the magnetic moment values ($1.65\ \mu_B$) within the required range for d^9 -system⁸. The electronic spectra of the Ni(II)- HL^1 complex shows two bands at 16129 and 27397 cm^{-1} assigned to the transitions ${}^3\text{A}_{2g}(\text{F}) \rightarrow {}^3\text{T}_{2g}$ and a charge transfer transition respectively, suggesting square planar geometry of the complex⁹⁻¹⁰. Also the diamagnetic nature supports to the structure. The electronic absorption spectrum of Co(II) complexes had three bands in range $10309\text{-}10204(\nu_1)$, $17543\text{-}18510(\nu_2)$, and $25777\text{-}25571(\nu_3)$ which may be attributed to three spin-allowed transitions ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{F})$, ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{A}_{2g}(\text{F})$ and ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{P})$, respectively, suggesting an octahedral geometry. The effective magnetic moment values ($5.12\ \mu_B$) were found to be well within the range as expected for octahedral geometry. The electronic spectra of the Mn(II) complex showed two bands at $16949\text{-}17543\text{ cm}^{-1}(\nu_1)$ and $23222\text{-}23809\text{ cm}^{-1}(\nu_2)$ assigned to the transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ respectively, indicating tetrahedral geometry. The magnetic moment values ($5.03\ \mu_B$) which is slightly lower than the spin only value expected for tetrahedral Mn(II) complexes¹¹. This may be due to the presence of magnetic exchange and small traces of Mn(II) species¹². In addition to the metal analysis, this is an additional evidence for the dimeric nature of Mn(II) complexes. The subnormal magnetic moment values are indicative of metal-metal interactions supporting dimeric nature¹³. The electronic spectra of the Fe(III) complexes showed three bands at $16129(\nu_1)$, $22727\text{-}23255(\nu_2)$ and $29411\text{ cm}^{-1}(\nu_3)$ assigned to the transitions ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}(\text{D})$, ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ and ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{2g}$ respectively and the magnetic moment values ($5.62\ \mu_B$) suggesting high spin octahedral geometry¹⁴.

Table 3. Magnetic and electronic absorption spectral data (in DMSO) of the complexes

Complex	$\mu_{\text{eff}} / \mu_{\text{B}}$	ν / cm^{-1}	Geometry
$\text{Cu}(\text{C}_{28}\text{H}_{24}\text{O}_6\text{N}_2\text{Cl})\text{Cl}_2$	1.65	12048,16163,27397	Octahedral (distorted)
$\text{Ni}(\text{C}_{28}\text{H}_{24}\text{O}_6\text{N}_2\text{Cl})\text{Cl}_2$	Diamagnetic	15384, 24390	Square-planar
$\text{Co}(\text{C}_{28}\text{H}_{24}\text{O}_6\text{N}_2\text{Cl})\text{Cl}_2$	5.12	10309,17543,25777	Octahedral
$\text{Mn}_2(\text{C}_{28}\text{H}_{24}\text{O}_6\text{N}_2\text{Cl})\text{Cl}_2$	5.03	17543,23222	Tetrahedral
$\text{Fe}(\text{C}_{28}\text{H}_{24}\text{O}_6\text{N}_2\text{Cl})\text{Cl}_2$	5.62	16129,22727,29411	Octahedral

Ligand field parameters

The relative strength 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 and the values are compiled in Table 4. The B and β values have been calculated only for the Ni(II)-L¹ and Co(II) complexes by following equations¹⁵. The B values are lower than the free ion values, thereby indicating the orbital overlap and delocalization of *d*-orbitals. The β values obtained are less than unity suggesting considerable amount of covalent character of the metal ligand bonds¹⁰. The ratio of ν_2/ν_1 being less than 2 as required for octahedral complexes, which is further supported the distortion from octahedral geometry by the values of Dq and B¹⁶. The LFSE values shows that the Cu(II) complexes are more stable than the other complexes.

Table 4. Ligand field parameters of some complexes

Compound	Dq, cm^{-1}	B, cm^{-1}	β	ν_2/ν_1	LFSE (kcal.mol^{-1})
Cu-L ¹	1176	-	-	-	33.52
Ni-L ¹	1041	720	0.79	1.54	29.58
Co-L ³	1020	801	0.82	1.68	29.08

Thermal analysis

The simultaneous TG/DT analysis of the Cu(II), Ni(II), Co(II), Mn(II) and Fe(III) metal complexes was studied from ambient temperature to 1000 K under a nitrogen atmosphere using alumina as the reference. The TG curve of the Cu(II) and Ni(II) metal complexes exhibited no mass loss up to 280 K indicating the absence of coordinated water¹⁷. Therefore, the complexes exhibits high thermal stability and the TG thermogram show single step exothermic peaks at 343.5 K which indicate the decomposition temperature of the complexes. The complexes starts decomposing partially giving metal oxide at 343.5 K, the organic part completely decompose in the temperature range 335 K -492 K as indicating by DT curve. The TG curve of Co(II) complexes shows two stage decomposition the weight loss encountered at 110.5 K supported by broad exothermic peak in TG curve which is characteristics of lattice water¹⁸. The second step was encountered at 240 K the organic constituent of the complex starts breaking and decomposes at 337 K shown in TG curve supported the two endothermic peaks at 312 K and 486 K in DTA curve. The constant weight corresponds to cobalt oxide, as a final product. The TG thermogram of Mn(II) complex shows the decomposition temperature at 256.9 K indicated by sharp peak, the organic part completely decompose the range 231-289 K was supported by DTA curve. The TG curve of Fe(III) complex shows a exothermic peak at 87.9 K, however the temperature 274 K may be the decomposition temperature of organic matter and the exothermic peak at 328 K indicate decomposition temperature of the complex. The FeO is obtained the end product at 554 K showed in DT curve. All the complexes finally decomposed to their metal oxides¹⁴.

