

Synthesis & Structural Studies of Manganese(II), Iron(II), Cobalt(II), Nickel(II), Copper(II) & Zinc(II) Complexes with the Schiff Base Derived from 3-Acetyl- 6-methyl-2H-pyran-2,4(3H)-dione & Gly- cine†

N RAMA RAO, P VENKATESWARA RAO, V J TYAGA RAJU
& M C GANORKAR*

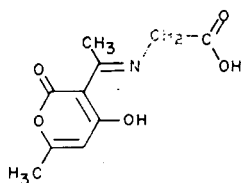
Department of Chemistry, Nizam College (O.U.), Hyderabad
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Complexes of the general formulae $[M(DHAGLY)_2 \cdot 2H_2O]_n$ and $[M(DHAGLY)_3 \cdot 3H_2O]$ where $M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)$ and $Zn(II)$; DHAGLY = schiff base derived from dehydroacetic acid and glycine and $n = 2, 3, \dots$ (polymer) have been prepared and characterised. The molar conductance values of the complexes in DMF indicate their non-ionic nature. The IR studies indicate dibasic tridentate chelating nature of the schiff base and also the participation of the lactone carbonyl in coordination except in the case of $Fe(II)$ and $Zn(II)$ complexes. The presence of coordinated water in these complexes is established by TG and DT analyses. ESR spectrum of $Cu(II)$ complex shows that the unpaired electron is in $d_{x^2-y^2}$ orbital. Magnetic moment and electronic spectral data show that all the complexes possess octahedral stereochemistry.

3-Acetyl-6-methyl-2H-pyran-2,4(3H)-dione (dehydroacetic acid, DHA), a potential chelating agent^{1,2}, has been observed to possess several biological properties. The acetyl carbonyl of DHA reacts with different amines to give the corresponding schiff bases^{3,4}. Iguchi *et al.*⁵ have studied the condensation products of DHA with different aminoacids and have noticed that carbonyl of C_3 -acyl participates in the reaction. Literature survey reveals that the complexing behaviour of schiff base derived from dehydroacetic acid and amino acids has not been investigated. In view of this the work on the title complexes was undertaken and the results are reported here.

Dehydroacetic acid was a Fluka reagent; all the other chemicals used were of AR grade.



I DHAGLY

The ligand (structure I) was prepared by the reported procedure⁵.

Preparation of metal complexes

The metal chelates were prepared by refluxing the ethanolic solutions of the respective metal(II) chlorides (0.01 mol) [except for $Fe(II)$ complex where aqueous ethanolic ferrous ammonium sulphate solution was used] and the ligand (0.01 mol) for 2-3 hr on a water-bath. The pH of the 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 ($60-80^\circ$) and dried *in vacuo*.

The IR spectra of the ligand and metal chelates were recorded in KBr in the range $4000-400\text{ cm}^{-1}$ on a Perkin-Elmer IR spectrophotometer model No. 377. Conductivity measurements 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 $1300-300\text{ nm}$ in nujol at room temperature. The ESR spectrum of $Cu(II)$ complex was recorded on a Varian EPR-E₄ spectrometer as powder at room temperature (frequency: 9.497 GHz ; field: 3370 G). DPPH (diphenyl picryl hydrazide) was used as the g maker. Thermogravimetric analysis was carried out on a manually operated thermobalance with a heating rate of $5^\circ/\text{min}$. Differential thermal analysis was carried out by using Leed and Northrup DTA unit (USA) with a heating rate of $10^\circ/\text{min}$; the instrument had a sensitivity of $100\text{ }\mu\text{V}/\text{inch}$. Magnetic susceptibilities of the complexes were measured at room temperature on a Faraday balance using $Hg[Co(SCN)_4]$ as the calibrant.

All the complexes are coloured, stable towards air and moisture, decompose at high temperatures and insoluble in common organic solvents.

The analytical data (Table 1) of the complexes indicate 1:1 stoichiometry (metal:ligand). Conductivities of their $1 \times 10^{-3}\text{ M}$ solutions in DMF ($8.2-22.0\text{ mhos cm}^2\text{ mol}^{-1}$) indicate their non-electrolytic nature.

