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

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ABSTRACT

Key Words:

Nickel (II) Complex, O-Vanillin, Coordination Chemistry

Transition elements are well-known for their unique ability to form coordination compounds due to the availability of vacant d-orbitals, allowing them to bond with a variety of ligands. In this study, a nickel(II) nitrate complex with the ligand 2-hydroxy-3 methoxybenzaldehyde (commonly referred to as ortho-vanillin or o-VAN) was synthesized. The resulting complex was thoroughly characterized using a combination of analytical techniques, including elemental analysis, molar conductance in non-aqueous solvents, electronic absorption and infrared spectroscopy, as well as magnetic susceptibility measurements. These methods provided valuable insights into the composition, geometry, and bonding nature of the complex, contributing to a better understanding of transition metal-ligand interactions.

Introduction

One of the most notable characteristics of transition elements is their ability to form coordination compounds, wherein the central metal ion is surrounded by multiple ligands bonded through coordinate covalent

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interactions. These coordination complexes exhibit a wide range of chemical and physical properties, making them highly effective as catalysts in various industrial processes. Furthermore, their involvement in biological systems and life processes underscores their significance in both inorganic and bioinorganic chemistry. Due to their central role in emerging scientific fields such as materials science, medicinal chemistry, and environmental studies, coordination compounds continue to be a major area of research in modern chemistry.

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,academicinterest,todayithasextendedtodisciplinesofscience.Thereasonforthepersistentinterest 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, 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,todayithasextendedtodisciplinesofscience.Thereasonforthepersistentinterest 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 them ost fascinating aspects in the study of coordination compound,in particular hose of polyfunctional ligands is the phenomenon of isomerisation particularly structural or positional isomerism and stereo or space isomerism.

The role of metal complexes in biological systems is well recognized, with many essential biochemical processes occurring through mechanisms involving coordination compounds. In this context, ortho-vanillin ($C_8H_8O_3$), a positional isomer of the more commonly known vanillin, has attracted interest due to its unique structural and functional properties. Found naturally in various plant extracts and essential oils, o-vanillin exhibits a range of bioactive behaviors, including weak inhibition of tyrosinase, as well as antimutagenic and mutagenic activities, the latter making it a compound of significant interest in genetic toxicity studies. Additionally, it demonstrates moderate antibacterial and antifungal effects and has found applications as a precursor in the synthesis of pharmaceutical agents. The present study focuses on the synthesis and comprehensive characterization of a nickel(II) complex with o-vanillin, aiming to explore its coordination behavior and potential for further biological or catalytic applications.

In this study, a novel Ni(II) nitrate complex incorporating the ligand 2-hydroxy-3-methoxybenzaldehyde (ortho-vanillin, abbreviated as o-VAN) has been synthesized under controlled conditions. The coordination behavior of o-VAN, featuring both phenolic and aldehydic donor sites, offers an interesting framework for complexation with transition metal ions. The synthesized complex was subjected to a detailed characterization protocol involving elemental composition verification, molar conductance analysis in non-aqueous media to assess ionic nature, and spectroscopic investigations including UV-Vis and FTIR to probe the electronic transitions and ligand–metal interactions. Additionally, magnetic susceptibility measurements were carried out to infer the geometry and electronic configuration of the nickel center. These combined techniques provide insight into the structural and bonding features of the complex, contributing to the broader understanding of Schiff base-type coordination chemistry with biologically relevant ligands

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 CaCI2.

Metal Estimation by Analytical Methods

The metal content in the synthesized complex was determined using gravimetric analysis.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 as light excess of dimethylglyoxime reagent (6mlof2%dimethylglyoxime) 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.

Analyticalandphysico-chemicalmethods

A combination of physico-chemical techniques was employed to characterize the synthesized Ni(II) complex. The analysis included gravimetric estimation of metal content, molar conductance measurements in non-aqueous solvents, infrared and electronic spectroscopy, and magnetic susceptibility studies. Molar conductance was determined using a dip-type platinum electrode cell (cell constant 1.05) connected to a conductivity bridge. Measurements were performed at 30°C in methanol, acetonitrile, and nitrobenzene with a complex solution concentration of 0.001 M. Infrared spectra were recorded using a Shimadzu IR-470 spectrophotometer in the 4000–400 cm^{-1} range, employing the KBr pellet technique. Solid-state electronic spectra were obtained using a Shimadzu UV-2050 spectrophotometer in the 400–900 nm range. Magnetic susceptibility was measured at room temperature with a Sherwood Scientific Magnetic Susceptibility Balance (MK-1). For thermal analysis, a sample mass of 1 g was subjected to heating at a rate of 70–80°C per minute.

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 Method

Evaluation of Central Metal Ion

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-VAN)$_2$(NO3)$_2$

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

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 the values suggested for non-electrolytes (Table 3.2).

