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DOI:

[10.1021/acs.inorgchem.9b00466](https://doi.org/10.1021/acs.inorgchem.9b00466)

Document Version

Accepted author manuscript

[Link to publication record in Manchester Research Explorer](#)

Citation for published version (APA):

Rajpurohit, J., Shukla, P., Kumar, P., Das, C., Vaidya, S., Sundararajan, M., Shanmugam, M., & Shanmugam, M. (2019). Stabilizing Terminal Ni(III)–Hydroxide Complex Using NNN-Pincer Ligands: Synthesis and Characterization. *Inorganic Chemistry*, 58(9), 6257–6267. <https://doi.org/10.1021/acs.inorgchem.9b00466>

Published in:

Inorganic Chemistry

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

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Abstract

The reaction of $[\text{Ni}(\text{COD})_2]$ (COD; cyclooctadiene) in THF with the NNN-pincer ligand bis(imino)pyridyl (L_1) reveals a susceptibility to oxidation in an inert atmosphere ($[\text{O}_2]$ level <0.5 ppm), results 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 $[\text{Ni}^{\text{III}}(\text{L}_1^{\bullet\bullet})^2(\text{OH})]$ (**1**). Various isotopically labelled experiments ($^{16}\text{O}/^{18}\text{O}$) assertively endorses that 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 shake-up satellite peaks for the primary photoelectron lines of Ni(2p) in the X-ray photoelectron spectroscopy (XPS) spectrum 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** show dominant antiferromagnetic interactions exist among the paramagnetic centres, results in an overall $S = \frac{1}{2}$ ground state. Variable temperature X-band EPR studies performed on **1** show evidence for $S = \frac{1}{2}$ ground state, which is consistent with magnetic data. The unusual g-tensor extracted for a ground state, $S = \frac{1}{2}$ is analyzed under a strong exchange limit of spin-coupled centres. 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 like 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 photo-elimination was shown by Nocera and co-workers⁵ and further its significance as a reactive catalyst is exemplified by Hillhouse and co-workers in HAT reactions.⁶

In general, to stabilize the Ni(III) oxidation state, ligands with hard donor atoms have predominantly been employed.⁷ However, in the majority of cases, the Ni(III) valance-state was mainly accessed, either through 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 alter the redox potential of the reactive metal centre 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 electrons¹¹. It is expected that the strong σ -donating capability and the extended π -cloud of L_1 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 L_1 (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 towards 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

Materials and Methods

Unless otherwise specified, all the reactions were carried out under anaerobic condition using a Schlenk technique and/or glove box. All the chemicals were purchased from commercially available sources, which were used without further purification. The ligand L_1 was synthesized according to the reported procedure.¹³ Single crystal data were collected on a Rigaku Saturn CCD diffractometer using a graphite monochromator (MoK_{α} , $\lambda = 0.71073 \text{ \AA}$). 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° , 16s 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 F^2 . 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 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 Easy Spin toolbox (5.2.18) for the Matlab program package.¹⁴

The X-ray photoelectron spectra were obtained on axis supra model of Kratos analytical electron spectrometer. The samples were mounted on carbon tape such that the sample cylinder was completely covered. The $\text{Al}(\text{K}_\alpha)$ X-ray line (1486.6 eV) was used for photoelectron excitation. C1s 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 Jaguar electronic structure package.¹⁶ Optimized geometries were obtained with 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 $\epsilon = 2.38$ (toluene). A time-dependent (TD) DFT calculations are performed using ω -B97X functional²⁰ in conjunction with def2-TZVP basis set²¹ using toluene as a solvent to obtain the lowest 30 doublet states performed in ORCA 4.0.1 electronic structure package.²²

Synthesis of $[\text{Ni}^{\text{III}}(\text{L}_1^{\bullet\bullet})_2(\text{OH})]^\#$ (**1**)

