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Synthesis and Characterization of New Mannich Base of 1-[(2-Hydroxy-Phenyl)-Phenyl Amino-Methyl]-Pyrrole-2-5-dione (L) with some Transition Metal Complexes

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Abstract: The present study deals with the structure of some metal complexes of Co(II), Cu(II) and Zn(II) with a new mannich base 1-[(2-hydroxy-phenyl)-phenyl amino-methyl]-pyrrole-2-5-dione (L) which is commonly known as N-[(2-hydroxy-phenyl)-phenyl amino-methyl]succinimide (L). The ligand and the complexes have been characterized by various physical-chemical techniques such as elemental analysis, molar conductance, magnetic susceptibility, infra-red, ultra-violet, ^1H & ^{13}C NMR and TGA/DTA. The corresponds patterns were recorded and discussed.

Keywords: 1-[(2-hydroxy-phenyl)-phenyl amino-methyl]-pyrrole-2-5-dione (L), Metal complexes, Thermal analysis, ^1H & ^{13}C NMR.

Introduction

Mannich base complexes have remained an important and popular area of research due to their simple synthesis, adaptability and diverse range of applications. Many of the mannich base compounds synthesized by the condensation of aldehyde, amine and amide have been recorded. Mannich condensation yields mannich bases which could display more potent pharmacological properties like antipsychotic, anticonvulsant, anthelmintic, antibacterial, antimalarial activities[1-4]. Literature studies revealed that during the past decades, their has been a great deal of interest in the synthesis and structural elucidation of transition metal complexes containing amide moiety. However, there is no study on any metal complexes of N-(1-piperidino salicylyl) acetamide. Earlier work reported that some drugs showed increased activity when administered as metal chelates rather than as organic compounds. The synthesized compounds have been characterized by elemental analysis, IR, UV and ^1H-NMR spectroscopy[5-8]. In the present work, synthesis and characterization of various substituted 1-[(2-hydroxy-phenyl)-phenyl amino-methyl]-pyrrole-2-5-dione (L) and its some metal complexes are synthesized and are characterized using different physico - chemical techniques.

Experimental Methods

Reagents such as salicylaldehyde, aniline, succinimide were of Merck products and were used as such. The melting points of all compounds were determined in open capillaries and uncorrected[9-10]. The elemental analysis of C, H, N, O were carried out at the elemental analyzer namely elemental model ratio EL(III), CECRI - Karaikudi. IR spectra were measured using KBr pellets with Perkin Elmer RX_1 spectrophotometer in the conventional range of 4000 - 400 cm^{-1}. ^1H & ^{13}C NMR spectra of the free ligand and its Zinc(II) complex in

DMSO- d_6 were recorded in a BRUKER, Switzerland Avance 400 MHz NMR spectrometer using Tetra Methyl Silane as internal standard.

Synthesis of ligand (L):

The ligand was synthesized by mannich condensation reaction between salicylaldehyde, aniline and succinimide in 1:1:1 mole ratio. Succinimide (1.47g) was mixed with salicylaldehyde (1.06mL) followed by adding aniline (0.91mL) into the mixture at room temperature with constant stirring for two hours. After 1 and ½ hours yellow colour solid mass was obtained and it was washed with ether. The compound is recrystallized from ethanol (yield: 80%). It melts at 110°C [11-12].

Synthesis of metal complexes:

Hot ethanolic solution of corresponding metal chlorides was slowly mixed with hot ethanolic solution of the respective ligand (1:1 mole ratio) with constant stirring. The mixture was refluxed for 5 - 6 hours at 70 - 80°C and cooling the contents, the coloured complexes were separated out in all the complexes. It was filtered and washed with ethanol and dried at vacuum desiccator (yield: 70 - 75%).

Results & Discussion

Infra-red spectra:

The comparison of the IR spectra of ligand and complexes suggested coordinating atom of the ligand and with metal ion in the complexes. The stretches found at 1706,1646 cm^{-1} in the spectrum of ligand are assigned to C=O stretches of the ligand. In the spectra of the complexes stretch at 1646 cm^{-1} is decreased by about 20 - 30 cm^{-1} and the other one found at 1706 cm^{-1} is increased by about 5 - 10 cm^{-1} suggesting that one of the carbonyl oxygen coordinated the metal ion and other is not. The stretch found at 3300 cm^{-1} which is assigned to N-H stretch of the ligand is shifted to lower frequency suggesting that is nitrogen of N-H group coordinated to metal ion. But due to the overlapping of N-H stretching frequencies of the Cu(II) complex with H_2O molecule, a shift at a higher frequency is observed for the N-H group. The new bands found in the spectra of complexes alone around at 770 - 750, 590 - 550 and 530 - 500 cm^{-1} in the spectra of the metal complexes were assigned to $\nu_{M\text{-}O}$, $\nu_{M\text{-}N}$ and $\nu_{M\text{-}X}$ stretching vibrations respectively. The IR absorption frequencies measured for the ligand and metal complexes are given in Table - 1.