The infrared spectrum of the ligand shows a broad band centered at 3400 cm^{-1} , which is attributed to intramolecularly hydrogen-bonded νOH ⁶. The bands observed at $1725, 1710$ and 1665 cm^{-1} are ascribed to $\nu\text{C}=\text{O}$ of carboxylic acid, $\nu\text{C}=\text{O}$ of lactone carbonyl and $\nu\text{C}=\text{N}$ of azomethine group respectively⁷. The $\nu\text{C}-\text{O}$ phenolic and $\nu\text{C}-\text{O}-\text{C}$ vibrations are displayed at 1245 and 1025 cm^{-1} respectively.

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Table 1—Analytical Data of the Complexes of DHAGLY

Complexes (Mol. formulae)	Found (Calc.) %			
	Metal	C	H	N
Mn(II)-DHAGLY (MnC ₁₀ H ₁₃ O ₇ N)	17.15 (17.50)	38.14 (38.22)	4.05 (4.14)	4.63 (4.45)
Fe(II)-DHAGLY (FeC ₁₀ H ₁₅ O ₈ N)	17.36 (17.52)	35.48 (35.73)	4.51 (4.46)	4.25 (4.16)
Co(II)-DHAGLY (CoC ₁₀ H ₁₃ O ₇ N)	18.29 (18.53)	37.53 (37.74)	3.95 (4.08)	4.62 (4.40)
Ni(II)-DHAGLY (NiC ₁₀ H ₁₃ O ₇ N)	18.19 (18.47)	37.52 (37.77)	3.97 (4.09)	4.19 (4.40)
Cu(II)-DHAGLY (CuC ₁₀ H ₁₃ O ₇ N)	19.45 (19.69)	37.09 (37.20)	4.16 (4.03)	4.52 (4.34)
Zn(II)-DHAGLY (ZnC ₁₀ H ₁₅ O ₈ N)	18.95 (19.09)	35.22 (35.05)	4.25 (4.38)	4.23 (4.08)

In all the complexes the 3400 cm^{-1} band disappears. Instead, a broad band characteristic of νOH of coordinated water is observed in the region $3500\text{--}3200\text{ cm}^{-1}$ in the spectra of all the complexes⁸. The presence of coordinated water is further confirmed by the appearance of a non-ligand band in the region $830\text{--}840\text{ cm}^{-1}$ (ref. 9) assignable to rocking mode of water and also by TG and DT analyses. The absence of νOH (phenolic) (occurring at 3400 cm^{-1} in the ligand) in the spectra of all the complexes suggests the cleavage of intramolecularly hydrogen bonded⁶ OH and subsequent deprotonation of the phenolic group and coordination of phenolic oxygen to the metal ion. This is further confirmed by an upward shift in $\nu\text{C}=\text{O}$ (phenolic) to the extent of $20\text{--}30\text{ cm}^{-1}$ (ref. 10). The absence of a band at 1725 cm^{-1} , which is present in the free ligand, and the appearance of strong new peaks in the range $1600\text{--}1620\text{ cm}^{-1}$ (due to νCOO^-) suggest the participation of $-\text{COOH}$ group^{11,12} in complexation, after deprotonation. A downward shift of $\nu\text{C}=\text{N}$ in all the complexes by $15\text{--}20\text{ cm}^{-1}$ shows the involvement of azomethine nitrogen in coordination¹³. An interesting phenomenon that has been observed is the lowering of $\nu\text{C}=\text{O}$ (lactone carbonyl) in the case of Cu(II), Ni(II), Co(II) and Mn(II) complexes by $20\text{--}35\text{ cm}^{-1}$ which suggests the participation of lactone carbonyl oxygen in coordination¹⁴. New peaks of medium intensities are observed in the range $600\text{--}400\text{ cm}^{-1}$, which are ascribed to $\nu\text{M}-\text{O}$ and $\nu\text{M}-\text{N}$ vibrations^{9,15}.

From the IR data it has been concluded that DHAGLY behaves as a dibasic tridentate ligand coordinating to the metal ions through the deprotonated phenolic oxygen, the carboxylate oxygen and the azomethine nitrogen. In the case of Cu(II), Ni(II), Co(II) and Mn(II) complexes, the oxygen of the lactone carbonyl is also involved in coordination.

