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Stabilizing Terminal Ni(III)-Hydroxide Complex Using NNN-Pincer Ligands: Synthesis and Characterization

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Supporting Information

ABSTRACT: The reaction of $[Ni(COD)_2]$ (COD; cyclooctadiene) in THF with the NNN-pincer ligand bis(imino)pyridyl (L_1) reveals a susceptibility to oxidation in an inert atmosphere ($[O_2]$ level <0.5 ppm), resulting in a transient Ni:dioxygen adduct. This reactive intermediate abstracts a hydrogen atom from THF and stabilizes an uncommon Ni(III) complex. The complex is crystallographically characterized by a molecular formula of $[Ni^{III}(L_1)^{2-}(OH)]$ (1). Various isotopically labeled experiments $({}^{16}O/{}^{18}O)$ assertively endorse the origin of terminal oxygen based ligand in 1 due to the activation of molecular dioxygen. The presence of proton bound to the terminal oxygen in 1 is well supported by NMR,



IR spectroscopy, DFT calculations, and hydrogen atom transfer (HAT) reactions promoted by 1. The observation of shakeup satellite peaks for the primary photoelectron lines of Ni(2p) in the X-ray photoelectron spectroscopy (XPS) unambiguously confirms the paramagnetic signature associated with the distorted square planar nickel ion, which is consistent with the trivalent oxidation state assigned for the nickel ion in 1. The variable temperature magnetic susceptibility data of 1 shows dominant antiferromagnetic interactions exist among the paramagnetic centers, resulting in an overall S = 1/2 ground state. Variable temperature X-band EPR studies performed on 1 show evidence for the S = 1/2 ground state, which is consistent with magnetic data. The unusual g-tensor extracted for the ground state S = 1/2 is analyzed under a strong exchange limit of spin-coupled centers. The electronic structure predicted for 1 is in good agreement with theoretical calculations.

INTRODUCTION

Nickel-containing enzymes catalyze various reactions such as the hydrolysis of urea, the disproportionation of the toxic superoxide radical, and the reversible oxidation of carbon monoxide, etc.¹ During the catalytic processes, especially with redox-active enzymes such as superoxide dismutase (SOD) and [NiFe]-hydrogenase, the Ni(III) ion is believed to be the reactive species responsible for the catalytic activity.¹ It has been shown by Jaun and co-workers that the Ni(III) species of the methanogenesis enzyme is involved in the activation of a C-H bond of CH₄ under anaerobic conditions.² In the recent past, selective mononuclear nickel complexes have been used in a number of organometallic transformation reactions, such as Negishi, Kumuda, and Suzuki cross-coupling reactions, where the Ni(III) ion was proposed as an intermediate.³ Mirica and his co-workers have exemplarily revealed the involvement of the Ni(III) ion as the reactive species for various cross-coupling and oxidative bond formation reactions.⁴ The importance of the Ni(III) ion in halogen photoelimination was shown by Nocera and co-workers,⁵ and further its significance as a reactive

catalyst is exemplified by Hillhouse and co-workers in hydrogen atom transfer (HAT) reactions.⁶

In general, to stabilize the Ni(III) oxidation state, ligands with hard donor atoms have predominantly been employed. However, in the majority of cases, the Ni(III) valence-state was mainly accessed, through either chemical/electrochemical oxidation or pulse radiolysis methods. It has been found that only a small number of Ni(III) complexes have been crystallographically characterized due to its high reactivity/ sensitivity and short-lived nature.^{7d,8}

On the contrary, such an unusual oxidation state is easily accessed under biological conditions through aerial or O₂ oxidation due to the low Ni^{III}/Ni^{II} redox potential (E_0), while for the pertinent inorganic mimics the E_0 value is not in the accessible range to utilize molecular oxygen as an oxidant; hence, stronger oxidizing agents or electrochemical methods are essential. It has been proposed that the presence of radicals in metalloenzymes alters the redox potential of the reactive

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metal center significantly,⁹ in addition to the formation of a strong in-plane metal–ligand interaction and the degree of ligand unsaturation.^{8a,10}

Keeping in mind all these factors, we sought to unveil the transient nature of the putative Ni(III) intermediate by employing the redox active ligand, bis(imino)pyridyl $(C_{43}H_{47}N_3, L_1)$, which can act as a reservoir to accommodate a maximum of three electrons.¹¹ It is expected that the strong σ -donating capability and the extended π -cloud of L₁ could potentially alter the electronic structure of the nickel complex, which should theoretically help to stabilize the Ni(III) oxidation state under mild conditions. This article reports the isolation and multiple spectroscopic characterizations of a trivalent nickel complex stabilized by a doubly reduced L1 (Scheme 1) via the activation of molecular oxygen. Although NCN $[C_6H_3(CH_2NMe_2)_2-2,6]$ and other modified pincer type ligands have been employed in the past toward the isolation of Ni(III) complexes, the trivalent oxidation state was accessed either by chemical or electrochemical oxidation exclusively.7d,12 The stabilization of Ni(III) ion in 1 using redox-active NNN pincer ligand (L_1) , however, is unprecedented in the literature.

