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NICKEL (II)-BIS (IMINOSEMIQUINONE) COMPLEX OF AMINOPHENOL DERIVATIVES: SYNTHESIS, STRUCTURAL CHARACTERIZATION AND CYCLIC VOLTAMMETRY STUDY

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ABSTRACT
In this study, a non-innocent bidentate ligand (H_2L) containing Ni(II) complex [Ni(L^{ISQ})$_2$], (1) was obtained under aerial conditions. The complex was defined by using FT-IR, UV-vis/NIR, ^{1}H-NMR, MASS and X-ray crystallography techniques. The results of the single crystal X-ray diffraction analysis revealed that the Ni(II) complex has a square planar configuration coordinated by two phenolate oxygen atoms and two nitrogen atoms from the two H_2L-ligands. Spectroscopic analysis also showed that the two H_2L ligands coordinated to the Ni(II) ion in the complex 1, two *ortho*-substituents -*Ph* groups were situated -*cis* to each other with respect to the square planar plane. ^{1}H-NMR spectrum of complex 1 suggested that it is a diamagnetic compound where two unpaired electrons of Ni(II) strongly couple with two one-electron radical ligands. In addition, cyclic voltammetry measurement of the complex 1 showed that the complex 1 underwent one two-electron oxidation and two one-electron reductions.
Keywords: Non-innocent Ligand, Ni(II)-Diradical Complex, Galactose Oxidase (GOase), Antiferromagnetic Coupling, Diamagnetic Complex, Cyclic Voltammetry.
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INTRODUCTION

Synthesis of radical-containing 3*d*-transition series metal complexes has been of great interest for the last three decades due to their unique electronic structure, distinctive magnetic properties, and remarkable activities in terms of the design of catalysts and for developing models that effectively mimic enzymatic reactions.[1] One of the most convenient ways for synthesising radical-coordinated 3*d*-transition series metal complexes involves the use of non-innocent ligands[2] in metal complexation reactions. These ligands actively participate in redox processes, facilitating the delocalisation of electron density between the metal centre and ligand framework. Non-innocent ligands, in particular, are defined as organic moieties that can change their redox state in the presence of metal ions and aerial oxygen, thereby enabling dynamic metal-ligand electronic interaction that plays a vital role in determining the complex's reactivity and stability.[3] Aminophenol-based non-innocent ligand is an attractive model for synthesising several metal complexes having catalytic, enzymatic and industrial perspectives. Ligand-centred redox feasibility allows those metal complexes to behave as a functional model for several metalloenzymes (e.g. *galactose oxidase*,[4,5,6] *amine oxidase* etc). Apart from their structural and electronic significance as biomimetic models, metal complexes derived from such non-innocent ligands have proven to be highly effective in various catalytic applications, synthesis of metal-quinone species[8], valence tautomeric interconversion[9], C–O/N/S bond activation[10], –CF_3 group transfer processes[11], and C–C cross-coupling reactions[12] Hence, aminophenol-based non-innocent ligands and their associated metal complexes represent a versatile class of compounds with substantial potential applications in catalysis, molecular electronics, and energy storage systems. In this context, the present study focuses on the synthesis, spectroscopic characterisation, and electronic structure analysis of new transition metal complexes derived from a non-innocent ligand, aiming to explore their potential redox activity and catalytic relevance.

A convenient and widely used strategy for synthesising radical-coordinated transition metal complexes is the utilisation of non-innocent ligands during metal complexation reactions. To investigate the role of

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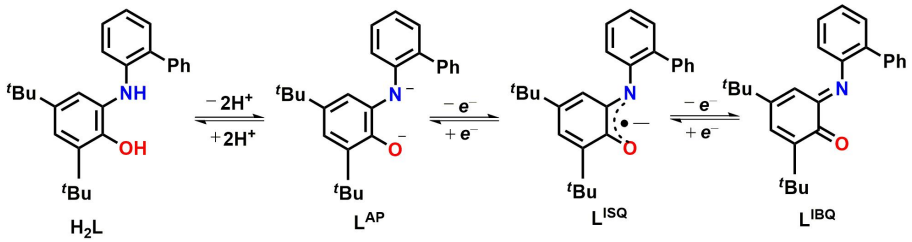
ortho-substituents, specifically a phenyl (*–Ph*) group, on the chemical and physical properties, including the reactivity of the transition metal complexes, an aminophenol-based non-innocent ligand H_2L was synthesized.[13] The introduction of the *ortho*-phenyl (*–Ph*) group into the ligand backbone is expected to modulate both the electronic and steric environment of the coordinated metal centre, thereby affecting the complex's stability, geometry and redox behaviour.