In an argon filled glove box, 50 mg of L_1 (0.082 mmol) and 23 mg of $[\text{Ni}(\text{COD})_2]$ (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. $\text{N}_2 + \text{CH}_3\text{CN}$). 0.2 mL of $^{16}\text{O}_2/^{18}\text{O}_2$ gas was injected into this solution with the help of a gas-tight syringe and slowly solution was allowed to warm up to room temperature (~ 30 -40 min). The colour 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 hours. The resulting maroon solution was evaporated to dryness, extracted into hexane (5 mL) and the filtrate was concentrated to 3-4 mL, which was kept for crystallization at room temperature. Within two days, brown colour block-shaped crystals were grown from the

filtrate upon slow evaporation. Yield (based on nickel): 23 mg (47 %). Anal calcd for ($\text{C}_{43}\text{H}_{48}\text{NiN}_3\text{O}$): 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 ^{18}O labelled atom. The m/z value of 681 along with 679 of equal intensity suggest the ^{18}O atom from $^{18}\text{O}_2$ gas (*vide infra*, also see ESI figure S1).

We have also observed that the reaction works very well even if we do not inject the $^{16}\text{O}_2/^{18}\text{O}_2$ into the reaction mixture externally i.e. the ppm level of oxygen gas present in the glove box is sufficient to isolate **1**.

Control experiment with H_2^{18}O : -

To probe the possible origin of –OH group in **1**, a similar synthetic procedure was followed as above, but ^{18}O labelled water (H_2^{18}O ; 1.7 μL) was used in place of $^{18}\text{O}_2$ gas. MALDI spectrum recorded for the crystals obtained in this reaction (see Figure S1 and related discussion are given in result and discussion section).

Synthetic procedure followed for the *in-situ* HAT reaction

In an argon-filled glove box, 25 mg of ligand, L_1 (0.0415 mmol), 12.5 mg of $[\text{Ni}(\text{COD})_2]$ (0.0415 mmol) were weighed and added into 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 minutes 81 mg of 2,4-di-tertbutyl 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 gas-tight 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 minutes, the rationale for this is described in the main text below (*vide infra*).

HAT reaction promoted by **1**

In an argon-filled glove box, 10 mg of **1** (1.47 μmol), 1.5 ml of THF was added into a 10 ml Schlenk tube, further 4 mg (22 μmol) of 9,10 dihydroanthracene or 2 μL (22 μmol) 1,4-cyclohexadiene was added. The reaction mixture was stirred for 24 h at room temperature. After completion of the reaction, 3 μL 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 were quantified with an internal standard by the means of GC and found the conversion of 11 % and 13 % for 9,10-dihydroanthracene and 1,4-cyclohexadiene respectively.

Results and discussions

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 colour 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 L_1 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 presence of the bulky substituents at the ortho-positions of the phenyl ring on the amine.

Scheme 1. General synthetic scheme followed for the synthesis of complex **1**.

The precursor $[\text{Ni}(\text{COD})_2]$ 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 ($\text{C14-N12} = 1.337(1) \text{ \AA}$) is shorter than a single bond ($1.465 \text{ \AA}$) and longer than a double bond ($1.279 \text{ \AA}$). The observed bond length is consistent with the other literature reports.²³

The fourth coordination site of the Ni ion is occupied by an oxygen atom in **1**, with a bond length of $1.824(5) \text{ \AA}$. The observed Ni1-O11 bond length is considerably shorter than $\text{Ni(II)-H}_2\text{O}$ ($2.044(4)$ - $2.107(3) \text{ \AA}$) and longer than Ni-oxo ($1.790(2) \text{ \AA}$; note: there is no terminal Ni-oxo complex structurally characterized in the literature until to date, but an oxo-bridged Ni(III) complex was structurally characterized^{23b}) complexes reported in the literature.²⁴ The oxidation state of nickel ion and the overall electronic structure of **1**, depending 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 labelling experiments have been employed to determine the identity of the terminal ligand.

