



SPECTRAL AND CHARACTERISATION OF METAL COMPLEXES FROM 2- THIOPHENE ALDEHYDE-2-IMINO GLYCINE

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ABSTRACT

Complexes of Mn⁺⁺, Co⁺⁺, Ni⁺⁺, Cu⁺⁺, Cr⁺⁺⁺, Fe⁺⁺⁺, with 2-thiophene aldehyde-2-imino glycine has been prepared. The structure of the complexes has been established on the basis of elemental analysis. Magnetic moment and infrared, spectra analysis.

Keywords:- Mn⁺⁺, Co⁺⁺, Ni⁺⁺, Cu⁺⁺, Cr⁺⁺, Fe⁺⁺ complexes, 2- Thiophene Aldehyde- 2- Imino Glycine.

INTRODUCTION

Co-ordination compounds of transition and inner transition metal complexes of heterocyclic Schiff bases have now been proved to be very active against several bacterial¹ and fungal² infections in 25 years, high coordination ability³⁻⁷ and Pharmacological activity⁸⁻⁹ of the Schiff bases have played prominent and venerable role in the development of coordination as well as medicinal chemistry. A large number of heterocyclic compounds have valuable properties as chemotherapeutic agents, drugs, copolymers etc. metal complexes derived from heterocyclic Schiff bases¹⁰⁻¹⁶ one known for a large number of Metals such as Cu(II), Ni(II), Co(II), Mn(II), Cr(III), and Fe(III) both amongst aldimines and Ketamines.¹⁷⁻²¹ Various analytical techniques such as magnetic measurements, electronic spectra, infrared spectra, electron spin resonance, massbauer, X-ray diffraction etc. has been proved very powerful tools in the development of transition metal coordination chemistry. Coordination compounds of Schiff bases of heterocyclic aldehyde and amino acids in view of its importance in biological systems. Although heterocyclic aldehydes are frequently used for preparation of Schiff bases but there is no systematic study have been done for the Schiff bases of thiophene-2 aldehyde with glycine and glutamic acid and their metal complexes. Future no systematic studies have been carried out on the effect of length of the skeletal carbon chain or the presence of a side chain in α -amino acids upon the formation of complexes and no studies have been reported on the difference between racemic and L- amino acids in the complexation. We are interested in the study of coordination compounds of heterocyclic aldehydes and amino acids with the view of its importance in biological system and co-related them for molecular structure and stereochemistry with electronic structure and magnetic measurements. An attempt has been made to bring together the theoretical basis for interpretation to the experimental results.

EXPERIMENTAL

All the chemicals used were of high purity (E-Merk, SD's, CDH, Qualigins-A.R. Grade). Metal contents were estimated by using standard methods. Liquid reagents and solvents were carefully purified by

distillation. The complexes prepared were recrystallised with the solvents depending upon their solubilities. The purity was checked by thin layer chromatography.

SYNTHESIS OF SCHIFF BASES

Preparation of 2-thiophene aldehyde-2-imino glycine(2-TAIGLY)

Schiff base was prepared by refluxing calculated amount of 2- thiophene aldehyde (1.25 gm. 10m mol in 25ml ethanol) and glycine (10m mol in minimum quantity of water) on a water bath for 2 hours with constant stirring at 50⁰-60⁰C to get a clear solution. The refluxing material was allowed to cool over night, when Creamish coloured precipitate was obtained. It was washed with ethanol water mixture and finally dried over there.

SYNTHESIS OF COMPLEXES

An aqueous solution of calculated amount of amino acid (10m,mol) was stirred with hot ethanolic solution of 2-thiophene aldehyde (10m, mol 25ml) in equimolar ratio for about 30 minutes. The aqueous ethanolic solution of metal acetate/chloride/sulphate were added to hot ligand solution in 1:1 molar ratio. The reactants were stirred for about 4 hours at 50⁰-60⁰C. The resulting solid products were washed with water-ethanol mixture/ether and dried in air. The purity of the complexes was checked by TLC.