EXPERIMENTAL SECTION

Materials and Methods. Unless otherwise specified, all the reactions were carried out under anaerobic condition using Schlenk techniques and/or a glovebox. All the chemicals were purchased from commercially available sources, which were used without further purification. The ligand L1 was synthesized according to the reported procedure.¹³ Single crystal data were collected on a Rigaku Saturn CCD diffractometer using a graphite monochromator (Mo K α , λ = 0.71073 Å). The selected crystals were mounted on the tip of a glass pin using mineral oil and placed in the cold flow produced with an Oxford Cryo-cooling device. Complete hemispheres of data were collected using ω - and ϕ -scans (0.3°, 16 s per frame). Integrated intensities were obtained with Rigaku Crystal Clear-SM Expert 2.1 software, and they were corrected for absorption correction. Structure solution and refinement were performed with the SHELX-package. The structures were solved by direct methods and completed by iterative cycles of ΔF syntheses and full-matrix least-squares refinement against F². CCDC number: 1498088. UV-vis-NIR measurement is performed on a Shimadzu (Japan) UV-vis-NIR-3600. The magnetic susceptibility measurements were performed on an MPMS-XL SQUID magnetometer equipped with 70 kOe magnet using toluene solution of 1. The magnetic data were corrected for the sample holder and diamagnetic contributions. ¹H NMR spectra were recorded on a Bruker Avance III 500. Mass spectra were obtained from MALDI-TOF (matrix-assisted laser desorption/ionization time of flight) to determine the solution stability of 1. The OTOF control analysis software was used to model the isotopic distribution patterns in mass spectra. Electron Paramagnetic Resonance (EPR) measurements were carried out using a Bruker EMX plus X-band EPR spectrometer operating in continuous wave (CW) mode, equipped with an Oxford variable-temperature unit and ESR900 cryostat with Super High-Q resonator. Simulations of the CW-EPR spectra were

performed using an Easy Spin toolbox (5.2.18) for the Matlab program package. 14

The X-ray photoelectron spectra were obtained on an axis supra model of a Kratos analytical electron spectrometer. The samples were mounted on carbon tape such that the sample cylinder was completely covered. The Al K α X-ray line (1486.6 eV) was used for photoelectron excitation. The C 1s peak from surface adsorbed carbon is used for internal calibration and corrected to be at 284.7 eV.

Computational Details. The electronic structure of 1 is further probed through density functional theory (DFT) calculations¹⁵ using a Jaguar electronic structure package.¹⁶ Optimized geometries were obtained with a B3LYP-D3 functional¹⁷ and 6-31G** basis set. For Ni, a Los Alamos LACVP basis set was used¹⁸ which includes effective core potentials. The energies of the optimized structures were readdressed by single-point calculations using Dunning's correlation consistent triple- ζ basis set cc-pVTZ(-f) basis set.¹⁹ Ni ion is treated with the modified version of LACVP, denoted LACV3P. Vibrational frequency calculations were conducted at the same calculating theory level as the geometry optimization calculations. We obtained solvation energies using the optimized gas phase structures from self-consistent reaction field (SCRF) calculations with dielectric constants $\varepsilon = 2.38$ (toluene). Time-dependent (TD) DFT calculations are performed using the ω -B97X functional²⁰ in conjunction with the def2-TZVP basis set²¹ using toluene as a solvent to obtain the lowest 30 doublet states performed in the ORCA 4.0.1 electronic structure package.²²

Synthesis of $[Ni^{III}(L_1^{-})^{2-}(OH)]$ (1). In an argon filled glovebox, 50 mg of L_1 (0.082 mmol) and 23 mg of $[Ni(COD)_2]$ (0.082 mmol) was weighed and transferred into a 25 mL screw cap fitted Schlenk tube in which 10 mL of dry THF was added, which was cooled to -40 °C (liq. N_{2} + CH_{3}CN). 0.2 mL of $^{16}\text{O}_{2}/^{18}\text{O}_{2}$ gas was injected into this solution with the help of a gastight syringe, and slowly solution was allowed to warm up to room temperature (\sim 30–40 min). The color of the solution was changed slowly from yellow to dark brown on stirring at room temperature, and the reaction mixture was allowed to stir for 12 h. The resulting maroon solution was evaporated to dryness and extracted into hexane (5 mL), and the filtrate was concentrated to 3-4 mL, which was kept for crystallization at room temperature. Within 2 days, brown color block-shaped crystals were grown from the filtrate upon slow evaporation. Yield (based on nickel): 23 mg (47%). Anal. calcd for (C₄₃H₄₈NiN₃O): C = 75.77; H = 7.09; N = 6.16. Found: C = 75.56; H = 7.15; N = 6.19. The compound obtained was further characterized by MALDI spectrum to check the incorporation of ¹⁸O labeled atom. The m/z value of 681 along with 679 of equal intensity suggests the 18 O atom from 18 O₂ gas (vide infra, also see Figure S1).

[We have also observed that the reaction works very well even if we do not inject the ${}^{16}O_2/{}^{18}O_2$ into the reaction mixture externally; that is, the ppm level of oxygen gas present in the glovebox is sufficient to isolate 1.]

Control Experiment with H₂¹⁸O: To probe the possible origin of the –OH group in 1, a similar synthetic procedure was followed as above, but ¹⁸O labeled water (H₂¹⁸O; 1.7 μ L) was used in place of ¹⁸O₂ gas. A MALDI spectrum was recorded for the crystals obtained in this reaction (see Figure S1 and the related discussion given in the Results and Discussion section).

Synthetic Procedure Followed for the *in Situ* HAT Reaction. In an argon-filled glovebox, 25 mg of ligand, L_1 (0.0415 mmol), and 12.5 mg of [Ni(COD)₂] (0.0415 mmol) were weighed and added into

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a 25 mL Schlenk tube. Into this Schlenk tube, 5 mL of dry THF was added. This sealed tube was connected to a Schlenk line and cooled down to -78 °C (methanol/liquid nitrogen bath) and stirred for 5 min. After 5 min, 81 mg of 2,4-di-*tert*-butyl phenol (0.415 mmol) was added into the Schlenk tube. To this reaction mixture, the required amount of dioxygen gas (0.5, 1.0, 2.0, and 4 mL) was injected with the help of a gastight syringe. This entire assembly remains in the methanol/liquid nitrogen bath, which was slowly allowed to attain room temperature with constant stirring. The reaction mixture was continued to stir for 6 more hours at room temperature. An aliquot of the reaction mixture was taken for quantitative analysis through GC using decane as an external reference.