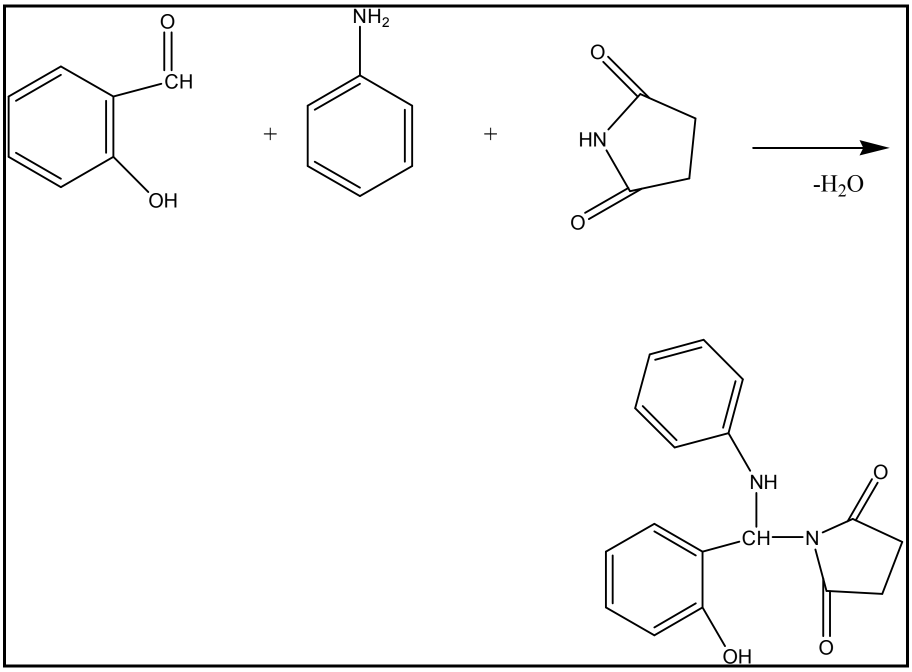

Figure - 1: Formation of mannich base (L)