RESULT AND DISCUSSION

The analytical data and Physical data are listed in Table-1. The magnetic moments of Mn(II) complexes showed a value in the range of 5.30-5.41 B.M., which is slightly lower than spin only value of 5.92 B.M. for high spin octahedral Mn(II) complexes. The stereo chemistry of these complexes can also be explained on the basis of electronic spectra. For spin free octahedral complexes of Co(II) complexes having d⁷ configuration, the observed magnetic moment fall in the range 4.30 B.M.- 5.20 B.M. The observed values are higher than the predicted spin only values 3.88 B.M. In high spin Co(II) complexes the ground state term is ⁴Tig(f). This ground state term carries enough orbital contribution and for the octahedral Co(II) complexes, the magnetic moment varies in the range reported earlier²². However, higher experimental values than spin only values can be accounted for considering electron delocalization and a low symmetry ligand field component. The magnetic moment of tetragonally distorted octahedral Ni(II) complexes²³⁻²⁴ magnetic moment of about 3.0-3.5 B.M. independent of temperature is expected²⁵. The experimental values are well within the range reported earlier for octahedral complexes.²⁶⁻²⁷ But are slightly higher than the spin only value of 2.38 B.M. This may probably due to slight distortion from the pure octahedral to D_{4h} Symmetry. The octahedral Ni(II) complex has ³A_{2g} ground state term, which has a considerable mixing with the ³T_{2g} term excited state term. This ground state term carries enough orbital contribution and for octahedral Ni(II) complexes, the magnetic moments due to orbital contribution would have been much more than what are actually measured.

The Cu (II) complexes gave magnetic moments in the range of 1.88-1.92 B.M. compared to one unpaired spin. As is well known Pauling's Valence Bond theory²⁸ assumes that the tetrahedral complexes of Cu (II) owing to their low symmetry have a greater orbital contribution to the magnetic moments. For perfectly tetrahedral structure the Cu (II) complexes are having μ_{eff} values in the range of 1.88-2.00 B.M. The crystal field theory predicts that Cu (II) complexes have a marked orbital contribution to the magnetic moment only when the ground state is orbitally degenerate²⁹⁻³⁰ for a distorted complex, the magnetic moment should be about 2.00 B.M. In the present investigation, the Cu(II) complexes have magnetic moments ~1.97 B.M. revealing octahedral geometry around the Cu(II) ion. These considerations suggest an octahedral configuration in the Cu (II) complexes.

The magnetic moment values of all the Cr (III) complexes at 27⁰C were found in the range 3.68-3.80 B.M. These experimental values of magnetic moments at room temperature though are very well in the range of reported values, yet they are considerably differing from spin only value of octahedral stereochemistry of d³ configuration³¹⁻³³. The small change in the magnetic moment with temperature leads to the presence of ⁴A_{2g} ground term of high spin Cr(III) ion in the present octahedral complexes.

The magnetic moment data show high spin octahedral geometry for all Fe(III) complexes since the magnetic moment values lie in the range 5.95-6.00 B.M. required for octahedral symmetry³⁴, The observed magnetic moment Fe(III) complexes were consistent with the presence of 5 unpaired electrons. Temperature change does not seem to affect magnetic moment to an appreciable extent and this independence of magnetic moment on temperature indicates the presence of ⁶A_{1g} ground term in all the complexes. The magnetic moment data indicate the formation of octahedral complexes by SP³d² scheme of bonding³⁵.

I.R. SPECTRAL STUDIES

In order to investigate structure and nature of the ligand and their complexes and stoichiometries of them, the isolated solids were analysed for their various important component elements. The infrared spectra were recorded to mark the different characteristic groups and bands in them. Comparison of IR data of ligand with those of complexes has been made to investigate structural changes in ligand, if any, during complexation with metal ions and to identify coordination sites.

ABNORMAL BEHAVIOUR OF THE LIGAND TO FORM COMPLEX

From the experimental study, it is confirmed that the ligand can not form complexes with metal ion, when the proton of -OH group forms intermolecular hydrogen bonding with nitrogen atom as in the case of 4-phenyl-2-aminothiazole and substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde³⁶. Therefore, complex is formed by taking 2-thiophene aldehyde, glycine and metal ion at a time (i.e. in situ) our goal is also to study the comparative behavior of glycine forming Schiff base with 2-thiophene aldehyde with various metal ions. The condensation of 2-thiophene aldehyde with glycine was attempted with the intention of preparing corresponding Schiff base. But it was all in vain as the ligand is unable to form complex with metal ion. It is clear from the I.R. spectra of ligand that ν_{OH} absorbs at 3181 cm^{-1} ³⁷ thus incapable of forming a complexes due to intra molecular hydrogen bonding between the proton and nitrogen atom. This marks the deprotonation of -OH group become difficult showing incapability to form complex with metal ion.

Due to insolubility of amino acids in common solvents, infrared spectrum of amino acids are usually taken in the solid states, its presence can be detected by the absorption of NH_3^+ and COO^- groups. Amino acids in the form of zwitter ion do not show N-N stretching at 3200 cm^{-1} , but shown a broad band lower than 3200 cm^{-1} . Lord and Merrifield³⁸ have shown that values of 2425 cm^{-1} for the hydrochlorides of a few tertiary amines examined in the solid state.