Note: The substrate is introduced into the reaction mixture after 5 min; the rationale for this is described in the main text below (*vide* infra).

HAT Reaction Promoted by 1. In an argon-filled glovebox, 10 mg of 1 (1.47 μ mol) and 1.5 mL of THF was added into a 10 mL Schlenk tube. Into that 4 mg (22 μ mol) of 9,10-dihydroanthracene or 2 μ L (22 μ mol) of 1,4-cyclohexadiene was added. The reaction mixture was stirred for 24 h at room temperature. After completion of the reaction, 3 μ L of *n*-decane was added as an internal standard. The resultant solution was subjected to GC-MS analysis to confirm the formation of the product. The formation of product via HAT reaction was quantified with an internal standard by the means of GC, and conversions of 11% and 13% were found for 9,10-dihydroanthracene and 1,4-cyclohexadiene, respectively.

RESULTS AND DISCUSSION

The reaction of bis(cyclooctadiene)nickel(0) with L_1 in the presence of a trace amount of oxygen under an argon atmosphere in THF (tetrahydrofuran) yielded brown crystals, which were suitable for single crystal X-ray diffraction measurements. The crystal structure analysis revealed the formation of a mononuclear nickel complex (1), which was crystallized in the monoclinic space group, C2/c (Table S1 of ESI). The asymmetric unit consists of only half of the molecule, and the complete structure is generated by rotation/inversion symmetry, with the rotational axis passing through O11, Ni1, N11, and C13 (Figure 1). The nickel ion exists in a distorted square-planar geometry and is surrounded by three nitrogen atoms of the reduced L1 ligand, which complete three of the four coordination sites. The average Ni1-N bond length is found to be 1.8622(3) Å, with the Ni1-N11(pyridine) bond being the shortest (1.8078(2) Å). This is likely due to the



Figure 1. X-ray structure of 1. Hydrogen atoms and side chain carbon atoms are removed for clarity. Selected bond lengths: Ni1–N11 = 1.808(4) Å; Ni1–N12 = 1.889(3) Å; Ni1–O11 = 1.824(5) Å. Selected bond angles: $\angle O1-1Ni1-N11 = 180^{\circ}$; $\angle N12-Ni1-N12\# =$ $165.3(2)^{\circ}$; $\angle N12-Ni1-N11 = 82.67(11)^{\circ}$; $\angle O11-Ni1-N12 =$ $97.33(11)^{\circ}$.

presence of the bulky substituents at the ortho-positions of the phenyl ring on the amine.

The precursor $[Ni(COD)_2]$ employed in the reaction reduces the ligand (L_1) by two electrons, and the evidence for the radical dianion formation directly comes from the crystal structure of 1, where the bond length of the imine group (C14-N12 = 1.337(1) Å) is shorter than a single bond (1.465 Å) and longer than a double bond (1.279 Å). The observed bond length is consistent with the other literature reports.²³

The fourth coordination site of the nickel ion is occupied by an oxygen atom in 1, with a bond length of 1.824(5) Å. The observed Ni1–O11 bond length is considerably shorter than Ni(II)–H₂O (2.044(4)–2.107(3) Å) and longer than Ni-oxo (1.790(2) Å; note: there is no terminal Ni-oxo complex structurally characterized in the literature to date, but an oxobridged Ni(III) complex was structurally characterized^{2.3b}) complexes reported in the literature.²⁴ The oxidation state of nickel ion and the overall electronic structure of 1 depend on the nature of the terminal ligand i.e., whether it is water or hydroxo or oxo (Scheme 1). Therefore, several analytical techniques and isotopic labeling experiments have been employed to determine the identity of the terminal ligand.

The single crystal X-ray diffraction confirms the presence of an oxygen donor bound to nickel ion which is firmly supported by the matrix-assisted laser desorption/ionization (MALDI) spectrum recorded for 1 (Figure 2). Figure 2 shows an m/z



Figure 2. (A–B) MALDI spectra of **1** showing the molecular ion (blue trace, panel A) and its first fragmentation isotopic distribution patterns (blue trace, panel B), respectively. Figure 2A Inset: MALDI spectrum of the reaction mixture of **1** carried out in the presence of ¹⁸O labeled ¹⁸O₂ gas.

peak at 679 (Figure 2A) and its first fragmentation peak observed at 663 (Figure 2B). The difference of 16 atomic mass units between the M+ and its first fragmentation peak unequivocally confirms the presence of an oxygen-based ligand bound to the Ni ion in 1 (Figure 2); however, the protonation state of this donor atom remains elusive.

Before probing the protonation state of the OH_x ligand in 1 (where x = 2 or 1 or 0), to shed light on the origin of oxygen-

based ligand in 1, ¹⁸O-isotopic labeling experiments were performed under the identical reaction conditions used to isolate 1. The reactions were carried out in the presence of (i) ¹⁸O-labeled ¹⁸O₂-gas and (ii) ¹⁸OH₂ (see the Experimental Section for details).

In the former case, the reaction did not proceed well, presumably due to the decomposition of the radical anionic ligand, as ¹⁸O₂ gas was introduced into the reaction mixture at room temperature. In contrast, a stable complex formation of 1 is noticed, if ¹⁸O₂ gas is introduced into the reaction mixture at low temperature (-78 to -40 °C) and subsequently warmed up to room temperature. The MALDI spectrum recorded for the solution unveils an almost equal intensity m/z peak of 679 and 681 (see the inset of Figure 2A). In contrast, the MALDI spectrum of 1 isolated using ¹⁸O labeled water does not show a m/z peak correspond to ¹⁸O-incorporation and the MALDI spectrum resembles that shown in Figure 2A (Figure S1). These two ¹⁸O-labeling experiments unequivocally confirm that the origin of the terminal oxygen based ligand ($-OH_x$) in 1 is due to molecular O₂ activation and not due to the (trace) water in dry THF solvent.

