SYNTHESIS AND CHARACTERISATION OF NICKEL (II) NITRATE COMPLEX OF O- VANILLIN

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Abstract

One of characteristic properties of transition elements is their ability to form co-ordination compounds, in which the central metal ions surrounded by several ligands which are attached to it by coordinate cov alent bonds. In the present investigation, the Ni(II)nitrate complex of the ligand 2- hydroxy-3-methoxy benzald ehyde (ortho-Vanillin abbreviated as o-VAN) has been prepared and characterized by elemental analysis, electrical conductance in non-aqueous solvents electronic and infrared spectra and magnetic susceptibility measurement.

Introduction

One of the characteristic properties of transition elements is their ability to form co-ordination compounds, in which the central mental ion is surrounded by several ligands which are attached to it by coordinate covalent bonds. Co-ordination complexes are good catalysts and they play a significant role in industry & life process. Because of the key role in new fields, co-ordination chemistry has an important role in science.

The scope of the chemistry of co-ordination compounds has becomes so great in these days that it is considered to be a separate branch of chemistry.The synthesis and study of coordination compound were once, academic interest, today it has extended to disciplines of science. The reason for the persistent interest in these compounds are many, but the important one among them must be there is case preparation, their diverse properties (physical and chemical), structural aspects and their model systems, which can help understanding several fundamental biochemical processes. One of the most fascinating aspects in the study of coordination compound, in particular those of poly functional ligands is the phenomenon of isomerisation particularly structural or positional isomerism and stereo or space isomerism.

Many of the biological process find its way of application through complex formation. The ligand used in the present study is o-vanillin, a compound of the formula C8H8O3, is distinctly different from its more prevalent isomer, vanillin. It is present in the extracts and essential oils of many plants[5]. It is a weak inhibitor of tyrosinase and displays both antimutagenic and comutagenic properties. However, its net effect makes it a "potent comutagen."ortho-Vanillin possesses moderate antifungal and antibacterial properties and today, it is used in the study of mutagenesis and as a synthetic precursor for pharmaceuticals[5]. The main objective of the present work is the synthesis and characterization of Ni (II) complex of o-vanillin.

In the present investigation, the Ni(II)nitrate complex of the ligand 2- hydroxy-3-methoxybenzaldehyde (ortho-Vanillin abbreviated as o-VAN) has been prepared and characterised by elemental analysis,

electrical conductance in non-aqueous solvents electronic and infrared spectra and magnetic susceptibility measurement.

Materials and Methods

Synthesis of the complex

1.2g of vanillin dissolved in methanol was taken in a beaker and then 0.6gm of the metal salt, Ni (NO3)2.6H2O, dissolved in methanol was added drop wise to it and then refluxed on a boiling water bath for about one hour. It was concentrated to get a viscous mass and then washed repeatedly with Diethyl ether to get the solid complex. The solid so obtained was kept over anhydrous $CaCI_2$.

Estimation of metal

The metal content in the present complex was estimated gravimetrically. About 0.1 g of the complex was accurately weighed and digested with 2 ml H_2SO4, diluted to 50 ml., heated to 70-80ºC and a slight excess of dimethyl glyoxime reagent (6 ml of 2% dimethyl glyoxime) was added followed by dilute ammonia solution. Filtered through a sintered glass crucible. Washed, dried, cooled in a desiccators and from the mass of the complex, percentage of the metal content was calculated.

Analytical and physico- chemical methods

The physico-chemical methods employed in the present investigation for the characterization of the complex were: Estimation of the metal content, Molar conductance in non aqueous solvents, IR and UV spectra and Magnetic susceptibility measurements.(sample mass = 1g: heating rate 70-80ºC).Conductance measurement were done in nitrobenzene, acetonitrile and methanol at 30ºC using a conductivity bridge having a dip type cell with platinum electrodes(cell constant 1.05)and solution of concentration 0.001M. I R spectra were recorded on a Shimadzu I R -470 spectrophotometer in the range 4000 – 400 cm^{-1} using KBr pellet technique and Electronic spectral studies in solid state were carried out on a Shimadzu U.V 2050 spectrophotometer in the range 400- 900 nm. Magnetic susceptibility measurements were done using Sherwood Scientific Magnetic Susceptibility Blance (MK – 1)

Results & discussion

Appearance and Solubility

The complex is brown in color, non hygroscopic, partially soluble in ethanol and methanol, aceto nitrile etc., but insoluble in CC14, diethyl ether, chloroform, benzene, nitrobenzene and ethyl acetate.