On the basis of above discussion, it is evident that metal ion can not be coordinated to the ligand formed due to intra molecular hydrogen bonding between the proton and nitrogen atom and difficulty to deprotonated and from free COO^- group. Therefore, the complexes was synthesised in situ process.

IR SPECTRAL STUDIES ON 2-THIOPHENE ALDEHYDE GLYCINE AND ITS COORDINATION COMPOUND

The IR spectral data with their tentative assignments of the frequencies of Schiff base 2-thiophene aldehyde-glycine abbreviated as 2-TAG and their coordination compounds are presented in Table no.-2.

The IR spectra of Schiff base derived from 2-thiophene aldehyde and glycine shows a band at 3161.1 cm^{-1} assigned as ν_{NH} and ring stretching band frequency band occur in the $1600-1400\text{ cm}^{-1}$ range. The highest frequency band in this region is of thiophene is at 1591 cm^{-1} . This moves to $1523+9$ on 2-substitution. This shows the substitution of substituents at position 2 in thiophene. The second bond of thiophene is present between 1435 and 1400 cm^{-1} is also ring stretching^{39ab}. The $\nu_{C=N}$ frequencies of the metal ion complexes shift towards lower frequencies as compared with those ($1640-1660\text{ cm}^{-1}$) of the free ligand, suggesting that ligands may be coordinated through the nitrogen atom to the metal ion⁴⁰. The band at 411.8 cm^{-1} is due to the C-H⁴¹ shows that complex may have such group. The ν_{C-S-C} band at 1443.6 also suggests about the C-S-C linkage. This frequency lowers, when the ligand gets coordinated with metal ions, showing the possibility of M-S linkage. It is evident from IR study that $\nu_{(C-S-C)}$ is lowered by $10-30\text{ cm}^{-1}$, when metal ion form complex with ligand. The carbonyl group (C=O), the other donor site of the ligand seems to participate in coordination⁴² as its frequency $\sim 1660.6\text{ cm}^{-1}$ is probably shifted towards higher frequency by $10-30\text{ cm}^{-1}$ in all complexes.

The assignment of the C-S band in aromatics has been discussed by Cymmermann and Willis⁴³ and by Allum et al⁴⁴. It appears that the C-S vibration couples very extensively with ring modes and that in consequences no useful group frequencies can be identified. The IR spectra shows two bands at around $= 1568\text{ cm}^{-1}$ and 1468 cm^{-1} region attributed respectively, to the antisymmetric and the symmetric stretching vibrations COO^- ⁴⁵. Below 600 cm^{-1} , we expect the metal ligand stretching frequency $\nu(M-L)$ ⁴⁶. In 2-TAG complexes $\nu(M-O)$, $\nu(M-N)$ and $\nu(M-S)$ are present and coupling between $\nu(M-O)$ and $\nu(M-N)$ will undoubtedly occur. Thus it is not astonishing to find a number of bands below 600 cm^{-1} , which are shifted towards lower frequencies. There are 2-3 bands within the range $370-550\text{ cm}^{-1}$. In general, the intensity of these bands increases with decreasing frequencies. The band due to (M-O) at $\approx 504\text{ cm}^{-1}$. The band near 379 cm^{-1} may be produced due to (M-S)⁴⁷⁻⁴⁸ linkage. A band occur at around 529 cm^{-1} is assigned as $\nu(M-N)$. From the above discussion it is clear that the ligand is tridentate in nature i.e. It coordinates through

carbonyl oxygen sulphur of thiophene and nitrogen atom on complexation with divalent and trivalent metal salts.

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Table-1 Analytical Estimations And Magnetic Moment Value Of The Complexes

