Chemical Behavior and Conductivity of a Nickel (II) Complex with Diphenylamine

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ABSTRACT

Nickel(II) complexes have attracted considerable attention due to their distinctive chemical behavior and application in various fields, such as catalysis, environmental monitoring, and material science. A nickel(II) complex with diphenylamine as the ligand was synthesized and characterized. The complex was prepared by reacting diphenylamine with nickel nitrate hexahydrate in methanol. UV-Vis spectra revealed a shift in the absorption maxima, indicating complex formation and highlighting diphenylamine as a stronger ligand than water. The empirical formula $Ni(diphenylamine)4(NO_3)2.6H_2O$ was derived from the Atomic Absorption Spectroscopy (AAS) report, which indicated a nickel concentration of 5.90 ± 0.05%. The combination seems to function as an electrolyte, with one nitrate ion coupled to the nickel ion and the other serving as a counter ion, according to electrical conductivity studies, which revealed a 1:1 charge ratio of cation and anion.

Keywords: Nickel, Diphenylamine, Conductivity, Nitrate, Electrical

INTRODUCTION

The electrochemical, structural, and catalytic features of nickel(II)-diphenylamine complexes have made them a hot topic in coordination chemistry. A transition metal with an atomic number of 28, nickel is well-known for its adaptable coordination behavior, capable of building complexes with an extensive array of ligands. Organic ligand diphenylamine (DPA) containing nitrogen and aromatic rings is exceptional among them because of its one-of-a-kind capacity to interact with metal centers. For many chemical reactions, nickel(II) complexes are useful because this ligand, which is normally employed in the production of different metal complexes, significantly improves their stability and reactivity. Research on nickel(II)-diphenylamine complexes has two purposes: first, it sheds light on metal-ligand interactions; second, it suggests ways these complexes might be used in environmental chemistry, materials science, and catalysis.
Thanks to its versatility in oxidation states and coordination geometries, nickel(II) has a well-documented history in coordination chemistry and the formation of several stable complexes. Specifically, the d8 electron configuration of the Ni(II) ion allows it to easily form coordination complexes with many different types of ligands, such as neutral molecules, chlorating agents, and anions. A neutral nitrogen-containing ligand called diphenylamine is commonly used to stabilize nickel complexes. Diphenylamine has a nitrogen atom that coordinates to the nickel center and acts as a donor site. The phenyl groups, on the other hand, offer extra stabilization through π-interactions. The capacity of DPA to chelate metal ions and create stable complexes makes it a desirable ligand for nickel in a variety of coordination settings.

Many structural motifs and reactivity of nickel(II)-diphenylamine complexes have been investigated. Complexes of this kind often display either an octahedral or square planar geometry; the exact shape depends on the coordination environment and any extra ligands present. Complexes with nickel centers can have their electronic characteristics fine-tuned by manipulating the DPA ligand's steric and electrical properties or adding additional ligands to the coordination sphere. Crucial for controlling the complex's reactivity, especially in catalytic reactions, is the capacity to change the electronic configuration of the metal. Aside from their structural variety, nickel(II)-diphenylamine complexes have demonstrated encouraging catalytic activity in many processes, such as hydrogenation, oxidation, and polymerization. Crucial to improving the complexes' catalytic effectiveness is the ligand's capacity to stabilize the metal center and help electron transfer activities.

Analysis of nickel(II)-diphenylamine complexes is primarily driven by their potential environmental uses, namely in the field of pollution degradation and remediation. Catalysts based on nickel are well-known for their capacity to facilitate the oxidative and reductive digestion of toxic substances, including organic contaminants. Enabling the complex to engage in electron transfer events that are necessary for environmental cleaning, the diphenylamine ligand can change the redox properties of the nickel center thanks to its electron-donating qualities. Additionally, these complexes are reactive and stable in water, making them promising candidates for use in water treatment systems to remove hazardous compounds or convert contaminants into less dangerous forms.

Possible uses in materials science have attracted interest in nickel(II)-diphenylamine complexes, which are also important for the environment. Conducting polymers, organic semiconductors, and molecular sensors are just a few examples of the high-tech materials that might benefit from these complexes' potential for electrical property tuning. By adding nickel(II)-diphenylamine complexes to these materials, their electrical characteristics may be improved, opening up new possibilities for the creation of ground-breaking innovations in areas including sensor technology, energy storage, and electronics. These complexes are appealing for developing solution-processable materials due to their stability and solubility in organic solvents; these materials are crucial for industrial-scale production and device fabrication.

