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Manganese(II), Iron(II), Cobalt(II), Nickel(II) and Zinc(II) Complexes of 2-(N-Salicylideneamino)-3-Carboxyethyl-4,5,6,7-Tetrahydrobenzothiophene

S. NIRMALA DEVI* and K. MOHANAN†
Department of Chemistry
Government College. Kariyavattom, Trivandrum-695 581, India

Condensation of 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzothiophene with salicylaldehyde gives a potentially tridentate Schiff base, *viz*., 2-(N-salicylideneamino)-3-carboxyethyl-4,5,6,7-tetrahydrobenzothiophene (HSAT). This Schiff base forms well defined metal complexes, with manganese(II), iron(II), cobalt(II), nickel(II) and zinc(II) ions. The complexes have been characterised by elemental analytical, molar conductance, magnetic susceptibility, UV, IR and NMR spectral data. The spectral studies reveal that the ligand moiety is bonded to the metal ion through the deprotonated phenolate oxygen, azomethine nitrogen and ester carbonyl. Manganese(II), iron(II) and cobalt(II) complexes exhibit 1 : 2 metal-ligand ratio; while nickel(II) and zinc(II) complexes show 1 : 1 ratio.

Key Words: Mn(II), Fe(II), Co(II), Ni(II), Zn(II), Complexes, 2-(N-Salicylideneamino) - 3 - carboxyethyl- 4, 5, 6, 7 - tetrahydrobenzothiophene

INTRODUCTION

Although metal chelates of Schiff bases have been extensively investigated, those of heterocyclic Schiff bases, particularly those containing thiophene ring system have received comparatively less attention.[1] A thorough survey of literature reveals that a few Schiff base complexes derived from thiophene-2-aldehyde and its derivatives with primary amines have been reported.[2–4] but those derived from aminothiophenes have been very less so far. This has been mainly due to the instability of aminothiophenes.[5] However, 2-aminothiophene has been made stable by suitable substitution[6] and the resulting compound, *viz*., 2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzothiophene has been condensed with salicylaldehyde to form a potentially tridentate Schiff base (HSAT), containing an ONO donor set. In this communication we describe the synthesis and characterisation of a series of 3d transition metal complexes with 2-(N-salicylideneamino)-3-carboxy ethyl-4,5,6,7-tetrahydrobenzothiophene.

EXPERIMENTAL

2-Amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzothiophene: This compound was prepared by a reported method.[6]

Synthesis of the ligand: The ligand was prepared by the condensation of

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†Department of Chemistry, University College, Trivandrum-695 034, India.

2-amino-3-carboxyethyl-4,5,6,7-tetrahydrobenzothiophene *with salicylaldehyde* in 1 : 1 molar ratio as detailed below.

To a solution of the amine (0.01 mol) in ethanol (30 mL), added salicylaldehyde (0.01 mol) in ethanol (20 mL). The resulting mixture was refluxed on a water-bath for 1 h. The colour of the solution changed to deep yellow and it was concentrated to about half of its original volume. The golden yellow crystals obtained on cooling the solution were filtered and dried. It was further purified by recrystallisation from ethanol. Yield: 90%; m.p. 155°C.

Synthesis of metal complexes

Manganese(II), iron(II) and cobalt(II) complexes: These complexes were prepared by the following general method: An aqueous solution (20 mL) of the metal salt (0.005 mol) was added to a hot magnetically stirred solution (70 mL) of the ligand (0.01 mol) in ethanol, after adjusting the pH to *ca.* 6.5. The resulting solution was refluxed on a water-bath for about 10 h and then concentrated. The hot solution was allowed to cool and the complex separated was filtered, washed successively with water, ethanol and ether and dried in vacuum.

Nickel(II) and zinc(II) complexes: These complexes were prepared by adopting the same procedure as for the cobalt(II) complex; but the metal-ligand ratio was kept to be 1 : 1 and the refluxing time was 8 h.