S. No.	Compounds	M.P.(°C)	% Found / Calcd							Ueff (B.M.)	Mol. Wt
			C	O	H	N	S	Cl	M		
1	[Mn(C ₇ H ₇ O ₂ NS).3(H ₂ O)]Cl ₂	180 – 183	24.08 (24.10)	22.91 (22.88)	3.753 (3.77)	4.012 (4.02)	9.185 (9.20)	20.31 (20.29)	15.73 (15.80)	5.41	349.09
2	[CO(C ₇ H ₇ O ₂ NS).3(H ₂ O)]Cl ₂	162-165	23.81 (23.73)	22.65 (22.72)	3.711 (3.69)	3.966 (3.95)	9.181 (9.17)	20.08 (20.09)	16.69 (16.58)	4.3	353.08
3	[Ni(C ₇ H ₇ O ₂ NS).3(H ₂ O)]SO ₄	155-160	22.24 (22.20)	38.09 (37.99)	3.466 (3.40)	3.705 (3.40)	16.96 (16.56)		15.52 (15.20)	2.9	378.00
4	[Cu(C ₇ H ₇ O ₂ NS).3(H ₂ O)]Cl ₂	160-162	23.50 (24.97)	22.36 (22.45)	3.663 (3.45)	3.915 (3.78)	8.964 (8.60)	19.82 (19.71)	17.76 (17.54)	1.5	357.69
5	[Cr(C ₇ H ₇ O ₂ NS).3(H ₂ O)]Cl ₂ (CH ₂ COO) ₃	180	34.51 (33.99)	38.90 (38.41)	4.901 (4.70)	3.096 (3.08)	7.088 (7.12)		11.49 (11.51)	3.6	452.37
6	[Fe(C ₇ H ₇ O ₂ NS).3(H ₂ O)]Cl ₂	186-192	24.02 (24.07)	22.85 (22.66)	3.743 (3.81)	4.001 (4.13)	9.161 (9.27)	20.25 (20.21)	15.95 (15.66)	5.6	349.99
7	[Mn(C ₁₀ H ₁₁ O ₄ NS).2(H ₂ O)]Cl ₂	182-185	29.79 (29.52)	23.81 (23.91)	3.750 (6.63)	3.474 (3.37)	7.954 (7.84)	17.58 (17.60)	13.62 (13.53)	5.32	403.13
8	[Co(C ₁₀ H ₁₁ O ₄ NS).2(H ₂ O)]Cl ₂	150-156	29.50 (29.47)	23.57 (23.60)	3.71 (3.80)	3.44 (3.39)	7.87 (7.19)	17.41 (17.37)	14.47 (14.50)	4.1	407.13
9	[Ni(C ₁₀ H ₁₁ O ₄ NS).2(H ₂ O)]SO ₄	150-153	29.79 (27.68)	37.03 (37.09)	3.49 (3.53)	3.24 (3.19)	14.84 (14.90)		13.58 (13.61)	3.1	432.05
10	[Cu(C ₁₀ H ₁₁ O ₄ NS).2(H ₂ O)]Cl ₂	180-184	29.17 (29.21)	23.31 (23.40)	3.67 (3.58)	3.40 (3.39)	7.78 (7.64)	17.22 (17.34)	15.43 (15.32)	1.7	411.74
11	[Cu(C ₁₀ H ₁₁ O ₄ NS).2(H ₂ O)] (CH ₂ COO) ₃	190	37.94 (37.88)	37.91 (37.87)	4.77 (4.69)	2.76 (2.72)	6.33 (6.42)		10.26 (10.30)	3.4	506.42
12	[Fe(C ₁₀ H ₁₁ O ₄ NS).2(H ₂ O)]Cl ₂	160-166	29.72 (29.84)	23.75 (23.68)	3.74 (3.81)	3.46 (3.52)	7.93 (7.84)	17.54 (17.61)	13.82 (13.94)	5.2	404.04

Table-2 Infrared Spectral Data of Legends (Derived From Thiophene-2-Aldehyde And Glycine And Its Metal Complexes)

S. No.	Ligand/ Complexes	Ligand modes				Coordination modes		
		V(C-N)	V(COO)	V(C-S-C)	V(OH)	V(M-O)	V(M-N)	V(M-S)
1	C ₇ H ₇ O ₂ NS	1660m	1464m	1443m	3640w	-	-	-
2	[Mn(C ₇ H ₇ O ₂ NS)(H ₂ O) ₂]Cl ₂	1605m	1478s	1451m	-	513m	477w	397m
3	CO[(C ₇ H ₇ O ₂ NS)(H ₂ O) ₃]Cl ₂	1612m	1410m	1443m	-	515m	461w	371m
4	Ni[(C ₇ H ₇ O ₂ NS)(H ₂ O) ₃]Cl ₄	1629w	1415m	1440m	-	528m	464m	379w
5	Cu[(C ₇ H ₇ O ₂ NS)(H ₂ O) ₃]Cl ₂	1600s	1413m	1450w	-	503m	441w	365w
6	Cr[(C ₇ H ₇ O ₂ NS)(H ₂ O) ₃](CH ₂ COO) ₃	1605m	1422m	1445m	-	515w	452m	379w
7	Fe[(C ₇ H ₇ O ₂ NS)(H ₂ O) ₃]Cl ₂	1610m	1428m	1443m	-	514m	459w	377w