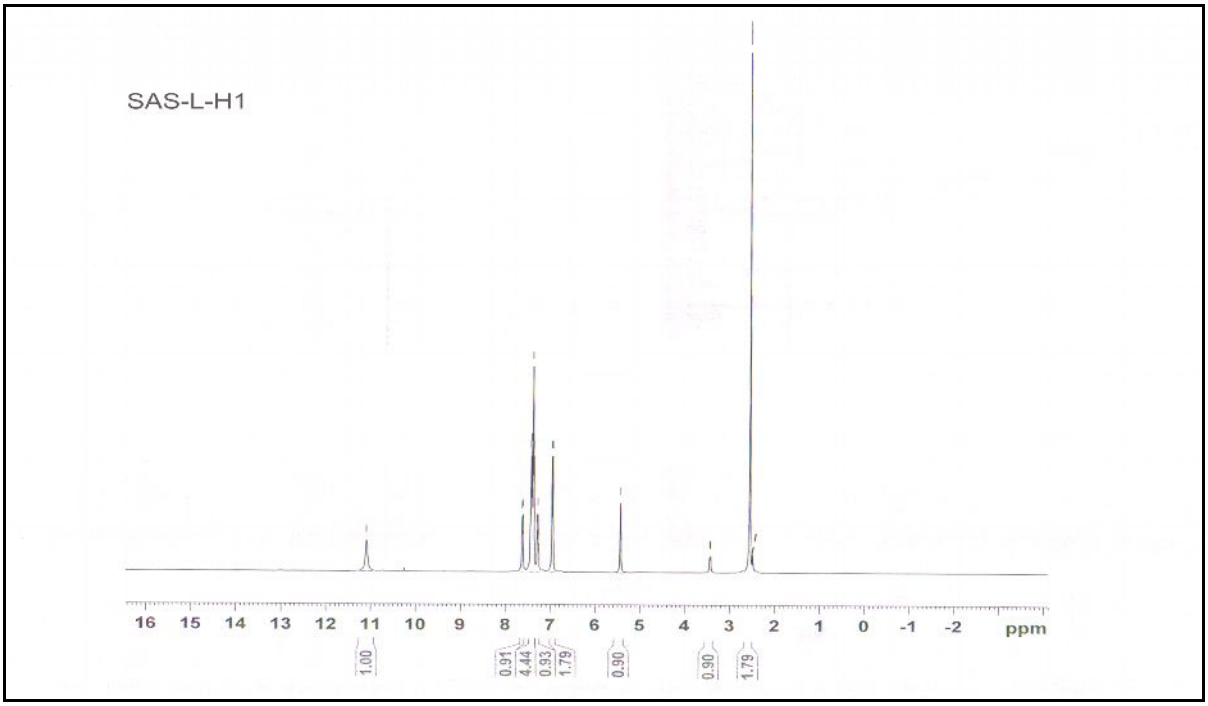

Figure - 2: ^{1}H NMR spectrum of ligand (L)

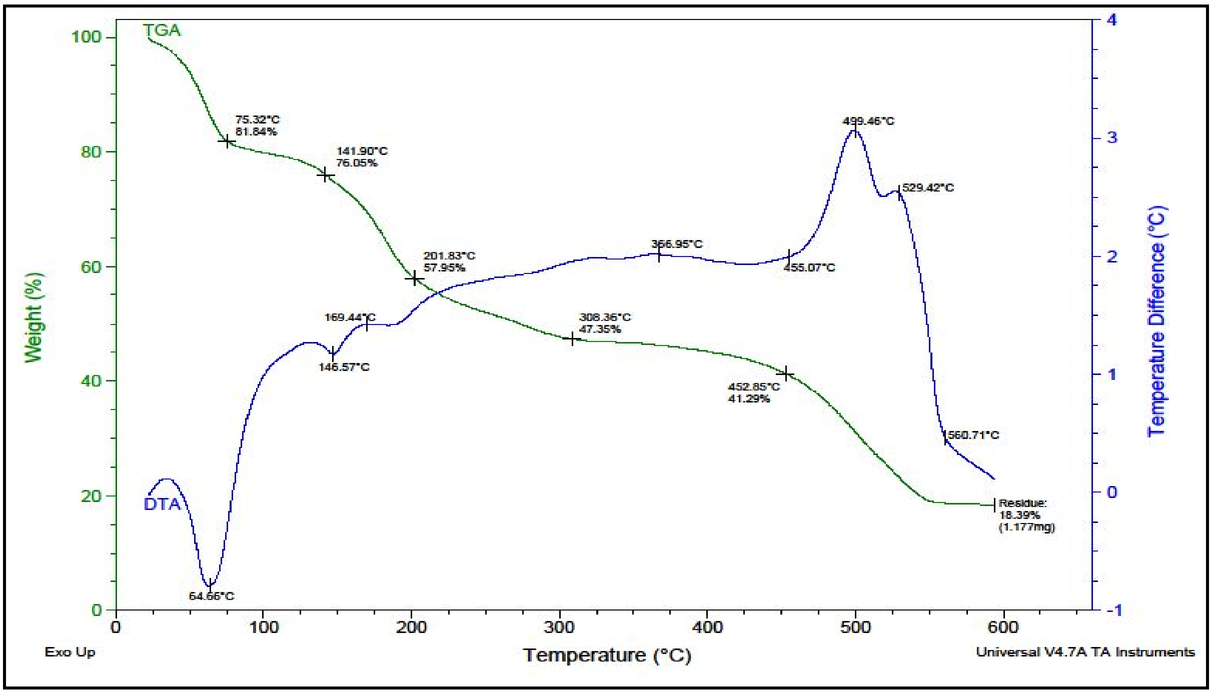

Figure - 3: TGA/DTA pattern of L.$CoCl_2$

Table - 1. IR spectral data of ligand (L) and metal complexes

Compound	$\nu_{C=O}$	ν_{N-H}	ν_{M-O}	ν_{M-N}	ν_{M-X}
L	1646	3300	-	-	-
L.$CoCl_2$	1628	3275	759	589	509
L.$CuCl_2$	1601	3444	770	552	530
L.$ZnCl_2$	1630	3240	757	582	505