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: $\angle \text{O1–Ni1–N11} = 180^\circ$; $\angle \text{N12–Ni1–N12\#} = 165.3(2)^\circ$; $\angle \text{N12–Ni1–N11} = 82.67(11)^\circ$; $\angle \text{O11–Ni1–N12} = 97.33(11)^\circ$.

The single crystal X-ray diffraction confirms the presence of an oxygen donor bound to nickel ion which is firmly supported by matrix-assisted laser desorption/ionization (MALDI) spectrum recorded for **1** (Figure 2). Figure 2 shows an m/z 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**, to shed light on the origin of oxygen-based ligand in **1**, ^{18}O -isotopic labelling experiments were performed under the identical reaction condition used to isolate **1**. The reactions were carried out

in the presence of (i) ^{18}O -labeled $^{18}\text{O}_2$ -gas and (ii) $^{18}\text{OH}_2$ (see the experimental section for details).

Figure 2. A-B) MALDI spectra of **1** show 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 ^{18}O labelled $^{18}\text{O}_2$ gas.

In the former case, the reaction did not proceed well, presumably due to the decomposition of the radical anionic ligand, as $^{18}\text{O}_2$ gas was introduced into the reaction

mixture at the room temperature. In contrast, a stable complex formation of **1** is noticed, if $^{18}\text{O}_2$ gas 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 that 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 ^{18}O labelled water does not show m/z peak correspond to ^{18}O -incorporation and the MALDI spectrum resembles that of shown in Figure 2A (Figure S1 of ESI). These two, ^{18}O -labeling experiments unequivocally confirm that the origin of the terminal oxygen based ligand ($-\text{OH}_x$) in **1** is due to molecular O_2 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**, Infra-Red (IR) spectrum was recorded for **1** in Nujol mulls.

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

The IR spectrum of **1** markedly shows a sharp peak at 3605 cm^{-1} (Figure 3), which is assigned to the $\nu_{(-\text{OH})}$ stretching frequency. In addition, routine $-\text{C}-\text{H}$, $-\text{C}=\text{C}$ and $-\text{C}=\text{N}$ stretching frequencies are observed in the usual fingerprint regions. IR experiment irrefutably reveals that 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 $-\text{OH}$ band centred at 3000 cm^{-1} in the IR spectrum. The absence of such broadband and the presence of a sharp peak at 3605 cm^{-1} hints 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 adds confidence to our notion.

To further probe the protonation state of the OH_x (x = 1 or 2), ¹H-NMR and ¹H-¹³C HSQC spectra were recorded for **1** in dry C₆D₆. 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 C₆D₆) spectra of **1** and **2** recorded at room temperature in C₆D₆ solvent (# = Grease, * = THF, \$ = Toluene, @ = Residual C₆D₆). Inset: expanded region of 5.2-6.0 ppm. B) O₂ concentration-dependent biphenol product formation in the presence of

[Ni(COD)₂] and L₁. The values $\pm$ SE reported here are an average value of three independent experiments carried out under identical experimental conditions.

The ¹H-¹³C 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 ¹H-¹³C spectrum (Figure S2). This scenario evidently confirms our assignment that the NMR signal observed at 5.56 ppm corresponds to a proton, which is attached to a heteroatom (such as oxygen). Although IR spectrum of **1** signals the presence of a hydroxyl group, due to the broadening of ¹H NMR signal and absence of an absolute molecular ion peak in MALDI, the number of proton(s) bounds to the oxygen donor cannot be determined accurately. However, using X-ray photoelectron spectroscopy we did identify the oxidation state the terminal ligand bound to nickel ion, subsequently the oxidation state of nickel ion in **1** (*vide infra*).

Next, we turned our attention to answer, 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) labelling experiments ii) *In-situ* HAT reaction which is detailed below

Deuterium labelling 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 C₆D₆ 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 enacts as the source of the proton.