In addition, the production of nickel(II)-diphenylamine complexes lends itself to investigations into the basic concepts of coordination chemistry, such as molecular orbital theory, crystal field theory, and ligand field theory. Examining the electronic structure and bonding in these complexes allows researchers to learn more about the variables that affect the stability and reactivity of coordination compounds, how metal ions interact with ligands, and more. Additionally, by studying these complexes, novel ligand design methodologies may be explored. By modifying the diphenylamine ligand, more stable or reactive nickel-based catalysts can be developed for specific applications.

Spectroscopic Techniques

The study of molecular structure, composition, and behavior is greatly enhanced by the use of spectroscopic methods. All of these methods give light on the characteristics of the molecules under investigation by observing how electromagnetic radiation interacts with matter.

1. UV-Visible Spectroscopy (UV-Vis)

Molecular absorption of visible light (400-700 nm) and ultraviolet (200-400 nm) is the basis of ultraviolet-visible spectroscopy. In these areas, light may be absorbed by molecules, which raises the energy level of the electrons already present in the molecule. The molecule's electrical structure determines the wavelengths that are absorbed. The existence of conjugated systems, such π bonds or lone pairs, in both organic and inorganic substances frequently causes unique absorption peaks.

2. Infrared (IR) Spectroscopy

Absorbing infrared light and allowing it to vibrate the molecular bonds is the basis of infrared spectroscopy. The absorption of infrared light causes various bonds inside a molecule to vibrate at frequencies that are proportional to their mass and strength. This causes the infrared spectra to show distinct absorption peaks. The fingerprint area (1500-400 cm^{-1}) and the functional group region (4000-1500 cm^{-1}) are the two primary divisions of the IR spectrum. O-H, C=O, N-H, and C-H stretching—among others—are detailed in the functional group section. Each molecule has its own unique fingerprint area that can authenticate a compound's identification and give precise information about the chemical structure as a whole.

3. Nuclear Magnetic Resonance (NMR) Spectroscopy

To study the magnetic characteristics of atomic nuclei, nuclear magnetic resonance spectroscopy employs radiofrequency radiation and powerful magnetic fields. Some nuclei, like hydrogen (^{1}H) or carbon (^{13}C), have frequencies that are dependent on their chemical surroundings when they are subjected to a magnetic field. This paves the way for the discovery of molecular dynamics, connection, and structure. The chemical shifts of protons in ´H NMR show how close they are to other protons or electronegative atoms like nitrogen or oxygen. The information about nearby nuclei is provided by the splitting of these peaks, which is known as spin-spin coupling. The concepts are identical in ^{13}C NMR, but the carbon atoms in the molecule are the main emphasis.

4. X-Ray Crystallography

For big organic and inorganic compounds, as well as coordination complexes, X-ray crystallography is a potent tool for elucidating their three-dimensional structures. By focusing X-rays on a crystalline sample, this method may determine the electron density distribution inside the crystal by analyzing the resulting diffraction pattern. This allows one to ascertain the locations of atoms and the lengths of their bonds.

5. Mass Spectrometry (MS)

Mass spectrometry is a method that determines the ion concentration in a sample by measuring their mass-to-charge ratio (m/z). It entails ionizing a sample, sorting the ions that come out of it according to their mass-to-charge ratio, and then detecting them to get a mass spectrum. One may infer the molecular structure from the spectrum, which gives information about the molecular weight, compound composition, and fragmentation patterns.

6. Fluorescence Spectroscopy

After absorbing light of a certain wavelength, fluorescent spectroscopy detects the amount of light emitted by a molecule. Molecules exhibit light emission (fluorescence) when they absorb photons, which excite them to a higher energy state. Light that is emitted has a longer wavelength (less energy) than light that is absorbed, and the emission spectra provide important details about the molecule's electrical environment. For substances at low concentrations, fluorescence spectroscopy is the gold standard due to its extreme sensitivity. One way to explore complexes involving nickel(II) and diphenylamine is to use fluorescence spectroscopy to see how the fluorescence changes as the metal ion is coordinated. Because of this, we may learn more about the complex's electrical characteristics and how the ligand and metal center interact with one another.