Kinetic calculations

The kinetic and thermodynamic parameters *viz.*, energy of activation (E_a), free energy change (ΔF), Entropy change (ΔS), the pre-exponential factor (Z) for non-isothermal decomposition of the metal complexes, were determined by the Horowitz-Metzer (HM) approximation method¹⁹⁻²⁰. The obtained data are given in Table 5.

The thermograms of the Cu(II) and Ni(II) complexes show one stage thermal decomposition with single DTG peak at 314.6 K and 343.5 K respectively. The thermograms of the Co(II), Mn(II) and Fe(III) complexes show more than one stage thermal decomposition. Theoretically, with decreasing the value of E_a , the value of Z increases and the higher value of activation energy suggest the higher stability²¹. However some other inherent physical and chemical factors may cause a change or deviation in this trend. The higher values of Cu(II) and Ni(II) complexes show higher stability than Co(II), Mn(II) and Fe(III) complexes. Higher values of activation energy (E_a) (Table 5) and lower values of frequency factor (Z) favour the reaction to proceed slower than normal. In present studies, the numerical values of activation energy, frequency factor and entropy of activation altogether indicate about the smoothness of the feasibility and reaction rate of the initial reactants and intermolecular stage compounds. The negative values for entropy of activation indicates that the activated complexes have more ordered or more rigid structure than the reactants or intermediate and the reactions are slower than normal which is further supported by low values²². The order to thermal stability of compound comes to be 2>1>5>4>3 (on the basis of decomposition stage) and 4>3>5 (on the basis of second decomposition stage). The order of the stability of compounds on the basis of activation energy can be set as 1>2>4>5>3 (for first stage) and 5>4>3 (for second stage)²³⁻²⁴. The variation in the trend might be interpreted to be due to some intermolecular interactions (structural as well as electronic) occurring there in.

Table 5. Thermal kinetic parameters of the metal complexes calculated by Horowitz-Metzer (HM) method

Complexes	Stage/temp, K	E_a , kJ mol ⁻¹	ΔS , JK ⁻¹ mol ⁻¹	ΔF , kJ mol ⁻¹	Z , S ⁻¹
L ¹ -Cu(II)	I/587	96.59	197.00	110.10	623
L ¹ -Ni(II)	I/610	66.08	164.57	78.15	302
	I/513.4	22.22	197.03	123.33	549
L ¹ -Co(II)	II/610.4	15.70	199.74	137.54	470
	III/824	14.31	199.24	137.54	653
L ¹ -Mn(II)	I/529.9	63.6	203.61	174.43	264
	II/722	30.45	204.31	153.24	167
L ¹ -Fe(II)	I/547	24.74	205.49	133.63	204
	II/601	38.93	209.74	190.41	168

Fungicidal activity

To evaluate antifungal activity of the ligand and the corresponding metal complexes, their effect on the growth of *Aspergillus niger* was studied. For fungicidal activity, compounds were *in vitro* against *Aspergillus niger* by mycelia dry weight method²⁵ (Table 6). The fungus was grown on standard glucose-nitrate (GN) medium prepared by adding 10 g glucose, 2.5 g KNO₃, 1 g of KH₂PO₄ and 0.5 g of MgSO₄ to 1 lit. Of distilled water and fungus was cultivated on the GN media. The ligands and complexes under investigation were added to the GN medium of either 300 or 500 ppm to prepare solution/ suspension.

The medium either alone or with the ligand and complexes, was taken in conical flask, autoclaved at 15 lbs for 30 min., inoculated with *A. niger*, inoculated for 7 days and the mycelium obtained was collected by filtration through Whatmann filter paper. The yield of mycelial dry weight (MDW) Table 6 for each treatment was recorded which enhanced with that obtained on standard GN medium. The ligands show 60 to 70% inhibitions. The complexes have greater antifungal activity than the corresponding ligands. The toxic effects of metal complexes were augmented and restricted the growth of *A. niger* from 80 to 100%. All the copper complexes arrested the total growth of the fungus. Growth inhibitions were not found only due to the metal ions but the cumulative effect of metal and ligand. Thus the metal complexes show synergistic combinations. It was also found that during incubation, there was a change in colour of the media. This could be because of degradation of the complexes brought about by *A. niger* by enzyme activity. The order of inhibition with respect to the metal ion was Cu(II)>Ni(II)>Fe(III)>Mn(II)>Co(II). The results obtained are in good agreement with earlier finding²⁶⁻²⁸.

Table 6. Antifungal activities of ligand and their metal complexes by mycelial dry weight (MDW) at 250 and 500 ppm

Compound	<i>Aspergillus niger</i>	
	250 ppm	500 ppm
L ¹	45	40
Control	65	63
Cu(L ₂)Cl ₂	31	20
Ni(L ₂)Cl ₂	25	15
Co(L ₂)Cl ₂	34	18
Mn ₂ (L ₂)Cl ₂	43	31
Fe(L ₂)Cl ₂	46	35

Conclusion

Based on the physicochemical and spectral data discussed above, distorted octahedral geometry for the Cu(II) complexes, Square planar(L₁) for the Ni(II), Octahedral stereochemistry for the Co(II) and Fe(III) complexes and tetrahedral geometry for Mn(II) complexes are proposed. The ligands behave as bidentate, coordinating through carbonyl oxygen and the imino nitrogen of dehydroacetic acid moiety. The complexes are biologically active and exhibit enhanced antifungal activities compared to their parent ligands. The thermal study revealed that the all complexes are thermally stable.

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