In an effort to identify the protonation state of the OH_x (x = 0, 1, or 2) ligand in 1, the infrared (IR) spectrum was recorded for 1 in Nujol mulls.

The IR spectrum of 1 markedly shows a sharp peak at 3605 cm⁻¹ (Figure 3), which is assigned to the $\nu_{(-OH)}$ stretching



Figure 3. IR spectrum of 1 recorded in Nujol mulls.

frequency. In addition, routine -C-H, -C=C, and -C=N stretching frequencies are observed in the usual fingerprint regions. IR experiment irrefutably reveals that a proton(s) is(are) bound to the oxygen donor atom in **1**. In general, a water molecule (i.e. OH_2) bound to the metal ion is expected to show a broad -OH band centered at 3000 cm⁻¹ in the IR spectrum. The absence of such a broad band and the presence of a sharp peak at 3605 cm⁻¹ hint that the peak presumably originates from a $-OH_x$ (x = 1) group. A hydroxyl ligand terminally bound to a Cu(III) ion reported elsewhere²⁵ shows a sharp peak in the same region as shown by **1**, further adding confidence to our notion.

To further probe the protonation state of the OH_x (x = 1 or 2), ¹H NMR and ¹H-¹³C HSQC (heteronuclear single quantum coherence) spectra were recorded for **1** in dry C_6D_6 . The ¹H NMR signals observed in the range of 0.99-3.30 ppm and 6.45-8.50 ppm are assigned to the isopropyl and the aromatic groups, respectively. In addition, a broad ¹H NMR signal is observed at 5.56 ppm, which is tentatively assigned to the OH_x ligand of **1** (bluish-green trace of Figure 4A and inset).



Figure 4. (A) ¹H NMR (400 MHz in C_6D_6) spectra of 1 and 2 recorded at room temperature in C_6D_6 solvent (# = grease, * = THF, \$ = toluene, @ = residual C_6D_6). Inset: expanded region of 5.2–6.0 ppm. (B) O_2 concentration-dependent biphenol product formation in the presence of $[Ni(COD)_2]$ and L_1 . The values \pm SE reported here are an average value of three independent experiments carried out under identical experimental conditions.

The ${}^{1}\text{H}-{}^{13}\text{C}$ HSQC spectrum of 1 shows correlation peaks correspond to the isopropyl and the aromatic groups in the respective chemical shift range. In contrast, no correlation peak is observed for the broad signal at 5.56 ppm in the ${}^{1}\text{H}-{}^{13}\text{C}$ spectrum (Figure S2). This scenario evidently confirms our assignment that the NMR signal observed at 5.56 ppm corresponds to a proton, which is bound to a heteroatom (such as oxygen). Although the IR spectrum of 1 signals the presence of a hydroxyl group, due to the broadening of the ${}^{1}\text{H}$ NMR signal and the absence of an absolute molecular ion peak in MALDI, the number of protons bound to the oxygen donor cannot be determined accurately. However, using X-ray photoelectron spectroscopy we did identify the oxidation state of the terminal ligand bound to nickel ion and subsequently the oxidation state of nickel ion in 1 (*vide infra*).

Next, we turned our attention to answer the question what is the source of a proton(s) which is(are) bound to the terminal oxygen ligand? In order to shed light on the origin of the proton, the following two experiments were performed; (i) deuterium (d8-THF) labeling experiments and (ii) *in-situ* HAT reaction which is detailed below.

Deuterium Labeling Experiments. As the reaction was performed in THF for the isolation of 1, we hypothesize that THF solvent could possibly be the source of a proton. To test this, the reaction was performed under identical conditions

used to isolate 1, except the THF solvent was replaced by d8-THF (99.95%). The single crystals obtained from the d8-THF reaction exhibit the same unit cell as 1. The ¹H NMR spectrum recorded on this sample in C_6D_6 reveals the disappearance of the peak at 5.56 ppm (wine-red trace in Figure 4A and its inset), while the remaining spectral features exactly overlap with the ¹H NMR of 1 isolated from regular THF (bluish-green trace in Figure 4A and its inset). This experiment apparently demonstrates that THF solvent acts as the source of the proton.

In-Situ HAT Reaction. The objectives of conducting these O_2 concentration-dependent HAT experiments are 2-fold: (i) to show that the O_2 molecule gets activated at the nickel site and produces a transient nickel:dioxygen adduct and (ii) to show that hydrogen atom abstraction by this adduct facilitates the formation of 1.

In 1, we have shown in the earlier section that the source of oxygen donor is an O_2 molecule. We surmise that O_2 molecule that gets activated at the nickel site results in the formation of a transient nickel:dioxygen adduct whose identity (3-dimensional structure) is currently unknown. This adduct could conceivably be stabilized in a high valent (could be $Ni^{IV} = O$ or $Ni^{IV} = O_2^2$ or Ni^{III}—O₂⁻) oxidation state. To prove the hydrogen atom abstraction ability of the transient species and the oxygen tolerance of the radical containing the nickel:dioxygen adduct, O2 concentration-dependent HAT experiments were performed using 2,4-di(tert-butyl)phenol substrate (see Experimental Section for details and also see Figure S3). Here, we would like to point out that the HAT reaction is promoted by $[Ni(COD)_2]$ itself with a phenolic substrate (2,4-di(*tert*butyl)phenol); however, to avoid the involvement of [Ni- $(COD)_2$ in HAT reactions, the substrate was added after 5 min. By this time $[Ni(COD)_2]$ is absolutely consumed by L_1 (before the addition of substrate) as evident by the UV-vis spectrum (Figure S3).