***In-situ* HAT reaction:**

The objectives of conducting this O_2 concentration-dependent HAT experiments are of two-fold I) to show that O_2 molecule gets activated at the nickel site and produce a transient nickel: dioxygen adduct ii) 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 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 $\text{Ni}^{\text{IV}}=\text{O}$ or $\text{Ni}^{\text{IV}}-\text{O}_2^{2-}$ or $\text{Ni}^{\text{III}}-\text{O}_2^{\cdot-}$) 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, O_2 concentration-dependent HAT experiments were performed using 2,4-di(*t*-butyl)phenol substrate (see experimental section for details also see ESI figure S3). Here, we would like to point out that, the HAT reaction is promoted by $[\text{Ni}(\text{COD})_2]$ itself with phenolic substrate (2,4-di(*t*-butyl)phenol), however, to avoid the involvement of $[\text{Ni}(\text{COD})_2]$ in HAT reactions, the substrate was added after 5 minutes. By this time $[\text{Ni}(\text{COD})_2]$ 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 $[\text{Ni}(\text{COD})_2]$ 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(*t*-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 See ESI Figure S4).^{26a,}

^{26b}, ^{26c}, ^{26d} 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 centre 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, the transient Ni:dioxygen adduct abstracts 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) labelled 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 proton abstraction) in **1**. The characteristic (shake-up 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

The Ni(2p) X-ray photoelectron spectrum recorded for **1** (Figure 5) reveals the presence of two main peaks with the binding energy of 853.87 eV and 871.77 eV which are attributed to the primary photoelectron lines of 2p_{3/2} and 2p_{1/2}, respectively. In addition, there are two shake-up satellite peaks associated with the 2p_{3/2} and 2p_{1/2} lines respectively, observed at 860.12 eV 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 ± 0.1 to 857.5 ± 0.2) reported in the literature.²⁸ This is attributed to the strong electron donating nature of nitrogen donors of **L**₁, 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 $[\text{Ni}(\text{diars})\text{Cl}_2](\text{ClO}_4)_2$ complex were observed at 854.7 eV and 872.6 eV respectively, for the photoelectron lines $2p_{3/2}$ and $2p_{1/2}$.

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

Although the formal oxidation state of the nickel ion in the above molecular formula represent +4, the experimentally observed binding energy is in the range observed for +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 shake-up satellite peak gives invaluable information not only about the geometry of the metal ion but also reveal the nature of 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 shake-up satellite peaks are described in details elsewhere.²⁹ To summarize the literature reports, shake-up 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 forbidden nature of shake-up lines.^{28, 29b} The square planar geometry around the nickel ion and the two-electron reduction of L₁ 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 state for the square planar nickel ion namely [Ni^{IV}(L^{••})²⁻(O)] (**1a**), [Ni^{III}(L^{••})²⁻(OH)] (**1**), [Ni^{III}(L^{••})²⁻(O[•])] (**1b**) and [Ni^{II}(L^{••})²⁻(H₂O)] (**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 results in the diamagnetic signature. As state above, diamagnetic nickel ion does not show shake-up satellite peaks, but this contradicts the experimental observation, therefore, one can safely neglect the possible models of **1a** and **1c**. The observation of shake-up satellite peak for both the primary photoelectron peaks apparently reveals that nickel ion must be trivalent and paramagnetic (low spin Ni³⁺ = 3d⁷ 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 suggests that proton(s) is(are) 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 non-integer spin state rather integer spin state (*vide infra*). Further, a non-integer spin state for the model **1b** is not possible as it contains even number (total four) of

unpaired electrons (two from L₁, 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 L₁ 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, 4b, 4, 7a, 7c, 7d, 12a} It is because there is no distortion in the plane formed by N11, N12, O11, N12# (where # represent the symmetrically generated atom, dihedral angle N11, N12, O11, N12# = 0°) and also the Ni(III) ion resides at the centre 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*).

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

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.