Thus the structural formula may be represented as [Ni(0-VAN)2(NO3)$_2$] where o-VAN is the ligand, ortho-Vanillin**.**

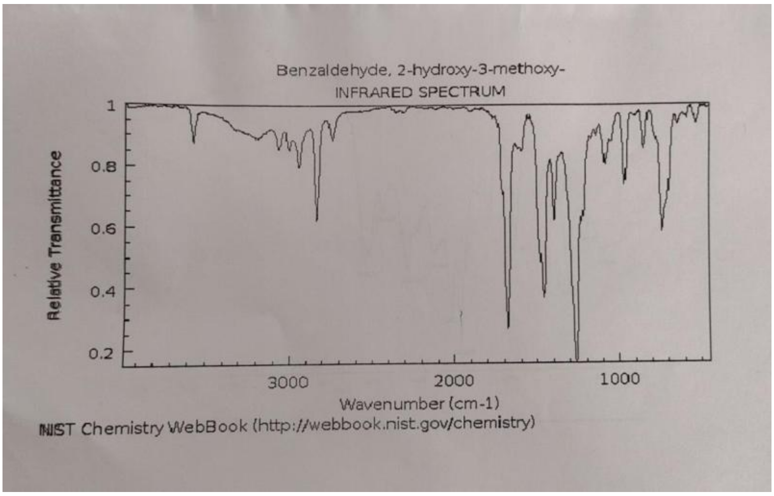
Molarconductanceinohm^{-1}cm^{2}mol^{-1}

Table3.2Molar Conductance Values of Ni (II)Complex of o-Vanillin

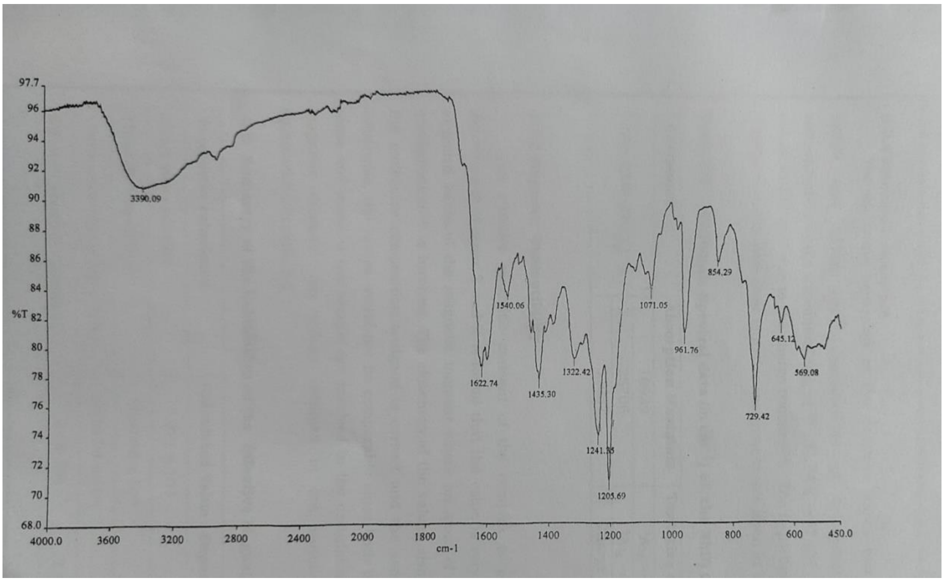
Compound	**Solvent**	**Molar Conductance***
[Ni(0-VAN)2(NO3)$_2$]	Nitrobenzene	7.30
	Acetonitrile	83.40
	Methanol	55.40

InfraRed Spectrum

The infrared spectral analysis provides valuable insights into the coordination behavior of the ligand and nitrate ion in the Ni(II) complex. The free o-vanillin ligand exhibits a strong absorption band at 1680 cm^{-1}, characteristic of the carbonyl (C=O) stretching vibration. Upon complexation, this band shifts to 1623 cm^{-1}, indicating coordination of the carbonyl oxygen to the metal center, confirming the role of the ligand as a neutral monodentate donor. Additionally, the complex displays two prominent bands at 1540 cm^{-1} and 1322 cm^{-1}, attributed to the asymmetric (ν_4) and symmetric (ν_1) stretching vibrations of the coordinated nitrate group. The observed separation of approximately 218 cm^{-1} between these bands suggests a bidentate coordination mode of the nitrate ion, consistent with C_{2v} symmetry. Based on these observations, a coordination number of six is proposed for the nickel(II) ion, likely resulting in an octahedral geometry around the metal center.



IRSpectrum ofO-Vanillin



IR Spectrum of [Ni(0-VAN)$_2$(NO3)$_2$)

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

Table3.3ImportantInfraredSpectraldata*ofNi(II)complex of VAN

ElectronicSpectrum

The U V spectrum of the complex shows two peaks at 18939 and 25706cm-1 characteristic of octahedral complexes corresponding to the transitions ^{3}A2g →3T1g/F), 3A2g→ 3T1g(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.