Into the reaction mixture of $[Ni(COD)_2]$ and L_1 , various amounts of dioxygen gas (0.5, 1.0, 2.0, and 4.0 mL) were injected externally in the presence of 2,4-di(*tert*-butyl)phenol at low temperature (-78 to -40 °C). The hydrogen atom abstraction promoted by the transient nickel:dioxygen adduct is quantified by the formation of 3,3',5,5'-tetra-*tert*-butyl-(1,1'biphenyl)-2,2'-diol (Figure 4B and Figure S4).^{26a-d} From Figure 4B, it is evident that the biphenolic product formation increases with an increase in concentration of molecular oxygen. This unambiguously confirms that the O₂ becomes activated at the nickel center and the resultant adduct is capable of promoting hydrogen atom abstraction. The reaction was therefore performed in the absence of a phenolic substrate in THF, results in transient Ni:dioxygen adduct abstracting a hydrogen from THF, thus accounting for the stabilization of **1**.

Through MALDI, NMR (both 1D ¹H NMR and 2D NMR (¹H–¹³C HSQC)) and isotopic (¹⁸O/²H) labeled experiments, respectively, we have proven unequivocally that (i) an oxygen donor atom bound to nickel ion, (ii) proton is bound to oxygen atom, and (iii) the proton is originated from THF solvent (through hydrogen atom abstraction) in 1. The characteristic (shakeup satellite peaks) XPS spectrum observed for 1 helped us to assign the oxidation state of the nickel ion in 1 and provide indirect support for the protonation state of the terminal $-OH_x$ (x = 1) ligand (*vide infra*). The oxidation state of the nickel ion in 1 is further decisively substantiated by catalytic and spectroscopic investigations (superconducting quantum interference device (SQUID) measurements and electron paramagnetic resonance (EPR) spectroscopy).

X-ray Photoelectron Spectroscopy (XPS). The Ni(2p) X-ray photoelectron spectrum recorded for 1 (Figure 5) reveals



Figure 5. X-ray photoelectron spectrum of the Ni(2p) binding energy region for 1.

the presence of two main peaks with the binding energy of 853.87 and 871.77 eV which are attributed to the primary photoelectron lines of $2p_{3/2}$ and $2p_{1/2}\text{,}$ respectively. In addition, there are two shakeup satellite peaks associated with the $2p_{3/2}$ and $2p_{1/2}$ lines respectively, observed at 860.12 and 878.27 eV. The latter two peaks which are approximately 6 eV higher than the primary lines observed for 1. It is very well exemplified in the literature that just by looking at the binding energy of Ni(2p) primary lines alone one cannot determine the oxidation state of the metal, as the binding energy of the metal ion depends on the charge on the metal ion.²⁷ The charge on the metal ion is governed by the nature of the coordinating ligand bound to the metal ion or in other words how well the ligands are able to alter/remove the charge on the metal ions. Circumstances that lead to increase the charge on metal ion, for example, strongly electron donating ligand such as nitrogen (as in case 1) or arsenic etc., binding energy of the primary lines will shift to lower energy, while a vice versa scenario is observed if the ligand bound to the metal tends to remove the charge on the metal ion (example, halide ion bound to a metal).

The photoelectron line of $2p_{3/2}$ observed at 853.87 eV for nickel ion in 1 is significantly lower than the binding energy observed for Ni(III) ions (855.1 \pm 0.1 to 857.5 \pm 0.2) reported in the literature.²⁸ This is attributed to the strong electron donating nature of nitrogen donors of L₁, which consequently increases the charge on Ni ion. It is a well-accepted mechanism among the community and has been used widely to explain the unusual results of various metal complexes; for example, the binding energies of the [Ni(diars)Cl₂](ClO₄)₂ complex were observed at 854.7 and 872.6 eV, respectively, for the photoelectron lines $2p_{3/2}$ and $2p_{1/2}$.

Although the formal oxidation state of the nickel ion in the above molecular formula represents +4, the experimentally observed binding energy is in the range observed for the +2 oxidation state of nickel ion.^{27a} Significantly low binding energy in this complex is attributed to the electron donating nature of arsenic ligand bound to the nickel ion.^{27a} In contrast, the presence of a shakeup satellite peak gives invaluable information not only about the geometry of the metal ion but also about the nature of the magnetic property associated with the metal ion, i.e. whether the nickel ion is paramagnetic or diamagnetic. The origin and the selection rule for observing shakeup satellite peaks are described in detail elsewhere.²⁹ To



Figure 6. (A) Packing diagram of 1. Panel B shows the intermolecular H-bonding between the two molecules in the crystal lattice of 1.

