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Deprotonation Induced Ligand Oxidation in a Ni^{II} Complex of a Redox Noninnocent *N*¹-(2-Aminophenyl)benzene-1,2-diamine and Its Use in Catalytic Alcohol Oxidation

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S Supporting Information

ABSTRACT: Two nickel(II)-complexes, [Ni^{II}(H₃L)₂](ClO₄)₂ (**1**)-(ClO₄)₂ and [Ni^{II}(HL)₂] (**2**), containing the redox-active tridentate ligand *N*¹-(2-aminophenyl)benzene-1,2-diamine (H₃L) have been synthesized. Complex **1** is octahedral containing two neutral H₃L ligands in a facial coordination mode, whereas complex **2** is a singlet diradical species with approximately planar configuration at the tetracoordinate metal atom with two pendant NH₂ side arms from each of the coordinated ligands. Both complexes are found to be chemically interconvertible; complex **1**²⁺ gets converted to complex **2** when exposed to base and oxygen via simultaneous deprotonation and oxidation of the coordinated ligands. Molecular and electronic structures of the isolated complexes are scrutinized thoroughly by various spectroscopic techniques, single crystal X-ray crystallography, and density functional theory. The observed dissociation of a ligand arm upon oxidation of the ligand was exploited to bring about catalytic alcohol oxidation using coordinatively saturated complex **1** as a catalyst precursor. Both the complexes **1** and **2** were tested for catalytic oxidation of both primary and secondary alcohols.

INTRODUCTION

Exploring the chemistry of transition metal ions with redox noninnocent ligands has been an active research area over the past years.¹ Redox noninnocent ligands not only offer interesting (ambiguous) electronic structures to its complexes, but can also participate in electron transfer processes during bond activation processes, particularly in catalysis.²

Among the various redox noninnocent ligands available, the diamine³ and the aminophenol⁴ ligand systems have been studied most thoroughly. Other than exploring the ambiguous electronic structures of its complexes, the ligand centered redox events have also been utilized to bring about useful chemical transformations. Consequently, keeping the basic redox active diamine/aminophenol part intact, several other new ligands were designed and synthesized.^{5,6} Attaching an additional donor-moiety to phenyl ring (B) (Scheme 1) of diamine/aminophenol ligands produces tridentate pincer type ligands. The coordination behavior along with its redox properties can thus be tuned to some extent by choosing different substituents in the phenyl arm.

Recently Heyduk and co-workers reported a few of such tridentate redox noninnocent pincer and studied their coordination chemistry with suitable metal ions.^{5a-e} At the same time Kaim and co-workers explored the coordination behavior and redox properties of some hybrid redox-active

Scheme 1. Conversion of Diamine/Aminophenol Ligands to the Tridentate Congeners

iminobenzoquinone ligands with an additional thioether donor function.⁶ Interestingly, the soft S-donor arm was found to be involved in fluxional processes; often it coordinates to the central metal ion and sometimes it remains pendant. Such type of fluxional behavior shown by the coordinated ligands is of interest in synthetic coordination chemistry and catalysis, in particular because it can provide vacant coordination sites at the metal during catalytic turnover, sites that are masked in the

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Scheme 2. Deprotonation and Oxidation of Ligand H₃L

ground state structures thus enabling stabilization of such reactive unsaturated intermediates.

Herein, we report the synthesis, isolation, and crystallographic characterization of the octahedral and square planar nickel(II) complexes **[1]**(ClO₄)₂ and **2**, respectively. These complexes differ not only in their geometry around the central nickel(II) atoms, but also have different ligand oxidation states. The fluxional coordination of the ligand is revealed by reversible interconversion between **[1]**²⁺ and **2** upon exposure to base and oxygen or protons and a reducing agent. Complex **[1]**(ClO₄)₂ is hexacoordinated, bound to two tridentate N¹-(2-aminophenyl)benzene-1,2-diamine ligands in a facial coordination mode. Complex **[1]**(ClO₄)₂ upon deprotonation in the presence of molecular oxygen as the oxidant transforms to its square planar analogue **2** via oxidative dehydrogenation. Complex **2** is a singlet diradical species with approximately planar configuration around the tetracoordinate metal atom with two pendant NH₂ side arms from each of the coordinated ligands. Beyond mere characterization of the complexes isolated, catalytic alcohol oxidation reactions were carried out to test the fluxional coordination behavior of the coordinated ligand in complex **[1]**(ClO₄)₂. The hexacoordinated Ni(II) complex **[1]**(ClO₄)₂ showed excellent catalytic activity in oxidizing both primary and secondary alcohols, even though it does not have vacant coordination sites available in its ground state structure. Both complexes **[1]**(ClO₄)₂ and **2** show excellent activity in the catalytic oxidation of both primary and secondary alcohols. Notably, catalytic alcohol oxidation reactions are of contemporary interest because of their relevance to chemical energy conversion using renewable resources.⁷

