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Studies on Complexes of Mn(II) and Cu(II) with 2-Thiophene Hydroxamic Acid

SANJAY KUMAR SINGH†, SHIKHA SINGH†, S.C. SINGH†
and RAJESH DHAKAREY*
Department of Chemistry, R.B.S. College, Agra-282 002, India

The complexes of Mn(II) and Cu(II) with 2-thiophene hydroxamic acid have been synthesised and characterised by elemental analysis, magnetic susceptibility measurements, IR and electronic spectral data. An octahedral geometry has been assigned to all the isolated complexes.

Key Words: Mn(II), Cu(II), Complexes, 2-Thiophene hydroxamic acid.

INTRODUCTION

Hydroxamic acids are an important class of organic molecules playing a key role in many chemical/biochemical, analytical, pharmaceutical and industrial fields[1-6]. An oxime function (>NOH) with a very easily anchoring acidic nitrogen is a very effective binding site for Mn^{2+} and Cu^{2+} ions[7-10]. When protonated the hydroxyl moiety of the oxime group may be involved in a very effective way and specific hydrogen bond, when deprotonated, can act as a bridging donor between metal ion in oligomeric species.

EXPERIMENTAL

2-Thiophene hydroxamic acid (THA) was prepared by the reported method[11]. All other reagents used were of AR grade.

Preparation of Metal Complexes

The metal acetate/chloride (0.005 M, 15 mL) in ethanol was added dropwise to a solution of the ligand 2-thiophene hydroxamic acid. (0.01 M, 25 mL) in the same solvent. The resulting mixture was stirred for 30 min and refluxed for 1.5 h on a water bath; 2 mL ammonia solution was slowly added to this solution and again refluxed for 1 h. After this the hot solution was filtered and the filtrate was kept at room temperature for crystallization. The crystals were obtained after 24 h, washed with water, alcohol and followed by ether. Finally the crystals were dried over P_2O_5 in a vacuum desiccator.

†Department of Chemistry, C.L. Jain College, Firozabad-283 203, India.

The elemental analyses of carbon, hydrogen and nitrogen were done on CHN microanalyzer. Infrared spectra of metal complexes were recorded in KBr on Perkin-Elmer 577 spectrophotometer in the region *ca.* 4000–200 cm^{-1} at RSIC, CDRI, Lucknow. Magnetic susceptibility measurements of the synthesized complexes were carried out at room temperature on EG&G Model 155 VSM (vibrating sample magnetometer) at RSIC, IIT, Chennai. The electronic spectra of complexes in solution (H_2O/DMF) were recorded on Systronics-106 at room temperature at the Department of Chemistry, R.B.S. College, Agra.

RESULTS AND DISCUSSION

Elemental analysis of the Mn(II) and Cu(II) complexes show 1 : 2 metal : ligand ratio. The physical properties and analytical data are given in Table-1. These complexes are soluble in organic solvents such as DMF and DMSO, insoluble in benzene, ether, acetone and chloroform.

The magnetic moments of the Mn(II) and Cu(II) complexes are given in Table-1. The magnetic moment value is close to the spin only value (5.92 B.M.) for maganese(II) complexes, which is independent of temperature, the stereochemistry indicating the presence of five-unpaired electrons and hence the complexes are of high spin nature. Magnetic studies show the complexes to possess octahedral stereochemistry. The magnetic moment values observed for Cu(II) complexes, *i.e.*, in the range 1.78 to 1.75 B.M. indicate the possibility of octahedral geometry around the copper(II) ion.

The electronic spectra of Mn(II) complexes show the presence of two strong bands *ca.* 20,000 and *ca.* 26500 cm^{-1} corresponding to $^6A_{1g} \rightarrow {}^4T_{1g}(4g)$ (10B + 5C) and $^6A_{1g} \rightarrow {}^4E_g(4D)$ (17B + 5C) transitions and energies has been observed. These transitions are independent of Dq and depend only upon B and C and these have been used to calculate the values for parameters B and C. The value parameter Dq was calculated by the relation Dq/B = 1.1. The values of Slater-Condon-Shortley parameters F_2 and F_4, spin-orbit coupling constant (λ), nephelauxetic parameter for coordinated ligand (hx) and mean pairing energy π have been calculated. The lower value of β indicates the increase in covalent character respectively. The electronic spectra of Cu(II) complexes exhibit two bands in the range 14320–9720 cm^{-1} corresponding to the transitions[12] $^2B_{1g} \rightarrow {}^2A_{1g}(\nu_1)$ and $^2B_{1g} \rightarrow {}^2E_g(\nu_2)$ respectively. The electronic spectral bands observed in Cu(II) complexes are of a distorted octahedral geometry. The approximate value of 10 Dq can be calculated using the mean value of the two peaks. This d^9 system is very sensitive to Jahn-Teller distortion. The electronic spectral data of Mn(II) and Cu(II) are given in Tables 2 and 3 respectively.