REVIEW OF LITERATURE

Amalia, Yusica et al., (2021) Reacting Ni(NO3)2•6H2O with 4-aminoantipyrine (AAP) ligand yielded a 1:3 mole nickel(II) complex. Several analytical methods were used to characterize the complex, including thermogravimetry, conductivity tests, IR, TG/DSC, and UV-Vis. The compound is [Ni(AAP)3](NO3)2•5H2O. Through the carbonyl oxygen and nitrogen of the primary amine, AAP coordinated with the nickel ion as a bidentate ligand. The compound's electronic spectra showed two peaks at 646 nm and 385 nm, representing the 3A2g(F) → 3T1g(F) and 3A2g(F) → 3T1g(P) transitions. This material has paramagnetic characteristics, octahedral shape, and an effective magnetic moment (μeff) of 2.96 BM. This compound exhibited much more antibacterial efficacy than the metal and its unbound ligand.

Abdul Rezak, Furhan et al., (2021) We examined the electrical, structural, morphological, and thermal impacts of doping poly(diphenylamine) (PDPA) with nickel oxide (NiO) nanoparticles. The FTIR studies validated the polymerization of diphenylamine with NiO nanoparticles, revealing their unique absorption bands at 445 cm−1. The PDPA/NiO nanocomposites have better crystallinity according to XRD. Electron microscopy and HR-TEM images confirmed NiO nanoparticle uniformity in the polymer matrix. Elements and EDX analysis confirmed the presence of NiO nanoparticles in the PDPA matrix. Outerwear The results of thermogravimetric analysis (TGA) demonstrate that nanocomposites possess exceptional thermal stability, corroborated by the findings of Redfern's thermal activation energy study. The AC conductivity, dielectric loss tangent, and dielectric permittivity were all improved in nanocomposites including NiO nanoparticles with PDPA. The capacity of the synthesized nanocomposites to detect ammonia gas at room temperature was evaluated by monitoring the changes in electrical resistance following exposure to ammonia gas. The results showed that the composite with a 7-weight percent sample shown the highest efficacy in ammonia gas detection. These nanocomposites possess exceptional features that might be highly beneficial in gas sensors and nano-electronic devices.

Dalha, Umar et al., (2021) The Schiff base ligand was synthesized by reacting 2-aminothiophenol with 2-thiophene carboxyldehyde. Complexes of Ni(II) and Cd(II) were subsequently synthesized utilizing this ligand. For this purpose, we analyzed the synthesized ligands and complexes using infrared spectra, molar conductance, magnetic susceptibility, solubility, and thermodynamic degradation. The complexes are broken down using heats of 212 and 220 degrees Celsius, respectively. In particular, the specific capacitance is 12.60 ohm-1 cm-2 mol-1 and the molar conductance is 16.12 ohm-1 cm{-2 mol-1. The ϕ (M-N) and ϕ (M-S) vibrations were indicated by infrared bands in the complexes' spectra, which were seen in the 519-475 cm-1 and 462-448 cm-1 ranges, respectively. In terms of magnetic susceptibility, complexes of nickel (II) are paramagnetic whereas complexes of cadmium (II) are diamagnetic. We know that DMSO dissolves the ligand and complexes because of the solubility test having a metal-to-ligand ratio of 2:1, the study suggests producing complexes having the formula [ML2].liquid, water.The antibacterial capabilities of ligand and metal chelates have been tested against various bacteria and fungi using the well diffusion technique. The results show that metal complexes of nickel (II) and cadmium (II) inhibit the same test organisms more efficiently than Schiff base ligand.