Scheme-1: Different Oxidation States of the Aminophenol-Based Ligand H_2L.

The synthesised ligand H_2L can exist in its coordination complexes in multiple redox states, including two-electron oxidised iminoquinone form ($[L^{IBQ}]^0$), one-electron-oxidised iminosemiquinone radical form ($[L^{ISQ}]^{1\bullet-}$), and fully reduced amidophenolate form ($[L^{AP}]^{2-}$) (Scheme-1).[13] Herein, we report the synthesis and detailed characterisation of a Ni(II)-bis(iminosemiquinone) complex (1), formed through coordination-induced oxidation of the aminophenol-based non-innocent ligand H_2L.

EXPERIMENTAL

Materials and Methods

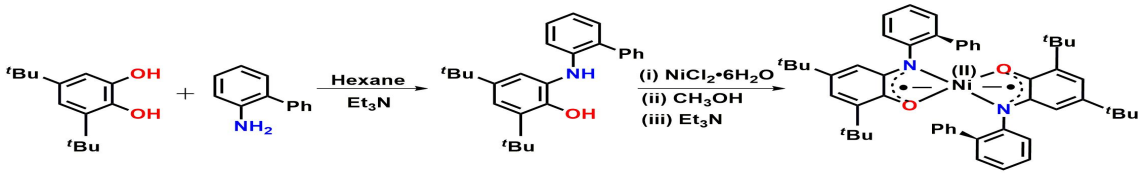
All chemicals were purchased from the Sigma-Aldrich company. To figure out compound structures, equipment like the Super Nova Eos diffractometer (for X-ray diffraction analysis) and CrysAlisPro performed the cell reductions and data refinement.[19] SHELXS-97 was used for direct structure solving, and SHELXL-97 was used for full matrix least-squares refinement.[20] A PerkinElmer Lambda 750 (for UV/vis/NIR study), a BRUKER 600 MHz NMR (for ^{1}H- and ^{13}C-NMR study) and a VersaSTAT 3 (for cyclic voltammetry study) were used.

Synthesis of H_2L Ligand

3,5-di-*tert*-bulyl catechol (1.117 g, 5.024 mmol) in hexane (20 mL) was treated with trimethylamine (0.05 mL) and stirred in open air for 15 minutes. 2-animobiphenyl (0.848 g, 5.011 mmol) was added, and the mixture was refluxed for 2 days, then stirred at room temperature for 48 hours. The product was purified by column chromatography (hexane: ethyl acetate = 98:2) to afford a light salmon-coloured solid. Yield: 1.65 g (88%). FTIR spectra (KBr pellet cm^{-1}): 3413, 3059, 3031, 2956, 2906, 2867, 1597, 1581, 1505, 1479, 1436, 1422, 1391, 1362, 1310, 1266, 1227, 1201, 1157, 1119, 1051, 1025, 1009, 973, 913, 880, 769, 750, 703, 649, 614. Mass: ESI – MS (CH_3CN) m/z for$[C_{26}H_{31}NO+H]^+$: Calculated, 374.2484; Found, 374.2490.

Synthesis of Complex 1

H_2L ligand (0.093 g, 0.25 mmol) was dissolved in methanol (10 mL), and $NiCl_2{\bullet}6H_2O$ (0.030 g, 0.125 mmol) was added. The colour of the solution changes from light brown to light green. Trimethylamine (0.05 mL) was then added, and the mixture was refluxed for 2 hours. A dark green precipitate was formed, filtered, air-dried, and recrystallised from a dichloromethane: methanol (3:1) mixture to afford dark-green block-shaped crystals. Yield: 0.069 g (69%). FTIR Spectra (KBr pellet cm^{-1}): 3055, 2960, 2904, 2865, 1579, 1524, 1475, 1438, 1381, 1360, 1323, 1290, 1255, 1243, 1228, 1201, 1175, 1106, 1030, 1002, 914, 853, 748, 697, 671, 589, 542, 513. Mass: ESI–MS (+ve) (CH_3OH) m/z for$[C_{52}H_{58}N_2O_2Ni]^+$: Calculated, 800.3863; Found, 800.3850.