■ RESULT AND DISCUSSION

The tridentate ligand, N¹-(2-aminophenyl)benzene-1,2-diamine, used in this study was prepared following the literature available.⁸ The coordination chemistry of the corresponding tris(amide) ligands having substitution in the two terminal -NH arms is quite well-known, but the coordination chemistry of the unsubstituted triamine (H₃L) has been less explored. These type of ligands are known for their redox noninnocent behavior;⁵ in its completely deprotonated trianionic form it offers catecholate type of binding [NNN^{cat}]³⁻, whereas upon coordination it can be oxidized by one electron to afford the radical iminosemiquinone form, [NNN^{sq}]²⁻, and by a second electron to afford the iminoquinone form, [NNN^q]⁻ (Scheme 2).

Reaction of Ni(ClO₄)₂ (0.387 mmol) with the ligand H₃L (0.774 mmol) in boiling methanol in a Schlenk tube under argon atmosphere produced a new, almost colorless dicationic complex [Ni^{II}(H₃L)₂](ClO₄)₂ (**[1]**(ClO₄)₂) in 85% yield. Elemental analysis along with positive-ion electrospray ionization mass spectra convincingly support its formulation

(see the Supporting Information (S1)). Complex **[1]**(ClO₄)₂ showed an intense peak due to the molecular ion **[1-H]**⁺ at *m/z*, 455 amu. Notably, the experimental spectral features of the complexes correspond well to the simulated isotopic pattern for the given formulation. A representative spectrum, that of **[1]**²⁺ along with the simulated spectrum, is shown in the Supporting Information (Figure S1). The room temperature magnetic moment μ_{eff} of complex **[1]**²⁺ is 2.68 μ_{B} , which is close to the spin-only value of a metal-centered *S* = 1 spin system, as expected for an octahedral Ni^{II} ion.⁹

The same reaction, however, in the presence of a strong base like NaOH and oxygen produced the new, bluish-green colored neutral complex **2** in 90% yield. Interestingly, complex **2** possesses an *S* = 0 ground state, as determined by magnetic susceptibility measurements at room temperature. It displayed sharp ¹H NMR signals in the normal range for diamagnetic compounds. The spectral pattern reveals that the two ligands in the complexes are magnetically equivalent on the NMR time scale. The aromatic protons of the coordinated ligand appear in the region δ 6.3–7.5. The broad peak at δ 6.37 is assigned to the -NH resonances. The most notable observation in the spectrum is the appearance of a broad singlet at δ 3.91, which is attributed to the uncoordinated -NH₂ groups, one from each of the two coordinated ligands. The intensity of the -NH signal decreases upon shaking a solution containing a droplet of D₂O. The ¹H NMR spectrum of **2** is shown in the Supporting Information (Figure S3).

X-ray Crystal Structures. X-ray diffraction (XRD)-quality single crystals of complex **[1]**(ClO₄)₂ were obtained by slow evaporation of its solution in dichloromethane-methanol (1:1) solvent mixture under nitrogen atmosphere, and the structure was solved. The molecular view of the cationic complex **[1]**²⁺ with partial atom numbering scheme is displayed in Figure 1, and the Oak Ridge thermal-ellipsoid plot (ORTEP) with

Figure 1. Molecular view of complex [Ni^{II}(H₃L)₂](ClO₄)₂ (**[1]**(ClO₄)₂). The ClO₄⁻ counterions are omitted for clarity (*i* means the symmetry operation *i* = −*x* + 1, −*y*, *z*).

