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Chelated tetradentateschiff base complexes of Cu(II), Ni(II), Mn(II) and Co(II): *A Case Study*

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Abstract

Cu(II), Ni(II), Mn(II) and Co(II) complexes were synthesized with *bis*-(salicylaldehyde)malonyldihydrazone a tetradentate ligand (L) and characterized by elemental analysis, molar conductance measurements, magnetic susceptibility, IR, electronic and EPR spectral studies. Metal(II) salts react with Schiff base ligand in 1:1 molar ratio. The ligand and its complexes are stable at room temperature and all of them are nonhygroscopic also. The elemental analysis for carbon, hydrogen and nitrogen were performed by micro analytical methods. Apart from this, the geometry of the newly synthesized compounds has been explained based on their elemental analysis, molar conductivity and spectral data. The molar conductance measurements of all the complexes in DMF solution correspond to electrolytic nature for the complexes except Mn(II) complexes.

Keywords: Malonoyldihydrazone, Salicylaldehyde, Tetradentate ligand, Transition metals,Spectroscopic studies.

Introduction

Schiff bases and their transition metal complexes have been investigated extensively since these types of molecules are important in chemistry and have many applications.[1] A great deal of work has been reported on the synthesis, structural investigations, various crystallographic features, mesogenic characteristics, structure-redox relationships and catalytic properties of different types of Schiff bases and their complexes with transition and non-transition elements**.** [2,3] Malonyldihydrazide and Salicylaldehyde compounds are capable to form complexes with transition metal ions in the form of Schiff bases. The complexes of Nickel(II) and Copper(II) have been prepared and characterized by elemental analysis, molar conductance measurements, infrared and electronic spectra. Henri et al. [4] have synthesized two new Schiff bases derived from 2,3-diaminopyridine and *o*-vanillin and their transition metal complexes (Cu, Ni, Fe, Zn). Rajavel and Krishnan [5] have reported the synthesis and characterization of Oxovanadium(IV) complexes of the Schiff bases derived by the condensation of 2-aminobenzaldehyde with various diamines as 1, 2-diaminoethane, 1, 3-diaminopropane and discussed the spectral data of the complexes. Erdalcanpolat et al. [6] have reported and synthesized a new 5-bromosalicylidene-*p*-aminoacetophenoneoxime and its complexes of Cu(II), Ni(II) and Zn(II). Jian-ning Lu et al. [7] have reported synthesis and

characterization of transition metal complexes. Nair et al. [8,9] have also reported synthesis and characterization of transition metal complexes of Cu(II), Ni(II) and Zn(II).

The present paper aims to synthesize and characterize the chemical structure of Schiff base complexes derived from Malonyldihydrazide and Salicylaldehyde.

Results and Discussion

The stoichiometry of the ligand and its complexes were confirmed by their elemental analysis. The elemental analysis of the ligand and its metal complexes show good support with the proposed structures of the ligand and its complexes (Table-1).

Table-1. Analytical and Physical data of the compound studied

Comp-ound	Empirical Formula	M. W.	C%	H%	N%	M%
			Calc. (Found)	Calc. (Found)	Calc. (Found)	Calc. (Found)
L	C17H18N4O4	342.33	59.68 (59.65)	5.34 (5.30)	16.39 (16.37)	— —
CuL	$Cu(C_{17}H_{16}N_4O_4)$	405.90	50.37 (50.31)	4.07 (4.05)	13.89 (13.80)	15.69 (15.66)
NiL	$Ni(C_{17}H_{16}N_4O_4)$	401.04	50.96 (50.92)	4.05 (4.02)	13.99 (13.97	14.70 (14.64)

(A) Molar Conductance

The molar conductance value (65-90 $ohm^{-1}cm^2mol^{-1}$) of the complexes of Cu(II), Ni(II) and Co(II), which was carried out in DMF solvent indicates that the complexes under study are 1:1 electrolytic nature [10,11]and Mn(II) has nonelectrolytic nature.

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(B) Infrared spectra

The IR spectra provides valuable information regarding the nature of functional group attached to the metal atom. The appearance of a broad strong band in the IR spectra of the ligand in 3431cm^{-1} is assigned to the O-H of the phenol group. Absence of the phenolic O-H vibration indicates that it is deprotonated in complexes. The spectrum of ligand shows two different –C=N bands in the region 1623 cm^{-1},which is shifted to lower frequencies in the spectra of Cu(II), Ni(II), Mn(II) and Co(II) complexes at 1620cm^{-1}, 1590 cm^{-1}, 1600cm^{-1} and 1610 cm^{-1} respectively indicates the involvement of –C=N nitrogen in coordination to the metal ion. [12,13] The occurrence of new bonds in the 410-580 cm^{-1} region in the IR of metal complexes confirm the presence of υM-N and υM-O bands respectively. [14,15] The main IR bands and their assignments are given in Table-2.