summarize the literature reports, shakeup satellite peaks are observed only for the paramagnetic nickel ion (example octahedral nickel(II) or tetrahedral Ni(II)), and the same will not be observed in diamagnetic square planar nickel(II) complexes due to the forbidden nature of the shakeup lines.^{28,29b} The square planar geometry around the nickel ion and the two-electron reduction of L1 are discernible directly from the X-ray diffraction. Therefore, the overall oxidation state of nickel ion in the complex is exclusively determined by the oxidation state of the terminal ligand coordinated to the nickel ion. Based on the terminal ligand oxidation state, one can safely assume the following three possible oxidation states for the square planar nickel ion, namely $[Ni^{IV}(L_1^{..})^{2-}(O)]$ (1a), $[Ni^{III}(L_1^{-})^{2-}(OH)]$ (1), $[Ni^{III}(L_1^{-})^{2-}(O\cdot)^{-}]$ (1b), and $[Ni^{II}(L_1^{\cdot})^{2-}(H_2O)]$ (1c). As nickel ion in both 1a (low spin 3d⁶ configuration) and 1c (low spin 3d⁸ configuration) exists in a square planar geometry, all the valence electrons are paired up, resulting in the diamagnetic signature. As stated above, diamagnetic nickel ion does not show shakeup satellite peaks, but this contradicts the experimental observation; therefore, one can safely neglect the possible models of 1a and 1c. The observation of a shakeup satellite peak for both the primary photoelectron peaks apparently reveals that nickel ion must be trivalent and paramagnetic (low spin $Ni^{3+} = 3d^7$ configuration) in nature. This situation leaves only two possible models now, i.e. 1 and 1b. But both ¹H NMR and IR experiments performed on 1 evidently suggest that a proton is bound to the oxygen atom, which is absolutely satisfied by the model 1, not 1b. This scenario is consistent with the experimental EPR spectra recorded for 1, which resembles that of a noninteger spin state rather than an integer spin state (vide infra). Further, a noninteger spin state for the model 1b is not possible as it contains even number (total four) of unpaired electrons (two from L_1 , one from nickel, and one from oxyl radical). This is further firmly supported by the room temperature $\chi_M T$ value (where χ_M is molar magnetic susceptibility) which substantiates the presence of three unpaired electrons (vide infra). By employing various analytical techniques, the molecular formula of 1 is unambiguously determined to be $[Ni^{III}(L^{-})^{2-}(OH)]$.

The multiple spectroscopic characterizations (X-ray, XPS, NMR, and MALDI) of 1 confirm that the nickel ion exists in a trivalent oxidation state. This is highly unusual, and the Ni(III) state stabilized by a redox active ligand, such as L_1 , is extremely scarce in the literature. The Ni–N bond lengths observed in 1

are relatively shorter than other trivalent nickel complexes reported in the literature.^{4a,b,4,7a,c,d,12a} This is because there is no distortion in the plane formed by N11, N12, O11, or N12# (where # represents the symmetrically generated atom, dihedral angle N11, N12, O11, N12# = 0°) and also the Ni(III) ion resides at the center of the plane. The short bond distances (Ni–N and Ni–O) in 1 have a significant influence on the electronic structure of 1 (*vide infra*).

As stated above, the majority of the trivalent nickel complexes have been accessed either by chemical or electrochemical oxidation. Therefore, **1** is a rare example, where molecular dioxygen acts as an oxidant, which facilitates to stabilize the unusual oxidation state for nickel, a unique method which is distinctly different from the other routes reported in the literature. In an unrelated report, it has been pointed out the importance of radical(s) in metalloproteins, which facilitate the stabilization of unusual metal ion oxidation states (by altering the redox potential) to carry out the complicated catalytic process with ease and elegance.^{1,30} It is likely that the presence of the two radicals along with the strong σ -donor atoms in **1** considerably lowers the oxidation potential of the nickel ion, allowing the isolation of **1** with trivalent oxidation state using a mild oxidant such as O₂.

With the protonation state of the terminal ligand and the oxidation state of the nickel ion in 1 proven, the crystal packing diagram of 1 was analyzed carefully to understand the supramolecular interactions in the crystal lattice (Figure 6). The closest Ni…Ni distance was found to be 8.644(8) Å (Figure 6). The crystal packing diagram evidently shows an array of molecules of 1 oriented along the b-axis. A similar scenario was witnessed for the adjacent array too; however, the adjacent array of molecules is correlated by an inversion symmetry (Figure 6). This unique packing diagram of the molecule in the crystal lattice leads to intermolecular Hbonding (Figure 6B; magenta trace) between the terminal -OH ligand of one molecule and the para-proton of the pyridinic ring of the adjacent molecule $(O11 \cdots H13 = 2.185(2))$ Å; see Figure 6B). Such supramolecular interaction might have a dramatic influence in the electronic structure of the molecules, particularly at a lower temperature (vide infra).

Direct Current (dc) Magnetic Susceptibility Studies of 1. Variable temperature (2-300 K) dc magnetic susceptibility measurements were performed on a toluene solution of **1**, using an applied magnetic field of 10 kOe (Figure 7). The observed



Figure 7. Temperature-dependent magnetic susceptibility measurement performed on the toluene solution of 1 with 10 kOe applied field in the temperature range of 2-300 K.

room temperature $\chi_M T$ value of 1.22 cm³ K mol⁻¹ is in close agreement with the expected value of three magnetically uncoupled spins (1.16 cm³ K mol⁻¹) with average $g_{Ni} = 2.1$ and $g_{rad} = 2.0023$ values. This apparently confirms the presence of three unpaired electrons and supports the trivalent oxidation state of nickel [two radicals on L₁ and an unpaired electron from low spin Ni(III)]. Upon decreasing the temperature, the $\chi_M T$ value decreases steeply until 70 K before increasing below this temperature and reaching a maximum of 1.06 cm³ K mol⁻¹ at 18 K.

Below 18 K, the $\chi_M T$ value abruptly decreases, reaching a value of 0.308 cm³ K mol⁻¹ at 1.99 K. The overall trend observed in the $\chi_M T = f(T)$ plot (up to 70 K) reveals that the unpaired electrons are coupled antiferromagnetically, which presumably stabilizes an overall ground state of S = 1/2. The variable temperature X-band EPR spectra recorded for this exchange coupled system are in good agreement with the magnetic susceptibility data recorded for 1 (*vide infra*).