Table - 2. Elemental analysis, colour, molar conductance, electronic spectra and magnetic susceptibility of the ligand (L) and metal complexes

Compound	Mol. Formula	Mol. Weight	Absorption Maxima	Transition Assignment	Yield %	Calculated / (Founded)						Colour	µ eff (BM)	Molar Cond.
						C	H	N	O	M	Cl			
L	$C_{17}H_{16}N_2O_3$	296	-	-	80	68.9 (68.4)	5.4 (5.3)	9.4 (9.7)	16.2 (16.0)	-	-	Yellow	-	-
L.CoCl$_2$	$C_{20}H_{28}Cl_2CoN_2O_5$	506	14,786	$^4A_2$ -$^4T_1$(P)	72	47.4 (47.2)	5.6 (5.4)	5.5 (5.4)	15.8 (15.7)	11.6 (11.5)	14.0 (13.8)	Violet	4.5	43
L.CuCl$_2$	$C_{20}H_{28}Cl_2CuN_2O_5$	511	19,215	$^2Eg \rightarrow ^2T_2g$	75	47 (47.2)	5.5 (5.3)	5.5 (5.5)	15.6 (15.7)	12.4 (12.3)	13.9 (13.8)	Brown	1.7	28
L.ZnCl$_2$	$C_{20}H_{28}Cl_2ZnN_2O_5$	513	-	-	75	46.8 (47)	5.5 (5.5)	5.4 (5.1)	15.6 (15.2)	12.7 (12.9)	13.8 (13.7)	Pale yellow	Dia	34

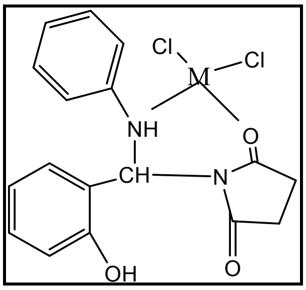

Figure - 4: Structure of L.MCl_2 (M = Co)

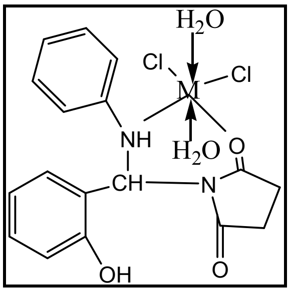

Figure - 5: Structure of L.MCl_2 (M = Cu,Zn)

Electronic spectra:

Electronic spectra and magnetic measurements were recorded in order to obtain information about the geometry of the complexes. The electronic spectra of the Co(II) complex display absorption bands in the regions of 14786 cm^{-1} which may be assigned to $^4A_2$-$^4T_1(P)$ transition respectively which indicates an Tetrahedral geometry. The splitting of the transition is due to spin orbit coupling. The electronic spectra of the Cu(II) complex display absorption band in the region of 19215 cm^{-1} which may be assigned to ^2Eg - ^2T_2g transition respectively which indicates an Octahedral geometry.

The complexes prepared were coloured microcrystalline powders; air stable, some of them are hygroscopic solids, insoluble in common organic solvents, but soluble in DMF and DMSO. The analytical, electronic spectra, colour and magnetic moments are summarized in Table - 2.

NMR spectral data of ligand (L):

^1H NMR (DMSO - d_6, δppm): 11 (OH), 3.4 (Ali - CH), 5.6 (N-H), 2.7 (Ali - CH_2 proton), 6.9 - 8.0 (Aro - CH proton)

^{13}C NMR (DMSO - d_6, δppm): 178 - 180 (Carbonyl carbon), 115 - 135 (Aro - carbon), 48(Ali - CH carbon), 27 - 30 (Ali - CH_2 carbon).

Thermal Analysis

The Co(II) complex is stable upto 75°C. An endotherm observed at ~ 75°C shows the loss of coordinated H_2O to give the anhydrous complex. Decomposition of the anhydrous complex occurs in the temperature range 140 - 450°C to form an intermediate of $CoCl_2$. When heated above 450°C the decomposition of $CoCl_2$ is decomposed to the final residue of CoO. The same is indicated by an exotherm at 530°C.

Conclusion

The new mannich base 1-[(2-hydroxy-phenyl)-phenyl amino-methyl]-pyrrole-2-5-dione (L) and Co(II), Cu(II) and Zn(II) metal complexes were synthesized and Characterized. The structural analysis data established on the basis of elemental analysis (C,H,N,O), Infra-red, UV, ^1H & ^{13}C NMR, Magnetic susceptibility and TGA/DTA patterns of complexes were recorded and discussed.

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