Table 1. Summary of Selected Experimental and Calculated Bond Lengths (Å) and Bond Angles (deg) of Complexes $[1]^{2+}$, **2**, and $[2]^{-}$

	$[1]^{2+}$		2		$[2]^{-}$
	X-ray	DFT	X-ray	DFT	DFT
Bonds					
Ni–N1	2.115(2)	2.1400	1.8262(19)	1.8404	1.8550
Ni–N8	2.139(2)	2.2115	1.8578(19)	1.8920	1.9199
Ni–N15	2.116(2)	2.1982			
N1–C2	1.447(3)	1.4539	1.341(3)	1.3395	1.3540
N8–C7	1.463(3)	1.4740	1.355(3)	1.3548	1.3743
N8–C9	1.450(3)	1.4556	1.427(3)	1.4237	1.4102
N15–C14	1.447(4)	1.4589			
C2–C3	1.389(4)	1.3979	1.414(4)	1.4197	1.4106
C2–C7	1.387(4)	1.3939	1.423(4)	1.4462	1.4395
C3–C4	1.388(4)	1.3976	1.362(4)	1.3810	1.3941
C4–C5	1.383(5)	1.3939	1.406(4)	1.4189	1.4037
C5–C6	1.386(4)	1.3980	1.371(4)	1.3793	1.3967
C6–C7	1.391(4)	1.4000	1.413(4)	1.4207	1.4082
Bond Angles					
N1–Ni–N8	81.26(9)	80.528	84.18(8)	89.945	83.351
N8–Ni–N15	78.62(9)	75.663			

complete atom numbering scheme is submitted in the Supporting Information (S4, S5). The metrical parameters are collected in Table 1.

The molecular structure of complex $[1](\text{ClO}_4)_2$ consists of one $[\text{Ni}(\text{H}_3\text{L})_2]^{2+}$ cation and two ClO_4^- anions leading to the molecular formula $[\text{Ni}^{\text{II}}(\text{H}_3\text{L})_2](\text{ClO}_4)_2$. The geometry of the cation $[1]^{2+}$ is a distorted octahedron comprising two facially coordinating ligands. Notably, none of the neutral σ -donating amine donors is deprotonated, and all six donors are bound to the central Ni-ion with their nitrogen lone-pairs. The bond distances are consistent with the nonoxidized neutral form of the ligand as revealed by density functional theory (DFT) studies. The average C–N and Ni–N bond distances are 1.455(3) Å and 2.123(2) Å, respectively. These Ni–N distances are typical of a Ni(II) center bound to neutral nitrogen donor atoms, as shown by a search carried in the Cambridge Structure Database (web CSD version 1.1.7)¹⁰ for compounds containing the NiN_6 fragment.

The packing diagram of complex $[1](\text{ClO}_4)_2$ is shown in the Figure 2. The crystal structure of this complex is stabilized by a two-dimensional (2-D) network of N–H $\cdots$ O hydrogen bonds in which layers of ClO_4^- alternate with layers of $[\text{Ni}^{\text{II}}(\text{H}_3\text{L})_2]^{2+}$. The geometric parameters of the hydrogen bonds are listed in Table 2.

In contrast to the structure of complex $[1]^{2+}$, the single-crystal X-ray diffraction analysis of complex **2** revealed a distorted square planar environment around the Ni center with a pendant NH_2 side arm from each of the two coordinating ligands at (averaged) nonbonding distances of 3.679(3) Å (Figure 3). The bond distances in complex **2** are similar to those observed in similar Ni^{II} complexes containing two partially oxidized *o*-diiminobenzosemiquinonato ligands.¹¹ The average C–N and Ni–N distances in **2** are 1.348(3) and 1.84175(19) Å, respectively. In similar bidentate di-imine type of ligands, C–N distances are considered to be an excellent indicator of the charge and the oxidation state of the coordinated ligand.¹² The iminosemiquinone oxidation state is characterized by C–N distances of 1.36 Å. Moreover, the one-electron oxidized *o*-diiminobenzosemiquinonato ligands also display partial localization of double bond character within