Scheme-2: Schematic Representation for the Preparation of Ligand H_2L of Complex 1

RESULTS AND DISCUSSION

Crystal Structure of Complex 1

Single crystal X-ray diffraction data for complex 1 were collected at 293(2) K. The complex 1 crystallises in the triclinic system with the $P\ \bar{1}$ space group. The molecular structure of complex 1 is shown in Fig.-1. Selected bond lengths and bond angles are summarised in Table-S1 (supporting information).

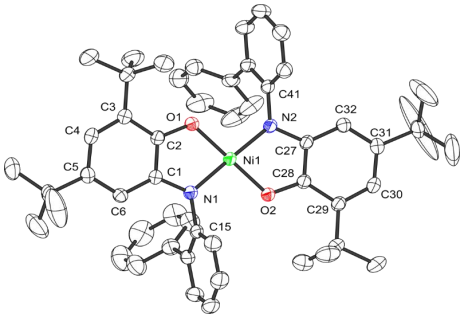


Fig.-1: ORTEP Molecular Structure of Complex 1

In complex 1, the central Ni(II) atom is coordinated by two nitrogen (N) and two oxygen (O) atoms from two monoanionic radical ligands, resulting in a nearly square-planar geometry. The ∠O1–Ni1–O2 and ∠N1–Ni1–N2 bond angles are 175.72(9)° and 178.56(10)°, respectively, consistent with an almost ideal square-planar ($\tau = 0.02$ where $\tau = \{360–(\alpha+\beta)\}/142$]; α and β are the two largest angles). The Ni–O and Ni–N bond lengths are Ni1–O1 = 1.837(2) Å, Ni1–O2 = 1.832(2) Å, Ni1–N1 = 1.838(2) Å, and Ni1–N2 = 1.846(2) Å, in good agreement with those expected for a Ni(II) center.[14,15] The C–C bond distances within the *tert*-butyl-containing phenyl rings are unequal and fall in the range of 1.40 ± 0.1 Å, deviating from the values expected for a fully reduced phenyl ring. The presence of four relatively long and two short C – C bonds (Table S1, supporting information**)** in an alternating long-short-long-short pattern indicates a quinoid-type distortion within the phenyl ring.[16] The observed C–N and C–O bond lengths C(1)–N(1) = 1.357(3) Å, C(27)–N(2) = 1.362(3) Å, C(2)–O(1) = 1.315(3) Å, and C(28)–O(2) = 1.312(3) Å are intermediate between single and double bonds, suggesting significant delocalization. These structural parameters indicate that the ligands are in their one electron oxidione-electronioxidisederefore, complex 1 can be described as a π–radical coordinated nickel (II) species in the neutral complex.

FT-IR Results of Complex 1

FT-IR was recorded on a PerkinElmer FT-IR spectrometer at room temperature using KBr pellets in the range of 4000–450 cm^{-1} and the data are given in Fig.-2.

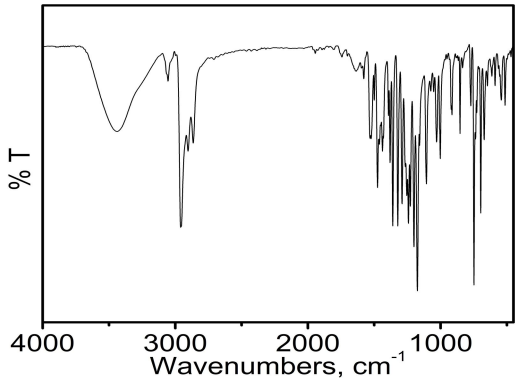


Fig.-2: FT-IR Spectrum of Complex 1

In the FT-IT spectrum of complex 1, the bands at 3059 cm^{-1} and 3031 cm^{-1} correspond to aromatic C–H vibrations, while the C–H stretching bands of the *tert*-butyl groups appear in the range 2956–2867 cm^{-1}. The strong absorption at 1597 cm^{-1} and 1580 cm^{-1} is assigned to C=C stretching vibrations of the phenyl rings.[13]

UV-vis-NIR Spectrum of Complex 1

The electronic absorption spectrum of complex 1 was recorded in CH_2Cl_2 at ambient temperature (Fig.-3). The spectrum exhibited a highly intense absorption band at 897 nm (ε = 36,217 M^{-1} cm^{-1}), which is attributed to a ligand-to-ligand charge transfer (LLCT) transition.[17] The strong intensity band further supports the presence of delocalized π-radical character within the coordinated iminosemiquinone ligand.

