

## Studies on Iron(II) and Manganese(II) Complexes with 2'-Hydroxychalcone

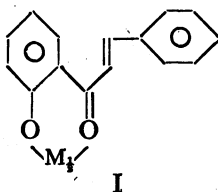
M. IRUDAYASAMY AND S. NAGARAJAN\*

*Department of Chemistry, Bharathidasan University,  
Tiruchirapalli-620 024, India.*

Fe(II) and Mn(II) bis-chelates of the type  $ML_2$ , where  $L = 2'$ -hydroxychalcone have been prepared and characterised on the basis of elemental analyses, conductance, magnetic susceptibility, electronic and infrared studies. Both the complexes have been found to be monomeric, low spin and square planar in configuration.

### INTRODUCTION

The biological activities, analytical applications and the formation constants of 2'-hydroxychalcone and its derivatives have been extensively reviewed quite recently<sup>1</sup>. The chelating action of 2'-hydroxychalcone has been reported for Cu(II), Co(II) and Ni(II)<sup>2</sup>. This paper deals with the preparation of complexes (I) of 2'-hydroxychalcone with Fe(II) and Mn(II) ions.



$M = Fe^{2+}, Mn^{2+}$

### EXPERIMENTAL

#### Materials and Methods

Benzaldehyde used was of reagent grade (SM), while ferrous ammonium sulphate and manganous chloride used were of AnalaR grade (BDH). Elemental analyses for two complexes were carried out at the I.I.Sc., Bangalore. The metals were estimated by volumetric procedure after decomposing the complexes with a mixture of conc.  $HNO_3$  and  $H_2O_2$ . Molecular weights were determined cryoscopically using diphenyl as solvent. Molar conductivities were obtained on  $ca\ 1 \times 10^{-3}$  M nitrobenzene solution in a Toshniwal conductivity meter. Magnetic susceptibilities were measured in a Gouy balance after appropriate calibration against the standard complex  $Hg[Co(NCS)_4]$ . Electronic spectral measurements were recorded on the solution of Fe(II) and Mn(II) complexes in chloroform as well as pyridine in a Carl Zeiss SPECORD UV-VIS

double beam recording spectrophotometer while the IR spectra (4000–200  $\text{cm}^{-1}$ ) were recorded in the KBr pellets at the I.I.Sc., Bangalore.

2-Hydroxyacetophenone was prepared by Fries rearrangement<sup>3</sup> and 2'-hydroxychalcone prepared by condensing the 2-hydroxyacetophenone with benzaldehyde in the presence of sodium hydroxide solution<sup>4</sup>.

(a) *Iron (II) chelate*  $\text{FeL}_2$ : A mixture of 2'-hydroxychalcone (10 m mol) in absolute alcohol (50 ml) and 1N aqueous NaOH (2 ml) was added slowly with constant stirring to a solution of  $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$  (5m mol) in water (100 ml) (a few drops of conc.  $\text{H}_2\text{SO}_4$  added to prevent the formation of hydroxide). The precipitated complex was filtered, washed with aqueous ethanol (1 : 1 v/v) and dried in vacuum over anhydrous  $\text{CaCl}_2$  (yield ca 70%).

(b) *Manganese (II) chelate*  $\text{MnL}_2$ : To a solution of  $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$  (5m mol) in water (100 ml) was added with constant stirring, a mixture of 2'-hydroxychalcone (10m mol) in absolute alcohol (50 ml) and 1N aqueous NaOH (2 ml). The precipitated solid was filtered, washed and dried as mentioned in the previous case. (yield ca 75%).

## RESULTS AND DISCUSSION

The iron (II) chelate appears to be orange brown whereas the manganese (II) chelate is dark brown in shade. Both are soluble in benzene and chloroform. The complexes have been assigned the general formula  $\text{ML}_2$  based on elemental analyses (Table 1). The complexes are non-electrolytes in nitrobenzene<sup>5</sup> as the molar conductance is of the order of 2  $\text{ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$ . Molecular weight determination by the cryoscopic method for both the complexes corresponds to monomeric species.

TABLE 1  
ANALYTICAL DATA AND MAGNETIC MOMENTS OF BIS  
(2'-HYDROXYCHALCONATO) METAL (II) COMPLEXES

Formula	Colour	Found (%)			Calcd. (%)			$\mu_{\text{eff}}$ (B. M.)	Molar conductance $\text{Ohm}^{-1} \text{cm}^2 \text{mole}^{-1}$	Mol. wt.	
		M	C	H	M	C	H			Found	Calcd.
$\text{FeL}_2$	Orange Brown	10.98	71.71	4.13	11.13	71.83	4.38	3.241	1.8	498.3	501.85
$\text{MnL}_2$	Dark Brown	10.73	71.48	4.52	10.96	71.86	4.39	3.620	2.3	501.7	500.94