Figure 2. Perspective view of 2-D network of N–H $\cdots$ O hydrogen bonding interactions along the $[100]$ direction displaying cationic layers of $[\text{Ni}^{\text{II}}(\text{H}_3\text{L})_2]^{2+}$ separated by ClO_4^- anions (C–H hydrogen atoms have been omitted for clarity).

the aryl rings. In agreement with the available literature,^{5a–c,11,12} in **2**, the partial double bond localization is also evident (Table 1). The DFT calculations reasonably reproduce the structures of $[1]^{2+}$ and **2**. DFT studies indeed confirm the presence of two one-electron semiquinone radicals in complex **2** (cf. below). Given the diamagnetic nature of **2**, as revealed by the magnetic susceptibility and NMR spectroscopic measurements (vide supra), the two unpaired electrons of these ligand radicals must be quite strongly antiferromagnetically coupled as observed in similar systems.^{5a–c,11,12}

Cyclic Voltammetry and Electron Paramagnetic Resonance (EPR). Cyclic voltammograms of $[1]^{2+}$ and **2** were recorded in CH_3CN solutions containing 0.1 M $[\text{NET}_4](\text{ClO}_4)$ at 25 °C. The potentials are referenced to the saturated Ag/AgCl electrode. The results are summarized in

Table 2. Hydrogen Dimensions of Compound $[1]^{2+}$

D–H...A	H...A/ Å	D...A/ Å	D–H...A/°
N(1)–H(1A) ...O(102) $[1/2 + x, 1/2 + y, 1/2 + z]$	2.32(3)	3.135(3)	146(2)
N(1)–H(1B) ...O(104)	2.16(3)	3.091(4)	168(3)
N(8)–H(8) ...O(101) $[1/2 - x, 1/2 - y, 1/2 + z]$	2.09(2)	2.940(3)	150(2)
N(15)–H(15A) ...O(101) $[1 - x, -y, z]$	2.60(3)	3.437(3)	150(3)
N(15)–H(15B) ...O(103)	2.09(4)	2.993(4)	162(3)

Figure 3. Molecular view of complex 2 $\text{Ni}^{\text{II}}(\text{HL})_2$ (ii means the symmetry operation ii = $-x, -y, -z + 1$).Table 3. The voltammogram of 2 is displayed in Figure 4 and that of $[1]^{2+}$ is shown in the Supporting Information (S6).Table 3. Cyclic Voltammetry Data^{a,b,c} of $[1]^{2+}$ and 2

compound	oxidation $E_{1/2}$, ^c V (ΔE_p , mV)	Reduction $E_{1/2}$, ^c V (ΔE_p , mV)
$[1]^{2+}$	0.68, 1.03, 1.37, 1.68	
2	0.34 (230)	−0.70 (85), −1.3 (140)

^aSolvent: CH_3CN ; supporting electrolyte Bu_4NClO_4 (0.1 M), and reference electrode SCE. ^bSolute concentration ca. 10^{-3} M. ^c $E_{1/2} = 0.5(E_{pa} + E_{pc})$, where E_{pa} and E_{pc} are anodic and cathodic peak potentials, respectively; $\Delta E_p = E_{pa} - E_{pc}$; scan rate = 50 mV s^{-1} .

Figure 4. Cyclic voltammogram of 2 in CH_2Cl_2 .

Complex $[1]^{2+}$ showed multiple irreversible oxidative waves in the potential range 0.5–1.7 V. Interestingly, after one or two scans the color of the solution changes to brownish-blue, and the initial voltammogram could not be reproduced. Complex 2 , on the other hand, showed two one-electron reductive responses in the potential range −0.7–1.3 V and a two-electron oxidative response at 0.34 V. Notably, the first reductive response is reversible, while the second one is quasi-reversible. The one-electron stoichiometry of the redox response has been confirmed by comparison of the current height with the redox response of the ferrocene/ferrocenium