RESULTS AND DISCUSSION

The complexes obtained analytically pure are listed in Table-1. All the complexes are fairly stable at room temperature and possess good keeping qualities. Formulation of these complexes has been made on the basis of their elemental analytical data, molar conductance and magnetic susceptibility measurements. Molar conductance values in DMF adequately confirm the non-electrolytic nature of the complexes.

TABLE 1

ANALYTICAL DATA AND MAGNETIC STUDIES OF METAL CHELATES OF HSAT

Complex (Colour)	Analytical data (%), Found (Calcd.)					Magnetic moment (BM)	Molar conductance (in DMF) ($\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$)
	Metal	C	H	N	S		
$[\mathrm{Mn(SAT)_2}]$ (Coffee brown)	7.51 (7.72)	60.30 (60.76)	4.92 (5.06)	3.76 (3.93)	8.87 (9.00)	5.85	13.1
$[\mathrm{Fe(SAT)_2}]$ (Light brown)	7.62 (7.84)	60.15 (60.68)	4.90 (5.05)	3.71 (3.93)	8.75 (8.99)	5.26	12.8
$[\mathrm{Co(SAT)_2}]$ (Purple)	8.31 (8.24)	60.03 (60.42)	4.76 (5.03)	3.65 (3.91)	8.80 (8.95)	4.84	11.6
$[\mathrm{Ni(SAT)NO_3}]$ (Red)	13.18 (13.08)	47.86 (48.13)	3.91 (4.01)	6.01 (6.24)	7.05 (7.13)	Diamag	10.5
$[\mathrm{Zn(SAT)NO_3}]$ (Pale yellow)	14.20 (14.35)	47.26 (47.43)	3.56 (3.95)	6.02 (6.14)	6.89 (7.02)	Diamag	13.4

Structure of the ligand has been established by UV, IR and NMR spectral data. Introduction of a hydroxy group at the position *ortho* to the azomethine group raises the possibility of phenolimine-quinoneamine tautomerism. In the UV spectrum of HSAT, bands have been observed at 250 nm and 320 nm characteristic of the phenol-imine form.[8]

Infrared spectrum of the ligand showed a strong and considerably broad band extending well over 3200–2950 cm^{-1} region and centred around 3100 cm^{-1}, attributable to hydrogen bonded phenolic OH group. An intense band observed at 1700 cm^{-1}, can be assignable to ester carbonyl group. The medium intensity band appearing at 1645 cm^{-1} is due to the azomethine group and the phenolic ν(C—O) is observed at 1280 cm^{-1}. The ester carbonyl group is also involved in hydrogen bonding with the phenolic OH, forming a sort of bifunctional hydrogen bonding. However in the competition with azomethine nitrogen for the phenolic OH, the ester carbonyl can manage only a meagre share. This explains why the ester carbonyl frequency in the Schiff base is relatively higher than that in the free amine (1660 cm^{-1}). Vibrations characteristic of the substituted thiophene nucleus have been observed at 1525, 1420 and 1370 cm^{-1}.

In conformity with the UV and IR spectral data, NMR spectrum of the ligand (recorded in DMSO d_6) has given signal at 12.85 δ, characteristic of strongly hydrogen bonded phenolic proton.[9] Signals for aromatic protons have been observed in the range 6.21–7.91 δ and the signal for hydrogen of the azomethine group has been found at 8.1 δ. Signals for methyl protons and methylene protons of the ester function have been observed at 1.2 δ and 3.7 δ respectively. However, the methyl proton signals have been merged with the signals of ring protons of cyclohexane moiety. The above spectral data adequately confirm that the ligand exists in phenol-imine form in a bifunctionally hydrogen bonded fashion.

Structure of the metal chelates

The UV spectra of the metal complexes have shown only a marginal shift of the characteristic bands observed for the phenol-imine form of the ligand, suggesting that no structural alteration of the ligand occurs on metal chelation. This is also an indirect evidence for the occurrence of strong internal hydrogen bonding in the free ligand (Table-2).