Proven the protonation state of the terminal ligand and the oxidation state of the nickel ion in **1**, 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 H-bonding (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....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 room temperature $\chi_M T$ value of $1.22 \text{ cm}^3 \text{ K mol}^{-1}$ is in close agreement with the expected value of three magnetically uncoupled spins ($1.16 \text{ cm}^3 \text{ K mol}^{-1}$) with an 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 L_1 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 $1.06 \text{ cm}^3 \text{ K mol}^{-1}$ at 18 K.

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

Below 18 K, the $\chi_M T$ value abruptly decreases reaching a value of $0.308 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.99 K. The overall trend observed in $\chi_M T = f(T)$ plot (up to 70 K) reveals that the unpaired

electrons are coupled antiferromagnetically, which presumably stabilize an overall ground state of $S = \frac{1}{2}$. The variable temperature X-band EPR spectra recorded for this exchange coupled system is 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 ≤ 80 K, the EPR spectrum is nicely resolved, with features centred around 3250-3450 Gauss. 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 Gauss suggest that the EPR transitions originate from an $S = \frac{1}{2}$ spin state.

When the EPR experiments of **1** were performed on either as a KBr pellet or frozen toluene solution, the observed trend in the temperature dependent behaviour is different. As in the case of KBr pellet, the maximum intensity is observed at 30 K and the intensity drops abruptly at 20 K (Figure 8 and also see ESI figure S6). Below this temperature, the intensities remain constant within experimental error (3332 G, 3352 G & 3393 G). The abrupt change in intensity at this temperature, 30 K–20 K is plausibly either due to the depopulation of excited states or intermolecular antiferromagnetic interactions, as **1** is an exchange-coupled spin system. In case of the frozen toluene solution, some of the EPR signals (3348 G & 3390 G; Figure S7) showed maximum intensity at 20 K, then drops significantly below this temperature. Other 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 behaviour 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 large spin ground state i.e. $S \geq 1$ and the observed EPR signals are consistent with half-integer spin-system only, specifically $S = \frac{1}{2}$. Although the $\chi_M T$ value ($1.06 \text{ cm}^3 \text{ K mol}^{-1}$) 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 $S = \frac{1}{2}$ spin states at this temperature with very weak ferromagnetic coupling between them.

Figure 8. Experimental (black trace) and simulated (red trace) EPR spectrum 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.

The EPR spectra of **1** were simulated with the following spin-Hamiltonian parameters; **1** as a KBr pellet; $g = [2.0123, 2.0031, 1.9764]$ ($g_{\text{iso}} = 1.9972$); Lorentzian line width of 14.5 Gauss 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 deviates 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 non-zero χ_{MT} value at 1.99 K ($0.31 \text{ cm}^3 \text{ K mol}^{-1}$) is consistent with an overall $S = \frac{1}{2}$ ground state. Considering the crystal structure of **1**, the unpaired electron spins ($S_{1_{\text{rad}}} = S_{2_{\text{rad}}} = \frac{1}{2}$ and $S_{3_{\text{Ni}}} = \frac{1}{2}$) could be treated as a triangle. Under this scenario, the total-ground state of $S = \frac{1}{2}$ can arise from two states namely, $|S_{12}, S\rangle = |0, \frac{1}{2}\rangle$ and $|S_{12}, S\rangle = |1, \frac{1}{2}\rangle$. Under the strong exchange limit, the g-value of these two different spin states are given by; $|0, \frac{1}{2}\rangle$ ($g = 0 \cdot g_{1_{\text{rad}}} + 0 \cdot g_{2_{\text{rad}}} + 1 \cdot g_{3_{\text{Ni}}}$) and $|1, \frac{1}{2}\rangle$ ($g = (2/3) \cdot g_{1_{\text{rad}}} + (2/3) \cdot g_{2_{\text{rad}}} - (1/3) \cdot g_{3_{\text{Ni}}}$). By using the typical $g_{\text{rad}} = 2.0023$ and $g_{\text{Ni}} = 2.1$ the effective g-value of the state $|0, \frac{1}{2}\rangle = 2.1$ and $|1, \frac{1}{2}\rangle = 1.97$ is observed. The analysis based on strong exchange limit indicates that $S = \frac{1}{2}$ ground state likely to originate from $|1, \frac{1}{2}\rangle$ rather than $|0, \frac{1}{2}\rangle$ state as the calculated effective g-value is in good agreement with the experimentally observed g_{iso} 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 ($g_{\text{eff}} = 2.48$) observed for a Ni_2Cr triangle using multi-frequency high-field EPR techniques elegantly.³¹ Overall, variable temperature EPR experiments not only rationalizes the origin of unusual g-values, but also confirms 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 centred 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}