Analytical and Physico-Chemical Methods

Estimation of Metal

The metal content of the complex was estimated as described in above. The percentage of Nickel in the complex is found to be very close to the theoretical value (Table 3.1) suggesting the molecular formula as Ni $(0\text{-VAN})_2(NO3)_2$

Compound	Metal	
$Ni(0\text{-VAN})_2(NO3)_2$	**% Theoretical**	**% Experimental**
	11.95	11.83

Table 3.1Analytical Data of Ni (II) Complex of o-Vanillin

Electrical Conductance

Molar conductance values provide us valuable information about the nature of the counter ions present in the complex. In the present study the molar conductance values are measured in nitrobenzene, methanol and acetonitrile. It was found that the conductance values are in good agreement with those values suggested for non-electrolytes (Table 3.2). Thus the structural formula may be represented as $[Ni(0\text{-VAN})_2(NO3)_2]$ where o-VAN is the ligand, ortho-Vanillin.

Compound	Solvent	Molar Conductance*
$[Ni(0\text{-VAN})2(NO3)_2]$	Nitrobenzene	7.30
	Acetonitrile	83.40
	Methanol	55.40

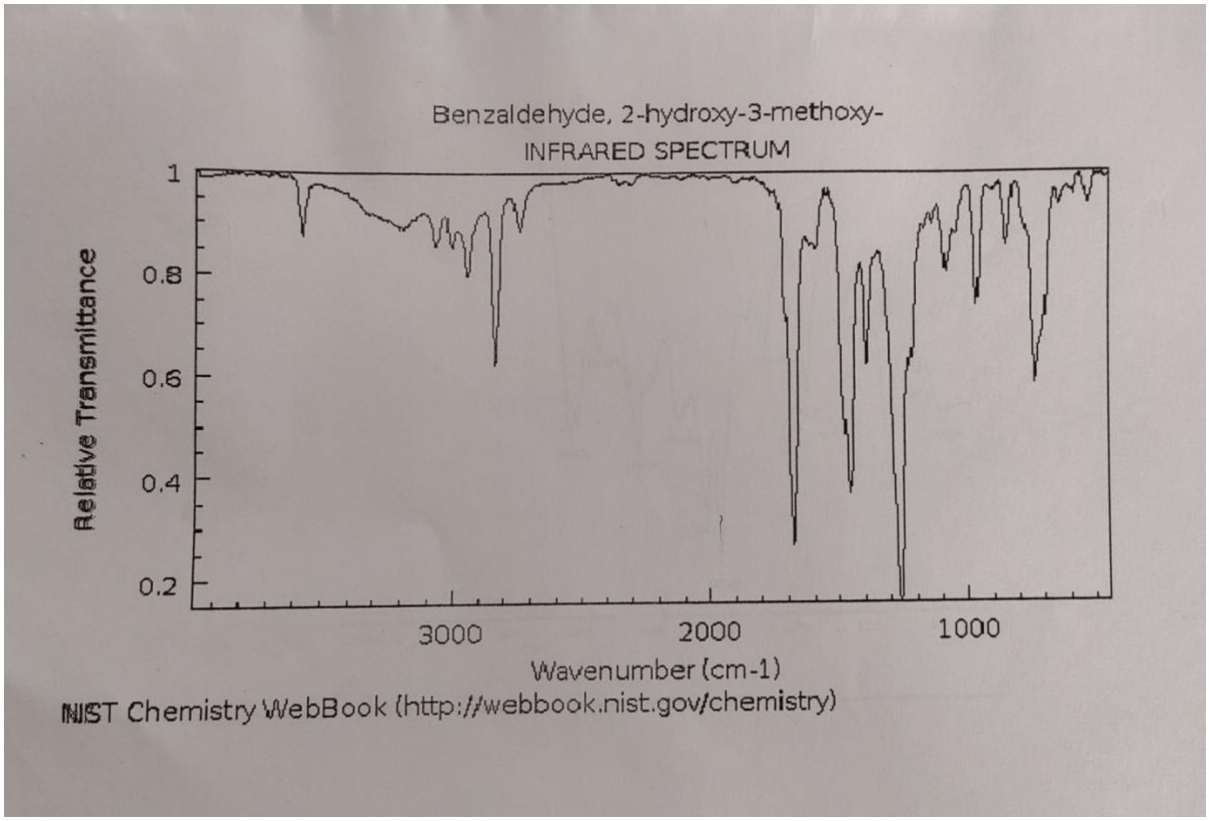
Molar conductance in $ohm^{-1}\ cm^2\ mol^{-1}$