Amalia, Yusica et al., (2019) Diphenylamine and Ni(NO3)2.6H2O were used to create a complex chemical with a methanol-to-metal ratio of 1:6. A shift in the maximum UV-Vis peak wavelength was detected, which pointed to the development of complexes. The analysis of the complex's nickel percentage by Atomic Absorption Spectroscopy (AAS) resulted in the identification of the empirical formula for the chemical as Ni(diphenylamine)4(NO3)2·6H2O. The conductivity test of the complex indicated a one-to-one ratio of cation to anion charges. The NO_3^{-} ion functioned in conjunction with the Ni^{2+} center ion, serving as both an ionic counter and a partner. The suggested chemical formula for the molecule is [Ni(diphenylamine)4(NO3)(H2O)](NO3).5H_2O. Infrared spectra indicate that the monodentate ligand diphenylamine interacts with nickel(II) through the secondary NH functional groups during dissociation. An octahedral structure was suggested by a transition peak observed in the electronic spectra at 25252 cm^{-1} and 13802 cm^{-1}. A μ eff of 2.99 BM is exhibited by the paramagnetic substance.

Kumar, Abhinav et al., (2013) Four potential complexes include Ni(II) diimine dithiolato, especially [Ni(S2C2Ph2)(1,10-Phenanthroline)]. Specifically, 3,3'-dicarboxy-2,2'-bipyridyl Nichrome(S2C2Ph2) (2). Formula for substance (3): Ni(S2C2Ph2)(4,4'-dicarboxy-2,2'-bipyridyl). Fourth element: [Ni(S2C2Ph2)(2,2'-bipyridyl)]. Using microanalysis, UV-Vis, IR, (1)H, and (13)C NMR, five compounds were produced from [Ni(S2C2Ph2)2] (1) and analyzed. The kinetics of charge transport inside these molecules has been attempted to be understood by means of quantum chemical calculations. Scientists have investigated the light-harvesting properties of these compounds by using them as photosensitizers in DSSCs based on TiO2. By shifting the anchoring group's position on the diimine derivative, nickel (II) dithiolate dyes can alter their electrical, structural, and light-harvesting properties.

Khalifa, K. et al., (2010) We synthesize and characterize 2-((4-aminophenyl)imino)-1,2-diphenyl-1-ethanone and its complexes with Cu(II) and Ni(II) ions. Mass, nuclear magnetic resonance, electronic, infrared, and elemental analysis were used to study the ligand and its complexes. The ratio of metal ligands was 1:1. Both complexes had square planar geometry predicted.

EXPERIMENTAL SETUP

Materials

Without additional purification, all of the compounds utilized were of analytical quality.

Physical measurements

The UV-Vis spectra of metal salts and metal complexes were recorded using a UV-Vis Double Beam Shimadzu 1601 spectrophotometer with methanol as the solvent. Atomic Absorption Spectroscopy (AAS) utilizing a Shimadzu AA-6650 was employed to determine the nickel content.

Synthesis of Ni(II) complex

The nickel(II) complex was prepared by dissolving 2.03 g (12 mmol) of diphenylamine in 10 mL of methanol. After that, a 0.58 g, 2 mmol methanolic solution of nickel nitrate hexahydrate was added dropwise to the mixture while stirring constantly for about three hours. The solution was then let to evaporate until its volume was within plus or minus 10 mL. The green precipitate was removed after about 48 hours after filtering, recrystallizing, washing with methanol, and drying under vacuum (1.63 g, 84.33%).

RESULT AND DISCUSSION

Complex formation

As illustrated in Figure 1, the UV-visible spectra of the nickel(II) complex and NiNO3.6H2O in methanol are present. The maximum wavelengths shrank to 724 nm and 396 nm in the ni(II) + diphenylamine compound, from 728 nm and 397 nm in the Ni(NO3)2.6H2O solution. By this shifting, it was shown that the complex was created and that diphenylamine was a more potent ligand than water.