couple under identical experimental conditions (for irreversible waves) and by exhaustive electrolyses of 2 at −0.9 V for the reversible waves. However, controlled-potential coulometry at +0.5 V produced a brown solution that immediately decomposes to give a mixture of unidentified products. The peak potential separations in the CV, $\Delta E = E_{p,ox} - E_{p,red}$ observed for the first reversible reduction wave is 85 mV which is close to that observed for the ferrocene/ferrocene couple at a scan rate of 50 mV s^{-1} . In contrast, ΔE for the $2e^-$ wave centered at 0.34 V using the same conditions is more than 230 mV at 25°C . Moreover, I_p for the oxidative redox couple (at 0.34 V) is significantly (~ 2.5 times) higher than that of the single-electron reductive wave. Similar Ni^{II} -complexes reported by others are also known to exhibit such type of single step two-electron redox events.^{11c,13} On the basis of our experimental results coupled with the available literature data,^{11c,13,14} we assign the first anodic response at 0.34 V as a two-electron process. Notably, the simpler analogue of complex 2 , the one without the additional aryl amine arm shows a one-electron reversible oxidation at −0.07 V and a one-electron reversible reduction at −1.21 V along with two additional quasi reversible responses at 0.21 and −1.89 V respectively.^{3b}

To obtain more insight into the nature of the electronic levels associated with the reversible reduction process at −0.7 V, electrogenerated monoanion $[2]^-$ was studied by EPR spectroscopy in $\text{CH}_2\text{Cl}_2/0.1 \text{ M TBAH}$ at 77 K. The one-electron reduced complex $[2]^-$, generated by exhaustive electrolysis of $[2]$, displayed a single line at $g = 2.005$ characteristic for a ligand radical complex. No resolved hyperfine couplings were observed at 77 K. These results are in agreement with DFT calculations, which show that both the highest occupied and lowest unoccupied molecular orbitals (HOMO, HOMO−1 and LUMO, LUMO+1) of complex 2 are primarily ligand-centered. Therefore, both oxidation and reductions are expected to occur at the ligands rather than at the metal. The one-electron ligand centered reduction in 2 produces the monoanionic complex $[2]^-$ with an electronic structure $[(L^{\bullet-})\text{Ni}^{\text{II}}(\text{L}^{2-})]$. However, the DFT results reveal a spin-delocalized alternative electronic structure with two equivalent ligands $\text{L}^{1.5-}$.

Electronic Structures and UV–Vis Spectra. To get a better insight into the electronic structures of the synthesized complexes, the geometries of the complexes $[1]^{2+}$ and 2 , were optimized, using DFT (B3LYP and LANL2DZ on Ni; 6-31G* on C, H, N; see Experimental Section). The structural parameters of the DFT optimized geometries match quite well to the experimental metrical parameters. Selected calculated bond lengths and angles are compared with the corresponding experimental ones in Table 1.

The most stable structure of $[1]^{2+}$ proves to be a triplet state ($S = 1$), as expected for an octahedral nickel(II) complex. The *fac* coordination mode of the H_3L ligand proved to be more stable than the *mer* coordination mode, also in DFT geometry optimization (energy difference $9.46 \text{ kcal mol}^{-1}$). Spin density

Figure 5. Spin density plots of [1]²⁺ (A); 2 (BS, $S = 0$) (B); and [2]⁻ (C).

analysis indeed confirms the presence of two unpaired electrons on the Ni center, as expected for octahedral Ni^{II}. Complex 2, on the other hand, is computed to be a singlet diradical complex with an approximately planar configuration around the tetra-coordinate metal atom with the two iminosemibenzoquinone ligand radicals coupled antiferromagnetically. This is in good agreement with all experimental data described above. Broken symmetry density functional calculations (BS, $S = 0$), clearly shows that the two coordinated ligands are open shell, π -radical monoanions ($L^{\bullet-}$), as shown computationally for analogous systems.^{3a,11–13,15} The selected bond parameters along with the spin density analysis reveal the iminosemiquinone ($L^{\bullet-}$) oxidation state of the coordinated ligands with the valence configuration of [Ni^{II}($L^{\bullet-}$)₂]. One of these two ligands remains in the spin-up manifold, while the second one is in the spin-down manifold, yielding the observed antiferromagnetically coupled diamagnetic singlet ($S = 0$) ground state. Notably, the broken symmetry $S = 0$ state was found to be energetically more stable than the triplet $S = 1$ state by ~ 2.6 kcal mol⁻¹.