Table 3.2 Molar Conductance Values of Ni (II) Complex of o-Vanillin

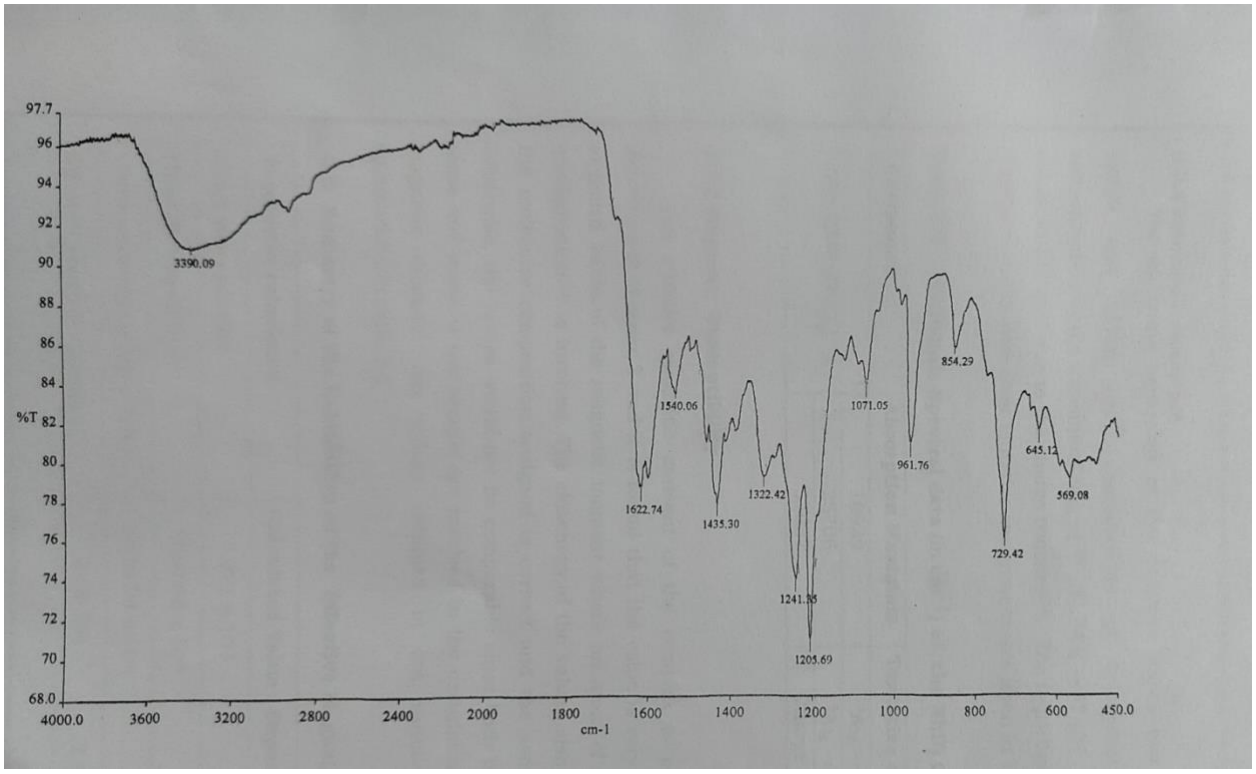
Infra Red Spectrum

The infrared spectrum of the free ligand shows absorptions characteristic of the carbonyl group at 1680 cm^1. But in the complex, the band at 1680 cm^{-1} characteristic of the carbonyl group is shifted to 1623 cm^1 indicating that the carbonyl group is coordinated to the metal ion in this complex. Thus, the ligand act as a neutral monodentate ligand..

The bands observed at 1540and 1322 cm^{-1} are due to the V4 and V_1 vibrations of the nitrate group of C_2, symmetry. The difference in wave numbers between the two highest frequency bands (v_1-v_1) of the C_2, nitrate is around 218 cm^1 indicating that the nitrate group is bidentately coordinated to the metal ion, in this complex. Thus, a coordination number of six may be assigned to the metal ion in this complex.