TABLE-2

INFRARED (cm^{-1}) AND UV SPECTRAL DATA OF METAL CHELATES OF HSAT

Complex	ν(C=O)	ν(C=N)	ν(C—O)	ν(M—N)	ν(M—O)	λ_{max} (nm)
$[Mn(SAT)_2]$	1652	1618	1324	515	424	320
$[Fe(SAT)_2]$	1654	1618	1330	512	418	320
$[Co(SAT)_2]$	1650	1620	1325	514	425	320
$[Ni(SAT)NO_3]$	1650	1615	1329	517	420	318
$[Zn(SAT)NO_3]$	1652	1619	1325	512	422	317

Infrared spectra of the metal chelates are closely similar among themselves. In the metal chelates, the broad band ranging from 3300–2950 cm^{-1} clears from this region, indicating deprotonation of the phenolic hydrogen and coordination of phenolate oxygen to the metal ion. The strong phenolic ν(C—O) band at 1280 cm^{-1} of the free ligand has been shifted upwards by *ca.* 45 cm^{-1}, in the spectra of the metal complexes, indicating the bonding to metal ion by the phenolate oxygen.[10] The ester carbonyl stretching frequency of the ligand is depressed by *ca.* 50 cm^{-1}, in the metal complexes. This is a clear evidence for the coordination by ester carbonyl. This type of bonding by ester carbonyl has been reported by several investigators.[11, 12] In the metal complexes, ν(C═N) is decreased by *ca.* 25 cm^{-1}, which is suggestive of coordination by azomethine nitrogen (Table-2). The substituted thiophene ring vibrations[13] of the ligand remain unaffected in the metal complexes and this rules out any possibility of coordination by the ring sulphur atom.

As far as the 1 : 1 complexes are concerned, the species formed after coordination of one molecule of the ligand to the metal ion served as a receptor capable of coordinating a univalent anion. Thus in the case of nickel(II) and zinc(II) complexes, the fourth coordination site has been occupied by a nitrate group. On coordination, the Δν value for the coordinated nitrate group have been found to be 115 cm^{-1} and 125 cm^{-1} respectively. These values clearly indicate that the nitrate group is coordinated in a monodentate fashion.[14]

Far IR spectra of the complexes showed medium intense non-ligand bands in the range 520-510 cm^{-1} and 425-415 cm^{-1}. These can be assigned to ν(M—N) and ν(M—O) vibrations respectively.[15] Thus the infrared spectral data reveal that the ligand acts as monobasic tridentate, coordinating through the phenolate oxygen, ester carbonyl and azomethine nitrogen. Manganese(II), iron(II) and cobalt(II) formed 1 : 2 complexes of the type $[M(SAT)_2]$, while nickel(II) and zinc(II) gave 1 : 1 complexes, represented as $[M(SAT)NO_3]$.

Electronic spectra and magnetic moments

Magnetic moment value of the manganese(II) complex indicated a high-spin octahedral environment around the metal ion. Electronic spectra of this complex exhibited weak absorption bands around 14500, 17050 and 19500 cm^{-1}, which are compatible with a distorted octahedral geometry around the metal ion.[16] The spectrum of $[Fe(SAT)_2]$ gave a weak absorption band at 11050 cm^{-1} which can be due to $^5T_{2g} \rightarrow {}^5E_g$ transition and is characteristic of a high-spin octahedral geometry[17] around iron(II). The spectrum of cobalt(II) complex exhibited two peaks around 9050 and 20500 cm^{-1}, which can be assigned to $^4T_{1g}(F) \rightarrow {}^4T_{2g}$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions respectively.[18] The electronic spectral data together with the magnetic moment value are very much like those reported for other octahedral cobalt(II) complexes which are consistent with an octahedral geometry around the metal ion.

For the nickel(II) complex, d-d transition occurred below 16660 cm^{-1}, which is characteristic of a square-planar or distorted square-planar structure.[19] It has been reported that tetrahedral geometry is the most preferred structure for four coordinated zinc(II) complexes.[20] Hence a tetrahedral geometry has been presumed for the zinc(II) complex.

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