Table-2. Characteristic IR bands (cm^{-1}) of the compounds studied

Compounds	υOH	υC=N	υC=O	υM-N	υM-O
L	3431	1623	1750	____	____
CuL	____	1620	1730	485	535
NiL	____	1590	1725	480	520
MnL	____	1600	1715	455	415
CoL	____	1610	1728	410	525

(C) Electronic Spectra

The UV-visible spectrum of the Schiff base ligand and its complexes were recorded in DMSO solution in the range of 200 to 1000 nm regions. The Electronic Spectra suggested Square Planar Geometry[16,17] for Cu(II), Ni(II) and Co(II) complexes (Table-3).

Table-3 Absorption Spectral data (nm) of the ligand and its Complexes

Compound	Absorption(λ_{max})		
	d-d	π -π* Benzene/imino	n- π* Azomethine
Ligand	-	260	370
CuL	536	265	320,430
NiL	505	250	320,390

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(D) EPR Spectra

The room temperature solid-state EPR spectrum exhibits axially symmetric g-tensor parameters with $g_{II} > g_{\perp} > 2.0023$ indicating that the Cu(II) site has a d_{x2-y2} ground state characteristic for square-planar stereochemistry. [18]

Experimental

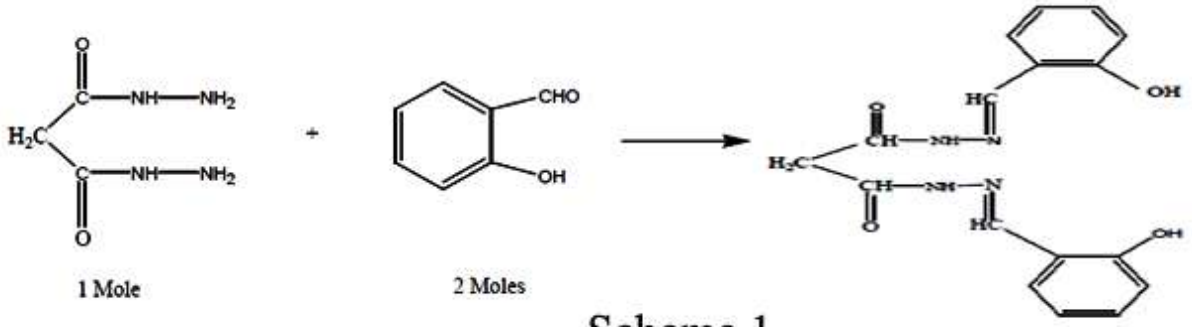
All chemicals used in this research work are reagent grade (Qualigen) including $NiCl_2.6H_2O$, $CuCl_2.2H_2O$, methanol, ethanol, DMSO and DMF. Double distilled water is used.

(A) Synthesis of Malonyldihydrazide

Malonyldihydrazide has been synthesized by reported earlier. [5]

(B) Synthesis of Bis-(Salicylaldehyde)Malonyldihydrazide

The ligand was prepared by reacting a warm dilute ethanol solution of Malonyldihydrazide (0.132 g ; 1 mmole) with Salicylaldehyde (0.21 ml ; 2 mmole). The reaction mixture was refluxed for six hours and suction filtered, washed with ethanol and dried over desiccator. The melting point of the product was found to be 215ºC. The colour of the product was light yellow (yield 75%) (Scheme-1).



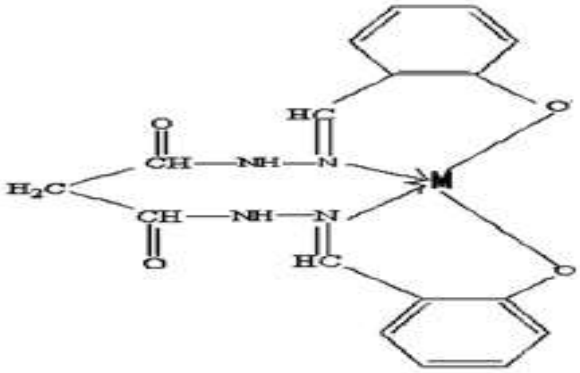
Scheme-1

(C) Synthesis of Complexes

(i) The ligand (0.342g; 1 mmole) was taken in hot ethanol (35 ml) and treated with a methanol solution of $CuCl_2.2H_2O$(0.170g ; 1 mmole). The light yellow transparent solution of the ligand

changed to blue after mixing the solutions. This was refluxed for 12 hours. The crystalline solid was separated out on cooling, filtered and dried over desiccator.

(ii) The ligand (0.342g; 1 mmole) was taken in hot ethanol(35 ml) and treated with a methanol solution of $NiCl_2.6H_2O$(0.237g ; 1 mmole). The light yellow transparent solution of the ligand changed to green after mixing the solutions. This was refluxed for 18 hours. The crystalline solid was separated out on cooling, filtered and dried over desiccator. (Figure-1).



Where: M=Ni(II) & Cu(II)

Figure-1

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