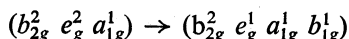
The magnetic moments of the complexes are listed in Table 1. The  $\text{Fe(II)}$  complexes has  $\mu_{\text{eff}}$  of 3.241 B.M. at room temperature (28°). This moment does not correspond to the spin-only moments of either the spin free configuration ( $b_{2g}^2 e_g^2 a_{1g}^1$ ) or the partial spin-paired configuration

( $b_{2g}^2 e_g^2 a_{1g}^1$ ) of respective  $\mu_{\text{eff}}$  values 4.899 B.M. ( $S = 2$ ) and 2.828 B.M. ( $S = 1$ ). As  $b_{1g}$  orbital is inaccessible in partial spin-paired state, it leads to a  $E_g^3$  term with a spin only moment of 2.828 B.M. The magnetic behaviour expected for that term compares well with the experimental result ( $\mu_{\text{eff}} = 3.241$  B.M.) since magnetic exchange interaction between adjacent molecules is possible alongwith orbital contribution<sup>6</sup>. The magnetic moment recorded for this sample can therefore be taken to correspond to square-planar environment with  $E_g^3$  term.

The  $\mu_{\text{eff}}$  for Mn(II) complex is 3.620 B.M. This is quite close to the partial spin pairing state ( $S = 3/2$ ). The experimental value more or less approaches the expected value ( $\mu_{\text{eff}} = 3.87$  B.M.). Hence, the value of  $\mu_{\text{eff}}$  noted for the Mn(II) complex is suggestive of the fact that the complex is in a square-planar environment with the ground term  $^4A_{1g}$  ( $b_{2g}^2 e_g^2 a_{1g}^1$ ).

The ligand field spectrum of Fe(II) complex in chloroform exhibits a broad shoulder around 528 nm. This leads to the proposition that Fe(II) may be in a square-planar environment and the ligand field band can be traced to a transition from the partially spin-paired ground term  $^3E_g$  ( $b_{2g}^2 e_g^3 a_{1g}^1$ ) to the  $b_{1g}$  ( $d_{xy}$ ) orbital. The above transition is  $d-d$  in character. The broad shoulder near 528 nm gets shifted to 681 nm when the solvent is changed to pyridine.

The spectrum of Mn(II) complex displays a broad shoulder like absorption band near 554 nm and a very weak shoulder around 363 nm in chloroform. The high energy band may be assumed to be a charge-transfer one whereas the band near 554 nm may be assigned to a  $d-d$  transition from the partially spin-paired ground term  $^4A_{1g}$  ( $b_{2g}^2 e_g^1 a_{1g}^1$ ) to the  $b_{1g}$  ( $d_{xy}$ ) orbital i.e.



This may be consistent with a trans square-planar environment for Mn(II) complex.

The characteristic stretching vibrations of the ligand and the metal (II)-2'-hydroxychalcone complexes are recorded in Table 2. The assignment of the infrared bands observed in these complexes is more or less similar to that of metal (II)-2'-hydroxychalcone complexes.  $\nu_{\text{C=O}}$  occurs as an intense band in the 1627–1640  $\text{cm}^{-1}$  region for the metal-chalcone complexes and  $\nu_{\text{C=C}}$  is submerged in it<sup>7</sup>. A very small increase of 2  $\text{cm}^{-1}$  is observed in the  $\nu_{\text{C=O}}$  of the Fe(II) complex corresponding to the ligand whereas a large increase of about 45  $\text{cm}^{-1}$  is noticed in the case of Mn(II) complex. This can be explained on the basis of distortion of square-planar structure. It is likely that in the Mn(II) complex, the  $dsp^2$  hybridization may be tending towards  $sp^3$  hybridization resulting in distortion of bond angle of the carbon of the carbonyl with the other two carbons (one in phenyl and the other in alkene)<sup>8</sup>. This significant increase

TABLE 2  
 INFRARED VIBRATIONAL FREQUENCIES ( $\text{cm}^{-1}$ ) OF  
 2'-HYDROXYCHALCONE AND ITS METAL COMPLEXES

M	$\nu(\text{C}=\text{O})$	$\nu(\text{Ph}-\text{C}=\text{C})$	Ph-C-C in-plane	Phenolic C-O <sup>a</sup>	$\nu(\text{M}-\text{O})$
H	1640	1575	9486	1365, 1340	580 <sup>b</sup>
Fe	1642	1573	1485	1370, 1340	580
Mn	1685	1600	1458	1365, 1318	615 br