X-Band Electron Paramagnetic Resonance (EPR) of 1. To probe the detailed electronic structure of 1, variable temperature, X-band EPR spectra were recorded as a pure polycrystalline powder and also in a dilution matrix of KBr pellet/toluene solution from 80 to 5 K. At room temperature, the EPR spectrum of the polycrystalline powder sample of 1 shows a broad, single line EPR signal around the g = 2 region, due to the population of all possible spin states; however, at the temperature \leq 80 K, the EPR spectrum is nicely resolved, with features centered around 3250-3450 G. The intensity of all the observed EPR signals increases as the temperature is lowered and reached a maximum intensity at 5 K (Figure S5). The spectra showed no evidence for EPR signals appearing at low magnetic fields in the temperature range of 80-5 K. The lack of EPR signals at low magnetic fields and the shape of the EPR features in the field range of 3250-3450 G suggest that the EPR transitions originate from an S = 1/2 spin state.

When the EPR experiments of 1 were performed on either a KBr pellet or frozen toluene solution, the observed trend in the temperature dependent behavior was different. As in the case of a KBr pellet, the maximum intensity is observed at 30 K and the intensity drops abruptly at 20 K (Figure 8 and Figure S6). Below this temperature, the intensities remain constant within experimental error (3332 G, 3352 G, and 3393 G). The abrupt change in intensity at this temperature, 30 K–20 K is plausibly due to either the depopulation of excited states or intermolecular antiferromagnetic interactions, as 1 is an



Figure 8. Experimental (black trace) and simulated (red trace) EPR spectra of 1 measured as a KBr pellet at 10 K. Conditions; microwave power 22 dB (1.262 mW), modulation amplitude 1 G, sweep time 40 s, average microwave frequency 9.3829 GHz.

exchange-coupled spin system. In the case of the frozen toluene solution, some of the EPR signals (3348 G and 3390 G; Figure S7) showed maximum intensity at 20 K and then drop significantly below this temperature. Another EPR signal shows maximum intensity only at 5 K (3328 G; Figure S7). The above trend indicates both depopulations of excited states and population of low-lying ground states take place at the same time. This behavior is consistent with the variable temperature magnetic susceptibility measurements performed on the frozen toluene solution of 1. It is noteworthy to mention here that in all three cases, the EPR spectra showed no evidence for the presence of a large spin ground state i.e. $S \ge 1$, and the observed EPR signals are consistent with a half-integer spinsystem only, specifically S = 1/2, although the $\chi_M T$ value (1.06) cm³ K mol⁻¹) of 1 at 18 K indicates the population of a triplet state (S = 1), which is not consistent with the EPR observation at low temperature. In fact, observation of integer spin as a ground state is not quite possible for 1, as it contains an odd number of electrons. Nevertheless, the observed $\chi_M T$ at low temperature can be accounted, presumably due to the equal population of two distinct and nearly degenerate S = 1/2 spin states at this temperature with very weak ferromagnetic coupling between them.

The EPR spectra of 1 were simulated with the following spin-Hamiltonian parameters: 1 as a KBr pellet; g = [2.0123, 2.0031, 1.9764] ($g_{iso} = 1.9972$); Lorentzian line width of 14.5 G was used. The experimental and simulated EPR spectra of 1 as a polycrystalline powder and as a frozen solution are given in Figure S8 along with the simulated spin-Hamiltonian parameters. The observed g-tensors significantly deviate from both the radical as well as Ni(III) single ion g-tensor values, which is rationalized below.

The magnetic susceptibility data of **1** show dominant antiferromagnetic interactions and the nonzero $\chi_{\rm M}$ T value at 1.99 K (0.31 cm³ K mol⁻¹) is consistent with an overall S = 1/2 ground state. Considering the crystal structure of **1**, the unpaired electron spins $\left(S_{1_{rad}} = S_{2_{rad}} = \frac{1}{2} \text{ and } S_{3_{\rm Ni}} = \frac{1}{2}\right)$ could be treated as a triangle. Under this scenario, the total-ground state of S = 1/2 can arise from two states, namely, $|S_{12}, S\rangle = |0, 1/2\rangle$, and $|S_{12}, S\rangle = |1, 1/2\rangle$. Under the strong exchange limit, the

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g-value of these two different spin states is given by $|0, 1/2\rangle$ a n d $(g = 0.g_{1_{rad}} + 0.g_{2_{rad}} + 1.g_{3_{Ni}})$ |1. $1/2(g = (2/3). g_{1_{rad}} + (2/3). g_{2_{rad}} - (1/3). g_{3_{Ni}})$. By using the typical $g_{rad} = 2.0023$ and $g_{Ni} = 2.1$, the effective g-value of the state $|0, 1/2\rangle = 2.1$ and $|1, 1/2\rangle = 1.97$ is observed. The analysis based on a strong exchange limit indicates that the S =1/2 ground state is likely to originate from the $|1, 1/2\rangle$ rather than the $|0, 1/2\rangle$ state as the calculated effective g-value is in good agreement with the experimentally observed giso value (1.9972). Observation of unusual g-tensors for a strongly exchange coupled system is witnessed already in the literature. For example, Collison and co-workers have rationalized the unusual g-value ($g_{eff} = 2.48$) observed for a Ni₂Cr triangle using multifrequency high-field EPR techniques elegantly.³¹ Overall, variable temperature EPR experiments not only rationalize the origin of unusual g-values but also confirm the uncommon trivalent oxidation state observed for nickel ion in 1.