TG and DT analyses of the complexes show the presence of two mol of coordinated water in the case of

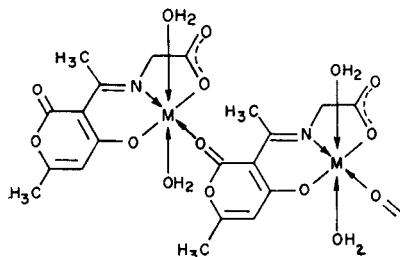
Mn(II), Co(II), Ni(II) and Cu(II) and three mol of water in Fe(II) and Zn(II) complexes. The loss of water in all the complexes except the Mn(II) complex is a one step process. Only one endothermic peak is observed in DT analysis which occurs at $187, 202, 240, 190$ and 210°C for Co(II), Ni(II), Cu(II), Fe(II) and Zn(II) complexes respectively. In the case of Mn(II) complex, it is a two step process; the two endothermic peaks in DT analysis occur at 195 and 220°C .

The Mn(II) complex possesses room temperature magnetic moment value of 5.65 B.M. which is low compared to spin-only value for high spin Mn(II) complexes. This can be attributed to the presence of Mn(III) species or spin-exchange in solid state¹⁶. The Fe(II) complex exhibits a value of 5.34 B.M. which is consistent with a high-spin octahedral geometry¹⁷. The magnetic moment of Co(II) complex is 4.24 B.M. suggesting a high-spin octahedral configuration¹⁶. The Ni(II) complex shows a μ_{eff} value of 3.09 B.M. which is expected for six coordinated Ni(II) complexes. The higher value compared to spin-only moment of 2.83 B.M. may be attributed to the slight mixing of a multiplet excited state in which spin-orbit coupling is appreciable¹⁸. The Cu(II) complex possesses a magnetic moment value of 1.95 B.M. which is well within the expected range of octahedral Cu(II) complexes¹⁶.

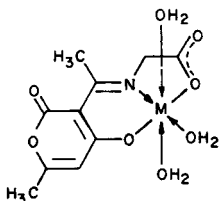
The electronic spectrum of Mn(II) complex shows weak bands at $8333, 15625, 25000$ and 29500 cm^{-1} which are of not much help in deciding the transitions¹⁷. The electronic spectrum of Fe(II) complex displays two absorption bands at 10101 and $20,000\text{ cm}^{-1}$ which are assigned to ${}^5T_{2g} \rightarrow {}^5E_g$ transition and charge-transfer respectively¹⁷. The Co(II) complex exhibits three main bands at $8771, 23809$ and 26666 cm^{-1} . These bands can be assigned to the transitions ${}^4T_{1g} \rightarrow {}^4T_{2g}, {}^4T_{1g} \rightarrow {}^4T_{1g}(P)$ (ref. 19) and charge transfer respectively. Ni(II) complex shows three bands at $9523, 17094$ and 26315 cm^{-1} which are attributed to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}; {}^3A_{2g} \rightarrow {}^3T_{1g}(F)$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}(P)$ respectively¹⁹. The Cu(II) complex exhibits an intense broad band at 16260 cm^{-1} which is assigned to transition¹⁹ ${}^2E_g \rightarrow {}^2T_{2g}$. Another band occurring at 25000 cm^{-1} is attributed to charge transfer.

The ESR spectrum of Cu(II) complex shows the $g_{\parallel}$ and $g_{\perp}$ values 2.224 and 2.068 G respectively. These values indicate the trend $g_{\parallel} > g_{\perp} > \text{free electron-spin}$ (2.0023) showing that the unpaired electron is in $d_{x^2-y^2}$ orbital of the Cu(II) ion. The $g_{\parallel}$ and $g_{\perp}$ values depart considerably from the free-spin value indicating a strong axial distortion of the molecule²⁰. These values suggest a tetragonally distorted octahedral structure with D_{4h} symmetry.

On the basis of analytical, conductivity, magnetic susceptibility, TG, DT, infrared, electronic and ESR spectral data, octahedral stereochemistry may be proposed for all the complexes. In the case of Mn(II), Co(II), Ni(II) and Cu(II) complexes, polymeric structures have been proposed in view of higher insolubility and participation of lactone carbonyl in coordination. Structures II and III are proposed for the complexes.



II $M = \text{Cu (II)}, \text{Ni (II)}, \text{Co (II)} \text{ \& } \text{Mn (II)}$



III $M = \text{Fe (II)} \text{ \& } \text{Zn (II)}$

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