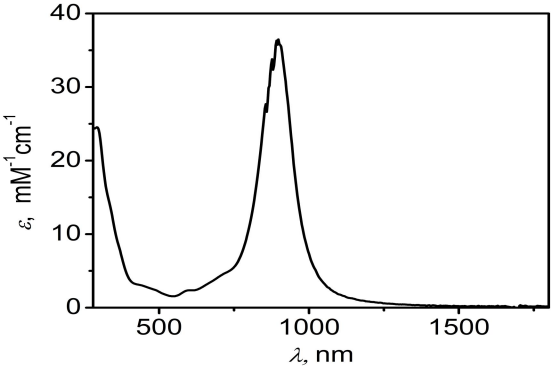


Fig.-3: UV-vis/NIR Spectrum of Complex 1 in CH_2Cl_2 at RT

^{1}H–NMR Spectrum of Complex 1

^{1}H-NMR spectrum of complex 1 was recorded in $CDCl_3$ at room temperature by using a BRUKER 600 MHz NMR instrument.

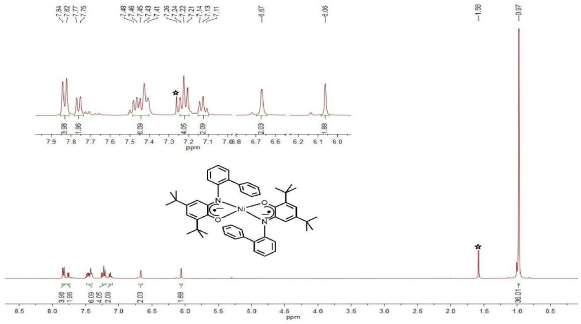


Fig.-4: ^{1}H-NMR of Complex 1 in CDCl3 at Room Temperature

The ^{1}H-NMR spectrum of complex 1 (Fig.-4) indicates that it is a diamagnetic compound, suggesting strong antiferromagnetic coupling between the two ligand-centred unpaired electrons and the Ni(II) centre. The absence of any noticeable paramagnetic shift or line broadening in the ^{1}H-NMR spectrum, even at ambient temperature, supports an overall S = 0 ground state. The diamagnetic nature of the complex is attributed to strong antiferromagnetic exchange interactions between the two radical centres mediated through the filled metal t_{2g} orbitals of the nickel ion (Fig.-5).

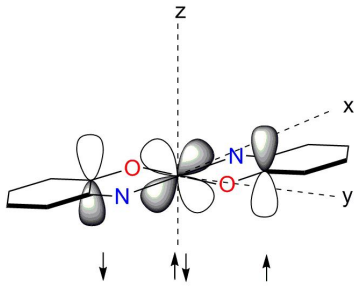


Fig.-5: Antiferromagnetic Coupling Pathway Between Two Radicals and Nickel Ion

Cyclic Voltammetry Study of Complex 1

Cyclic voltammetry (CV) measurements of complex 1 were carried out in CH_2Cl_2 using a glassy carbon working electrode, a platinum wire counter electrode, and an $Ag/AgNO_3$ reference electrode. The electrolytic solution contained 0.1 M $[(n\text{-}Bu)_4N]PF_6$ as the supporting electrolyte. All potentials were

referenced to the ferrocenium/ferrocene (Fc^+/Fc) redox couple, using ferrocene as an internal standard. The cyclic voltammograms data of complex **1** was recorded over the potential range +0.5 to −2.1 V (Fig.-6**)**.

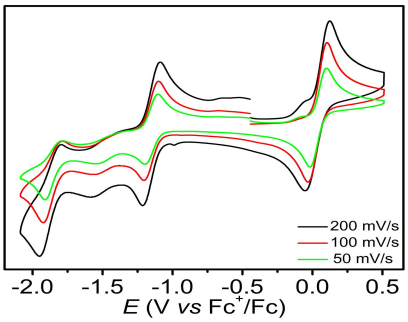
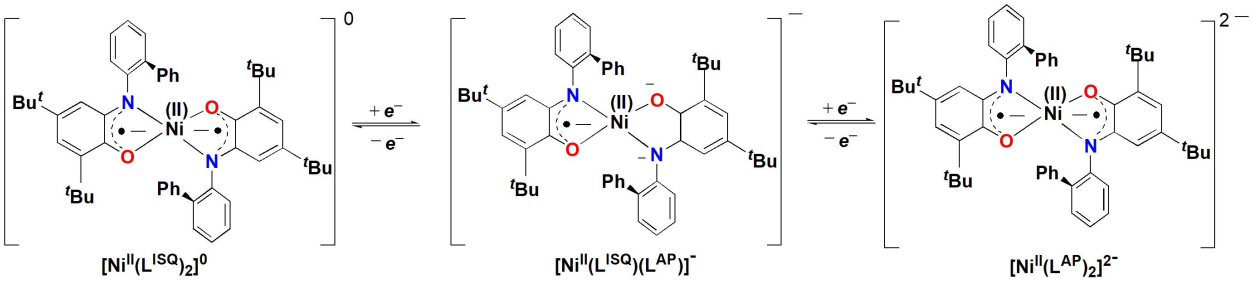