a : Mean taken for comparison

b : Ligand vibration

br : broad

is due to the bond angle variation from  $120^\circ$  for  $\text{C}-\text{CO}-\text{C}$  to a lesser value (below  $120^\circ$ ). Hence Mn(II) complex may be equilibrating between square-planar and tetrahedral structures based on the shift of  $\nu_{\text{C}=\text{O}}$ . In view of the extended conjugation, one would expect a much lower  $\nu_{\text{C}=\text{O}}$  value in these compounds; but a relatively higher value is observed. The  $\pi_3^*$  orbital of the conjugated system including the phenyl group of the chalcone complexes is found delocalized over the carbon nuclei<sup>9</sup>. As a result,  $d\pi-p\pi$  back-bonding involving these orbitals could cause a very small change in  $\text{C}=\text{O}$  bond order in the chalcone complexes and this is reflected in the very small decrease in  $\nu_{\text{C}=\text{O}}$  on co-ordination.

The effect of mesomeric electron release by the phenyl group is to increase the negative charge on the oxygen atom and caused a general strengthening of the  $\text{M}-\text{O}$  bonds. Super-imposed on this effect, there would be an increased tendency toward  $\pi$ -bonding in the  $\text{M}-\text{O}$  linkages. It can be seen that both these effects would strengthen the  $\text{M}-\text{O}$  and  $\text{C}-\text{C}$  bonds more than the  $\text{C}=\text{O}$  bond of the chelate ring<sup>10</sup> which would lead to significant shifts in the phenyl vibration. The intense band noticed in the region of  $1550-1600 \text{ cm}^{-1}$  can be traced to the phenyl-alkene vibration<sup>7</sup> and is found to be metal sensitive. This frequency varies as  $\text{Mn} > \text{Fe} \approx \text{H}$  which is also the sequence for  $\nu_{\text{C}=\text{O}}$ . There are also changes in the phenyl vibrations observed in the  $1445-1495$  and  $1465-1515 \text{ cm}^{-1}$  regions. These variations may reflect on the participation of the phenyl ring in mesomeric interaction with the metal. The phenolic carbonyl stretching vibration  $\nu_{\text{C}=\text{O}}$  occurs as an intense doublet in the  $1332-1370 \text{ cm}^{-1}$  region. The ligand field in complexes determines  $\text{M}-\text{L}$  vibration. Since the chalcone possesses higher ligand field strength,  $\nu_{\text{M}-\text{O}}$  must be greater for the chalcone complexes<sup>11</sup>. Thus, the band around  $600 \text{ cm}^{-1}$  in the IR spectra of the complexes is found to be metal sensitive and is tentatively assigned to  $\nu_{\text{M}-\text{O}}$ . The shift above  $600 \text{ cm}^{-1}$  for Mn(II) can be explained on the basis of mass number considerations. The close

agreement of the various frequencies of Fe(II) and Mn(II) complexes with those of Cu(II), Ni(II) and Co(II) chalcone complexes<sup>2</sup> may give support to the square-planar configurations for these complexes.

### ACKNOWLEDGEMENT

The authors are thankful to Prof. D. Venkapayya, Head of the Department of Chemistry, Regional Engineering College, Tiruchirapalli for valuable discussion and help in recording magnetic susceptibility and also to Mr. P. Suriyanarayanan, Teacher fellow (F.I.P.), I. I. Sc., Bangalore for his help in carrying out elemental analysis and recording IR data.

### REFERENCES

1. D. N. Dhar, *The Chemistry of Chalcones and Related Compounds*, Wiley-Interscience, New York (1981).
2. M. Palaniandavar and C. Natarajan, *Aust. J. Chem.*, **33**, 737 (1980).
3. A. I. Vogel, *Practical Organic Chemistry*, Longman, London p. 676 (1959).
4. V. I. Dubnitskaya, E. T. Oganesyana and A. L. Shinkarenko, *Izv., Sey. Kavk. Nauchn. Tsentra Vyssh Shk. Sev. Estestv. Nauk*, **3**, 74 (1975), *Chem. Abstr.*, **83**, 205884b (1975).
5. Sutton, *Aust. J. Chem.*, **12**, 122 (1959).
6. B. N. Figgis, *Introduction to Ligand Fields*, Wiley-Eastern Limited, New Delhi, p. 318 (1976).
7. L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Methuen, London, p. 89 (1966).
8. ———, *Advances in Infrared Group Frequencies*, Methuen, London, p. 132 (1968).
9. J. B. Hendrickson, D. J. Cram and G. S. Hammond, *Organic Chemistry*, McGraw-Hill, New York, p. 146 (1970).
10. K. Nakamoto, Y. Morimoto and A. E. Martell, *J. Phys. Chem.*, **66** 346 (1962).
11. C. G. Percy and D. A. Thornton, *J. Inorg. Nucl. Chem.*, **35**, 2719 (1973).

Received: 3 May, 1988; Accepted: 5 March, 1989]

AJC-36