Compound	**Absorption Maximum**	**Tentative assignment**
$[Ni(0\text{-}VAN)2(NO3)_2]$	18939	3A2g→3T1g(F)
	25706	3A2g→^{3}T1g(P)
	37037	Charge transfer

Table3.4ElectronicSpectraldata (incm1)of the Ni(II)Complex

Magnetic Behavior Analysis

The effective magnetic moment of the synthesized complex was calculated using the standard procedure outlined earlier. The obtained value closely matches the theoretical magnetic moment expected for a Ni(II) ion with a d^8 electronic configuration, which typically exhibits a paramagnetic nature with two unpaired electrons. This agreement between the experimental and theoretical values strongly supports the proposed molecular composition of the complex and affirms the purity of the sample. Any significant deviation in the magnetic moment would indicate possible impurities or inaccuracies in molecular weight determination, as both molecular mass and sample mass are critical factors in the calculation. A summary of the calculated parameters and corresponding values is presented in Table 3.5.

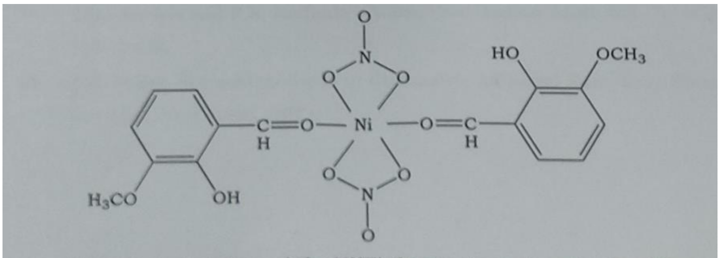
Parameter calculated	Computed Value	Expected Range
Mass Magnetic Susceptibility	7.271 x10-6	
Molar Susceptibility	3569.98 x10-6	
Corrected Molar Susceptibility	3719.98 x10-6	
Effective Magnetic Moment	2.98 BM	2.8 -4.0BM

Table3.5SummaryoftheCalculationoftheEffectiveMagneticMoment

Conclusion

The synthesized Ni(II) complex of o-vanillin was thoroughly characterized using a range of physico-chemical techniques, including elemental analysis, molar conductance in non-aqueous media, infrared and electronic spectroscopy, and magnetic susceptibility measurements. Elemental analysis supported the proposed molecular formula, Ni(o-VAN)$_2$(NO$_3$)$_2$, while the low conductance values in solvents such as methanol and acetonitrile indicated the non-electrolytic nature of the complex, consistent with the neutral structure [Ni(o-VAN)$_2$(NO$_3$)$_2$]. Infrared spectral data revealed a shift in the carbonyl stretching frequency of the free ligand upon complexation, indicating monodentate coordination of the carbonyl oxygen to the metal ion. Furthermore, the nitrate anion displayed characteristic splitting between ν_4 and ν_1 vibrational modes, confirming its bidentate coordination. These observations suggest an overall coordination number of six around the Ni(II) center. The electronic absorption spectrum exhibited bands typical of octahedral geometry, and the observed magnetic moment aligned well with that expected for a d^8 Ni(II) complex, further validating the structural assignment and confirming the integrity and purity of the complex.

Therefore, the structure of the complex can be proposed as follows, based on the collective experimental evidence:



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

References

1. S.F.AKettle,"Co-ordinationCompound",ELBS,(1975).
2. H.A.John and E. Teller, Prox. Sos. London,Ser. A 161,220 (1937)
3. J.E.Huheey,E.A.KeiterandR.L.Keiter"InorganicChemistryprinciplesofstructureand reactivity", 4th edn, Harper Collins, Cambridge (1993).
4. F.A.Cotton(Ed),"Encyclopaediaof InganicChemistry",JohnWiley&Sons,Vol.7 (1990)..5.
5. Watanabe,Kazuko;Ohta,Toshihiro;Shirasu,Yasuhiko.Enhancementandinhibitionofmutation by o-vanillin in Escherichia coli. Mutation Research, DNA Repair (1989), 218 (2), 105–109.
6. VogelA.I“AtextbookofQuantitative Inorganic Analysis,5thEdn. ELBS.

7. W.J.Geary, Coord. Chem. Rev, 7, 81 (1971).
8. Nakamoto"InfraredandRamanSpectraofInorganic&Co-ordinationCompounds",WileyNew York (1986).
9. CurtisN.F&CurtisY.M,Inorg.Chem.(1965) 804.
10. Burger.K,I.TMiller&D.NAllen"Co-ordination Chemistry
11. D.NSathyanarayana"ElectronicAbsorptionSpectroscopyandRelatedTechniques"Univerities Press, (2001)
12. Hathaway B.J, Holah D.Gand Hudson M.J Chem. Soc.(1963)4586.
13. SibyJosephand P.K.Radhakrishnan, Proc.IndianAcad.Sci-110(2) 107 (1998).
14. R.SDrago,PhysicalmethodsinChemistry,AffiliatedEast-WestPressPvt.Ltd.,NewDelhi. (1971).