Infrared Spectra

A band observed in the infrared spectrum of ligand around *ca.* 3211 cm^{-1} which may be assigned to hydrogen bonded OH stretching[13], disappears on

TABLE-1
PHYSICAL PROPERTIES AND ANALYTICAL DATA AND MAGNETIC MOMENT VALUES OF Mn(II) AND Cu(II) COMPLEXES

Complexes	Physical properties				Analytical data %, Found (Calculated)					μ_{eff} (B.M.)
	m.p. (°C)	Colour	m.w.	State	C	H	N	Cl	M	
$Mn(C_5H_5NO_2S)_2Cl_2$	140	Brown	412.7	Solid (Powder)	27.04 (29.14)	2.52 (2.44)	6.94 (6.79)	17.35 (17.20)	13.41 (13.32)	5.43
$Mn(C_5H_5NO_2S)_2(CH_3COO)_2$	110	Dark brown	459.35	Solid (Powder)	36.73 (36.60)	3.58 (3.51)	6.12 (6.09)	—	11.98 (11.95)	5.41
$Cu(C_5H_5NO_2S)_2Cl_2$	130	Brown	420.78	Solid (Crystalline)	28.62 (28.54)	2.41 (2.39)	6.72 (6.65)	16.88 (16.85)	15.18 (15.10)	1.78
$Cu(C_5H_5NO_2S)_2(CH_3COO)_2$	115	Light brown	467.96	Solid (Powder)	35.96 (35.93)	3.48 (3.44)	5.94 (5.98)	—	13.62 (13.57)	1.75

complexation indicating that proton of the —OH group is replaced by the metal ion upon chelation. A broad band at *ca.*1650 cm^{-1} may be due to (C=O) stretching frequency in the free ligand which is displaced towards lower frequency in the metal complex at *ca.* 1600 cm^{-1}, indicating the coordination through the keto group[14]. A (C—N) stretching frequency at *ca.* 1355 cm^{-1} in the free ligand which is displaced towards higher frequency in metal complex *ca.* 1400 cm^{-1}. The enhancement of the ν(C—N) frequency indicates that coordination of hydroxamic acid occurs through oxygen of carbonyl group. A weak band due to (N—O) stretching frequency in free ligand, *ca.* 944 cm^{-1} gets shifted to higher frequency side *ca.* 1120 cm^{-1} on complexation. Appearance of new bands at *ca* 480, 300 and 1380 cm^{-1} indicates the formation of ν(M—O), ν(M—Cl) and ν(M—CH_3COO) bonds respectively. The important IR frequencies are given in Table-4.

TABLE-2
ELECTRONIC SPECTRAL DATA (cm^{-1}) AND VARIOUS LIGAND FIELD PARAMETERS OF Mn(II) COMPLEXES

Band assignments and parameters	$Mn(C_5H_5NO_2S)_2Cl_2$	$Mn(C_5H_5NO_2S)_2(CH_3COO)_2$
$^6A_{1g} \rightarrow {}^4T_{1g}$	20202	18518
$^6A_{1g} \rightarrow {}^4A_{1g}$	21978	21739
$^6A_{1g} \rightarrow {}^4E_g$	26667	25000
$^6A_{1g} \rightarrow {}^4T_{1g}$	27786	26710
10 Dq (cm^{-1})	7350	7931
B	669	465
C	3057	3721
F^2	1154	995
F^4	87.3	106.3
β	0.77	0.54
λ	164.4	114.2
hx	3.17	6.56
f	0.9235	0.60
π	12029	19130.52
π/B	2.59	2.59

Thus from the IR spectra of metal complexes, the conclusion may be drawn that the ligand is bidentate.

TABLE-3
ELECTRONIC SPECTRAL DATA (cm^{-1}) OF Cu(II) COMPLEXES

S. No.	Complexes	Band position		Assignments	10 Dq
		ν_1	ν_2		
1.	$Cu(C_5H_5NO_2S)_2Cl_2$	14706	16129	$^2B_{1g} \rightarrow {}^2B_{2g}(\nu_1)$ $^2B_{1g} \rightarrow {}^2E_g(\nu_2)$	15417.5
2.	$Cu(C_5H_5NO_2S)_2(CH_3COO)_2$	15267	18692	$^2B_{1g} \rightarrow {}^2B_{2g}(\nu_1)$ $^2B_{1g} \rightarrow {}^2E_g(\nu_2)$	16979.5

TABLE-4
KEY INFRARED FREQUENCIES (cm^{-1}) OF Mn(II) AND Cu(II) COMPLEXES

S. No.	Complexes	Assignments						
		ν(OH)	ν(C=O)	ν(C—N)	ν(N—O)	ν(M—O)	ν(M—Cl)	ν(M—CH_3COO^-)
1.	$Mn(C_5H_5NO_2S)_2Cl_2$	—	1574 s	1425 s	1116 w	526 w	290 w	—
2.	$Mn(C_5H_5NO_2S)_2(CH_3COO)_2$	—	1594 s	1364 s	1117 b	510 w	—	1385 w
3.	$Cu(C_5H_5NO_2S)_2Cl_2$	—	1605 s	1426 s	1118 s	489 s	280 w	—
4.	$Cu(C_5H_5NO_2S)_2(CH_3COO)_2$	—	1603 b	1427 s	1117 m	474 s	—	1384 s

s = sharp; b = broad; m = medium; w = weak.

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