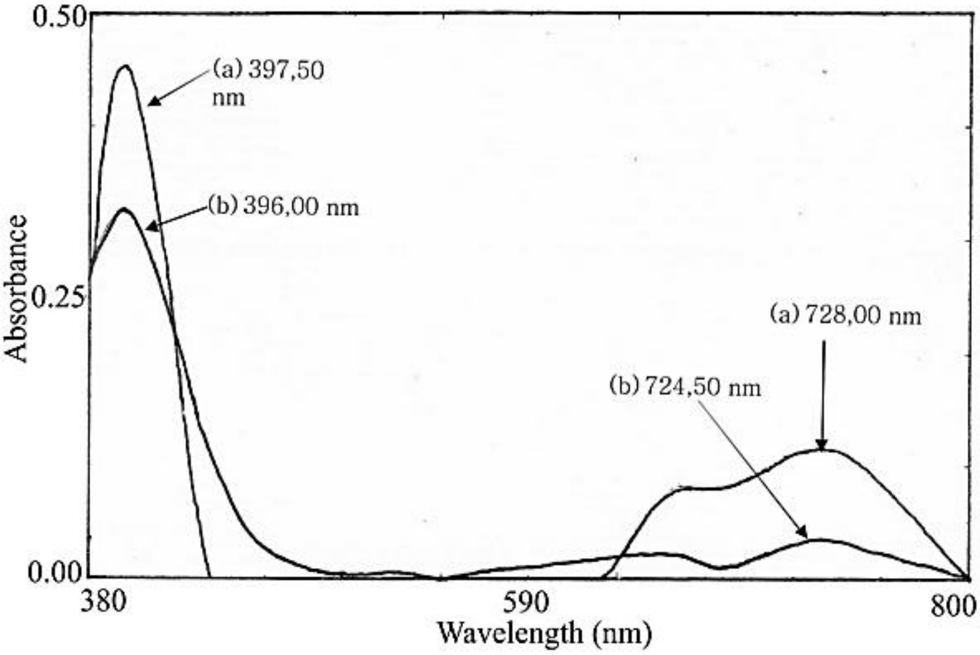

Figure 1. Emission spectra of a Ni (NO3)2.6H2O complex and a Ni(II)-diphenylamine combination in methanol

Analysis of the nickel content with Atomic Absorption Spectroscopy

The AAS measurement for the nickel concentration in the Ni(II)-diphenylamine combination was 5.90 ± 0.05%. Table 1 shows the theoretical nickel concentration, and comparing it to this measurement gives the possibility of a complicated formula. This suggests that Ni(diphenylamine)4(NO3)2.6H2O is a reasonable approximation of the nickel(II) complex formula.

Table 1. Concentration of nickel in the combination with diphenylamine

Empirical Formula	Mr	% Ni
Ni(dpa)4 (NO3)2.4H2O	931.65	6.32
Ni(dpa)4 (NO3)2.5H2O	949.65	6.17
Ni(dpa)4 (NO3)2.6H2O	967.65	6.08

Analysis of electrical conductivity

Table 2 displays the results of the electrical conductivity tests conducted in methanol (10-3 M) and the mixture of Ni(II) and diphenylamine. The Ni(II) complex's electrical conductivity was measured at 14.50 ± 0.18 S.cm2.mol-1. You may find out what the cation and anion charges are in the Ni(II)-diphenylamine complex by comparing its electrical conductivity to that of the reference solution. When Ni(II) and diphenylamine were combined, the findings showed that the ratio of cation to anion charges was 1:1. Two nitrate ions are coordinated on the Ni(II) central ion and one nitrate ion (NO3-) acts as a counter ion in the electrolyte Ni(II)-diphenylamine complex.

Table 2. Standard and Ni(II)-diphenylamine complex electrical conductivity in methanol

Solution	ΛM (S.cm2.mol-1)	Cation : Anion Charge
Metanol	0	-
NiSO4.6H2O	7.39	1 : 1
CuSO4.5H2O	8.62	1 : 1
CuCl2.6H2O	47.18	2 : 1
NiCl2.6H2O	53.18	2 : 1
AlCl3.6H2O	90.97	3 : 1
Ni(II)-difenilamin	14.50 + 0.18	1 : 1

CONCLUSION

By observing distinct changes in absorption wavelengths, UV-Vis spectral analysis verified the effective production of the Ni(II)-diphenylamine combination. Spectra analysis revealed that the diphenylamine ligand provided more effective coordination than water. The suggested empirical formula of Ni(diphenylamine)4(NO3)2.6H2O was supported by the results of Atomic Absorption Spectroscopy (AAS), which showed a nickel content of 5.90 ± 0.05%. With one nitrate ion coordinating to the Ni(II) ion and the other serving as a counter ion, the electrical conductivity studies revealed that the Ni(II)-diphenylamine complex functions as an electrolyte with a 1:1 cation-anion ratio. These results give light on the coordination chemistry and associated domains' possible uses of the Ni(II)-diphenylamine complex by revealing its structural and conductive characteristics.

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