UV-vis-NIR Data and Theoretical Calculation of 1. The UV-vis-NIR spectrum of 1 was recorded in toluene at room temperature in a sealed cuvette. The spectrum shows four distinct peaks, an intense band at 447 nm along with a shoulder at 548 nm: a relatively less intense peak at 717 nm and broadband with low intensity centered at 975 nm (Figure 9). The observation of a band in the near IR region is a characteristic signature of a Ni(III) ion d-d transition, which is well documented in the literature.^{8b,30}



Figure 9. UV-visible spectrum of 1 measured in toluene $(5.88 \times 10^{-4} \text{ M})$ at room temperature (red trace). Inset: the broad, weak near IR transition of 1. Green sticks represent the computed UV-vis spectrum from TD-DFT calculations (refer to Figure S10 for A–D details).

To obtain further insight into the electronic structure of 1, DFT calculations are carried out. Both ferromagnetic and antiferromagnetic S = 1/2 spin states are explored. The antiferromagnetic spin state is the most stable species by 1.6 kcal/mol, which is consistent with the dc magnetic susceptibility measured on 1. The optimized structure of 1 shows the Ni–OH bond length of 1.82 Å, which is good agreement with the single crystal X-ray structure (Figure S9). The computed O–H stretching of 3667 cm⁻¹ is in qualitative agreement with the experimental data of 3605 cm⁻¹ which further emphasizes the presence of terminal hydroxo species bound to Ni(III) ion.

As expected, the unpaired electron spins on reduced L₁ are fully delocalized; however, maximum spin density is found on imino and pyridinic carbon atoms due to extensive delocalization (Figure 10). Similarly, spin density localized on nickel ion is found to be 1.4 e⁻ with a major contribution from the $d_{r^2-r^2}$ orbital, which indeed corroborates the Ni(III) center having one unpaired electron. Likewise, the spin densities on the -OHanion and the two electrons reduced L₁ ligand are found to be 0.16 e⁻ and 1.44 e⁻, respectively. The significantly lower spin density on the ligated atoms suggests that spin density is delocalized onto the nickel center which rationalizes the increased spin density observed on the nickel site as compared to the expected value for an unpaired electron. The small radical character in the -OH moiety is sufficient to catalyze C-H activation through the radical mechanism, which rationalizes why 1 is promoting HAT reactions efficiently.

Finally, time dependent-DFT calculations were performed on the optimized structure of **1**. The computed spectrum also shows four distinct peaks (358, 397, 680, and 1099 nm), and the observed transition energies are in line with the experimental values (Figure 9 and Figure S10). The calculated transitions are rather strongly mixed. The computed weak d-d transition is predicted at 1099 and 680 nm. Overall, the calculations support the findings from the experiments that the oxidation state of the nickel ion is trivalent.

Chemical Reactivity of 1. Tolman and co-workers and other research groups have elegantly shown the hydrogen atom abstraction ability of various transition metal complexes (for example LCu(III)–OH, where L = NNN pincer ligand) from hydrocarbons.^{16,17a,25,26,32,33} As 1 is structurally similar to the copper(III) complex, HAT reactions were performed on hydrocarbon substrates, such as dihydroanthracene (DHA) and dihydrobenzene (DHB) in the presence of a THF solution of 1 at room temperature (Scheme 2).

Not surprisingly, 1 promotes the HAT reaction efficiently and results in the formation of anthracene and benzene, respectively (Figures S11–S12). The HAT reaction proceeds smoothly in these cases without any added external oxidant,



Figure 10. Computed Mulliken spin density on 1 at the B3LYP-D3/LAC3VP**/cc-pVTZ(-f) level.

Scheme 2. Schematic Representation of HAT Reaction Promoted by 1 at Room Temperature



implying the striking reactivity of **1**. The chemical reactivity of **1**, similar to that of a terminal Cu(III)–OH complex, undisputedly reveals that a –OH group bound to the nickel ion and rules out the possibility of the terminal $-OH_2$ group in **1**.

CONCLUSIONS

The reaction of zerovalent nickel precursor and L1 in the presence of trace amount of oxygen led to the formation of mononuclear nickel complex, which is crystallographically characterized with the molecular formula of $[Ni^{III}(L_1)^{2-}(OH)]$ (1). XPS measurement performed on 1 unambiguously confirms the paramagnetic signature of the nickel ion, which helped to rationalize the nature of the fourth coordinating ligand as a terminal -OH group. The origin of -OH ligand in 1 is confirmed by ${}^{18}O_2/{}^{2}H$ (d8-THF) labeled experiment upon activation of molecular oxygen followed by hydrogen atom abstraction from THF solvent. The appearance and disappearance of the ¹H NMR peak at 5.56 ppm in 1 and the HAT reaction catalyzed by 1 strongly corroborate the findings of XPS data. In line with the structural prediction by multiple spectroscopic analysis, the observed room temperature $\chi_M T$ value $(1.22 \text{ cm}^3 \text{ K mol}^{-1})$ is consistent with the three unpaired electrons (two from L_1 and one from Ni(III) ion) in 1. The temperature dependent $\chi_M T(T)$ profile implies a dominant antiferromagnetic interaction between the spins, which results in a doublet as an overall ground state. The X-band EPR spectra recorded for this complex are in excellent agreement with the magnetic data, and the observed g-tensors for 1 are rationalized under strong exchange limit of spin-coupled systems. Theoretical calculations shed light on the electronic structure of 1, and the computed UV-vis-NIR and stretching frequencies are in good agreement with the experimental absorption and IR spectra, respectively. Overall, a new synthetic strategy is revealed to stabilize the uncommon oxidation state of the nickel ion under the mild condition (for example, using molecular dioxygen as an oxidant). The reported method is distinctly different from the other literature reports to access the unusual oxidation state for nickel ion.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b00466.

Crystallographic table, HSQC spectra of complex 1, and GC and GC-MS spectra for HAT reactions (PDF)

Accession Codes

CCDC 1498088 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge

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Notes

The authors declare no competing financial interest.

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