I R Spectrum of O- Vanillin



I R Spectrum of $[Ni(0\text{-}VAN)_2(NO3)_2)$

The important infrared spectral bands of the ligand and its complex are described in Table 3.3.

Compound	v(C=0)	v4(NO3)	v1(NO3)
O-VAN	1680		
$[Ni(0\text{-}VAN)_2(NO3)_2)$	1623	1540	1322

*in cm^1

Table 3.3 Important Infrared Spectral data* of Ni (II) complex of VAN

Electronic Spectrum

The electronic spectrum of the complex shows two maxima at 18939 and 25706 cm-1 characteristic of octahedral complexes corresponding to the transitions $^3A_{2g} \rightarrow 3T_{1g}/F)$, $3A_{2g} \rightarrow 3T_{1g}(P)$ and another one at 37037 cm^1 due to the charge transfer. The important absorption maxima together with their tentative assignment are given in Table 3.4.

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Compound	Absorption Maximum	Tentative assignment
[Ni(0-VAN)2(NO_3)$_2$]	18939	3A2g →3T1g(F)
	25706	3A2g → ^{3}T1g (P)
	37037	Charge transfer

Table 3.4 Electronic Spectral data (in cm 1) of the Ni(II) Complex

Magnetic Susceptibility

The effective magnetic moment of the complex is calculated as described in above. And it is found that the value is very close to the expected value of the magnetic moment where an atom of d^8 electronic configuration is involved. The closeness of the values also reveals that the molecular composition assigned is correct and the sample is pure. Otherwise, the values would not be comparable since both the molecular mass and mass of the sample are involved in the calculation of effective magnetic moment. The values obtained in the various steps are summarized in table 3.5.

Parameter calculated	Calculated Value	Expected Range
Gram susceptibility	7.271 x 10-6	
Molar Susceptibility	3569.98 x 10-6	
Corrected Molar Susceptibility	3719.98 x 10-6	
Effective Magnetic Moment	2.98 BM	2.8 -4.0BM

Table 3.5 Summary of the Calculation of the Effective Magnetic Moment

Conclusion

Ni(II) complex of the ligand has been synthesized and characterized by elemental analysis, electrical conductance in non-aqueous solvents electronic and infrared spectra and magnetic susceptibility measurement .

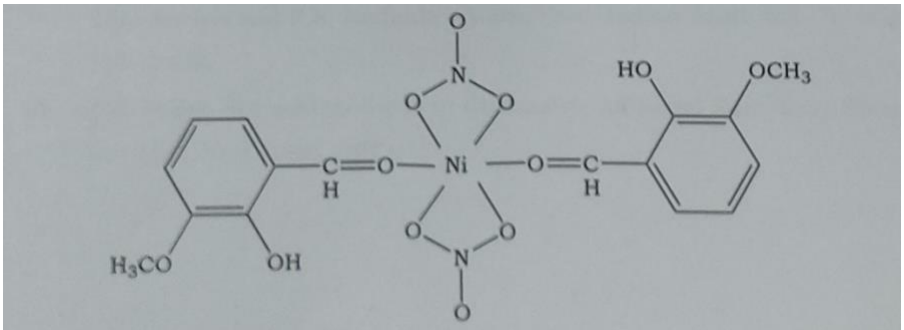
The analytical data suggests that the molecular formula is Ni(0-VAN)$_2$(NO_3)$_2$ and the non-electrolytic nature proposes the structural formula [Ni(o-VAN)$_2$(NO_3)$_2$].

The v(co) of the free ligand is found to be shifted in the IR spectrum of the complex, suggesting that the carbonyl group is co-ordinated mono dentately to the metal ion in this complex. The difference between the frequencies v4 and v_1 attributed to the nitrate ion revealed that the nitrate is bidentately coordinated.

Thus, the conductance values together with the infrared spectral data propose a co-ordination number of six to the metal ion in this complex.

In the electronic spectrum of the complex, absorption maximum is obtained in the region reported for octahedral complexes and Magnetic susceptibility value is in good agreement with the expected value confirming the molecular composition and purity of the prepared complex.

Thus, based on the above mentioned facts may be represented as:



Tentative structure of the Ni(II)nitrate Complex of o-Vanillin

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