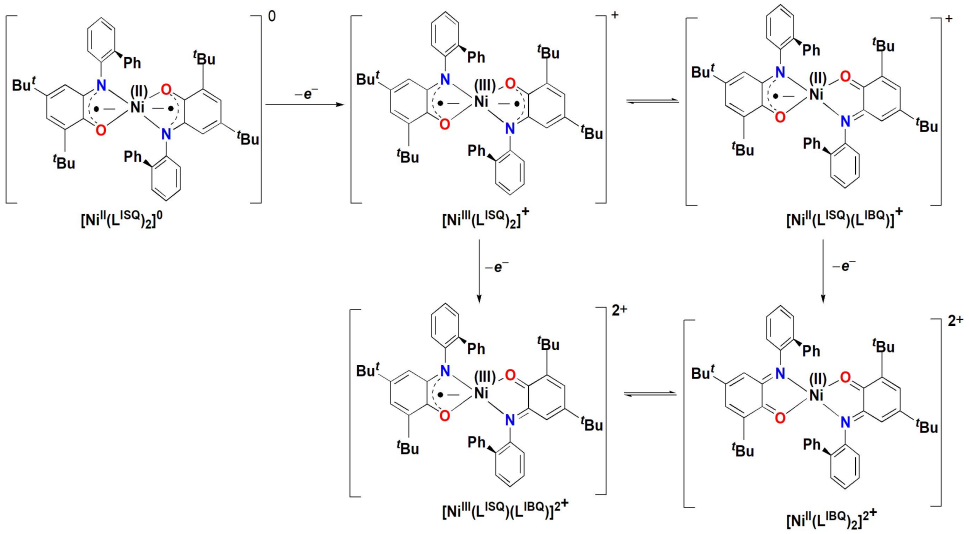
Fig.-6: Cyclic Voltammograms of Complex 1

Complex 1 exhibits two one-electron reductions and a two-electron oxidation in its cyclic voltammogram. The reduction occurs at $E_{1/2}$ = −1.822 V and −1.153 V versus Fc^+/Fc and is assigned as ligand-centred processes, corresponding to sequential reduction of the iminosemiquinone ligands (Scheme-3).



Scheme-3: Ligand-Centred Reductions Process During Cyclic Voltametric Study

A two-electron oxidation wave was observed at $E_{1/2}$ = +0.038 V versus Fc^+/Fc. This process involves a concerted two-electron transfer, which may proceed via sequential one-electron steps associated with metal-centred oxidation (Scheme-4). The transformation was found to be scan rate dependent (Fig.-6), indicating partial kinetic coupling between the two redox processes. Similar electrochemical behaviour has been reported previously for other Ni(II)-diradical complexes.[18]



Scheme-4: Metal Centre Oxidation Process During Cyclic Voltametric Study

CONCLUSION

In conclusion, a new Ni(II)-bis(iminosemiquinone) complex 1 has been synthesised using ligand H_2L. Single crystal X-ray diffraction analysis reveals a square planar geometry around the Ni(II) centre, with two phenyl (-Ph) substituents positioned *-cis* to each other. The complex is diamagnetic, indicating a strong antiferromagnetic coupling between the two ligand-based radical centres mediated through the metal t_{2g} orbitals. The UV-vis-NIR spectrum of the complex is dominated by an intense ligand-to-ligand charge transfer (LLCT) band centred at 879 nm. Cyclic voltammetry demonstrates that the complex undergoes two successive one-electron oxidations and two two-electron reduction processes. This work aligns with the objectives of SDG9 by contributing to the advancement of innovative molecular materials with potential applications in electronic devices, energy storage systems, and molecular magnetism.

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CONFLICT OF INTERESTS

No conflicts of interest are disclosed by the authors.

AUTHOR CONTRIBUTIONS

The present work is related to *SDG-9: Industry, Innovation and Infrastructure*. All the authors contributed significantly to this manuscript, participated in reviewing/editing and approved the final draft for publication. The research profile of the authors can be verified from their ORCID ids, given below:

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