To obtain further insight at the electronic structure of **1**, DFT calculations are carried out. Both ferromagnetic and anti-ferromagnetic $S=1/2$ spin states are explored. The anti-ferromagnetic 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.

Figure 9. The UV-Visible spectrum of **1** measured in toluene (5.88×10^{-4} M) at room temperature (red trace). Inset: shows 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 in ESI)

As expected, the unpaired electron spins on reduced L_1 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 $d_{x^2-y^2}$ orbital, which indeed corroborates that the Ni(III) centre having one unpaired electron. Likewise, the spin density on the $-OH$ anion and the two electrons reduced L_1 ligand is 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 centre 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.

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

Finally, Time Dependent-DFT calculations were performed on the optimized structure of **1**. The computed spectrum also shows four distinct peaks (358 nm, 397 nm, 680 nm, 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 680nm. 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.^{16a,16b, 17a,25-26, 32} 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 THF solution of **1** at room temperature (Scheme 2).

Scheme 2. Schematic representation of HAT reaction promoted by **1** at room temperature.

Not surprisingly, **1** promotes the HAT reaction efficiently results in the formation of anthracene and benzene respectively (Figures S11-S12 of ESI). The HAT reaction proceeds smoothly in these cases without any added external oxidant, implies 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 -OH₂ group in **1**.

Conclusions

The reaction of zero-valent nickel precursor and L_1 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 $[\text{Ni}^{\text{III}}(\text{L}_1^{\bullet\bullet})^2(\text{OH})]$ (**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 $-\text{OH}$ group. The origin of $-\text{OH}$ ligand in **1** is confirmed by $^{18}\text{O}_2/2\text{H}$ ($d_8\text{-THF}$) labelled experiment upon activation of molecular oxygen followed by proton 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 χ_{MT} 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 $\chi_{\text{MT}}(T)$ 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 is in excellent agreement with the magnetic data and the observed g-tensors for **1** is rationalized under strong exchange limit of spin-coupled systems. Theoretical calculations, shed light on the electronic structure of **1** and the computed the 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 uncommon oxidation state of 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. Crystallographic table, HSQC spectra of complex **1**, GC and GC-MS spectra for HAT reactions is given in supporting information. CCDC number: 1498088

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ACKNOWLEDGEMENTS

MS thanks the funding agencies (SERB (EMR/2015/000592), INSA (SP/YSP/119/2015/1264)), CSIR (01(2933)/18/EMR-II) for the financial assistance and the central facility IRCC, IIT Bombay for the access of ESCA, MALDI and EPR. MS acknowledges The University of Manchester and MIB for financial supports.

ABBREVIATIONS

HSQC, heteronuclear single quantum coherence; XPS, x-ray photoelectron spectroscopy, EPR, electron paramagnetic resonance, HAT, hydrogen atom transfer, MALDI, matrix-assisted laser desorption/ionization.

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A new synthetic strategy is revealed to stabilize trivalent oxidation state of nickel ion under the mild condition (example, using molecular dioxygen as an oxidant). This method is distinctly different from the other literature reports to access the trivalent oxidation state for Ni ion, with the molecular formula $[\text{Ni}^{\text{III}}(\text{L}_1^{\bullet\bullet})^2(\text{OH})]$. The electronic and magnetic properties of the complexes are discussed in details.