Geometry optimizations were also carried out on [2]⁻, i.e., the one-electron reduced redox partner of 2. Optimized structural parameters for the computed ground state of [2]⁻ are collected in Table 1, and the spin density plot is depicted in Figure 5. Notably, upon one-electron reduction, the remaining unpaired electron gets delocalized over the two ligands, as is clear from the spin density plot in Figure 5. Similar observations were reported for related systems.^{3a,11–13,15} This result is consistent with the experimentally observed ligand centered EPR data of complex [2]⁻. Analysis of the molecular orbitals reveals that both the occupied and unoccupied MOs of the complexes [1]²⁺ and 2 are mainly ligand-based, with a small contribution from the metal center in all cases (S7, S8).

The electronic spectrum of complex [1](ClO₄)₂ was recorded in acetonitrile and that of complex 2 was recorded in dichloromethane. The experimental spectral results are collected in Table 4, and the corresponding spectra are shown

Table 4. UV–Vis NIR Data^a

compound	λ_{max} , nm (ϵ , M ⁻¹ cm ⁻¹)
[1](ClO ₄) ₂	494 (5969, b), 293 (17450, s), 230 (38224)
2	240 (18841), 276 (10938, s), 325 (5969, s), 845 (22724)

^a[1]²⁺ in CH₃CN and 2 in CH₂Cl₂, b:broad; s:shoulder.

in Figure 6. Complex [1](ClO₄)₂ shows a broad weak intensity peak at 494 nm and a intense absorption at 230 nm with shoulder at 293 nm. On the other hand, complex 2 showed an intense peak at 845 nm along with a mid intensity peak at 240 nm. The intense peak at 845 nm is assigned as a spin and dipole allowed ligand-to-ligand charge transfer band. This spectral

Figure 6. Electronic spectra of [1]²⁺ (black), 2 (blue) in CH₃CN and CH₂Cl₂ respectively.

feature is similar to those reported for closely related Ni^{II} complexes containing two antiferromagnetically coupled *o*-iminobenzosemiquinone radical ligands.^{3b,6a,11}

Deprotonation Induced Interconversion. The [1]²⁺ → 2 transformation exemplifies an unprecedented interconversion of a hexa-coordinated Ni^{II} complex to a coordinatively unsaturated square planar Ni^{II} complex via simultaneous deprotonation and one-electron oxidation of each of the coordinated ligands. To get more insight into this redox-induced dissociation of a ligand arm upon oxidation, several reactions were carried out under continuous spectroscopic monitoring.

Deprotonation/Reprotonation Studies of [1]²⁺ and 2.

The conversion of [1]²⁺ to 2 is associated with the deprotonation (loss of four protons) of the coordinated ligands along with one-electron oxidation of each of the coordinated ligands, leaving the nickel(II) oxidation state of the metal unchanged. Deprotonation studies, using NaOH as base, were carried out in the presence of oxygen as well as under an inert atmosphere. Upon addition of NaOH to an acetonitrile solution of [1]²⁺ in the presence of molecular oxygen, the initial color of the solution gradually changes to bluish-green, and the color-intensity gradually increases over the time, corresponding to formation of complex 2. UV–vis monitoring of this reaction shows a gradual increase in absorption, which maximizes at 845 nm, and the final spectral pattern matches exactly with that of complex 2 (Figure 7). However, addition of NaOH or other bases to the acetonitrile solution of [1](ClO₄)₂ in the absence of oxygen (oxidant) produces a mixture of unidentified products. Similarly, complex [1](ClO₄)₂ when exposed to air in the absence of base also does not undergo conversion to 2, instead produced a mixture of unidentified products. However, chemical oxidation [1](ClO₄)₂ with ferrocenium cation or molecular iodine produce an intense blue-colored solution. Our repeated attempts to isolate the blue complex were however unsuccessful. These experimental

Figure 7. (a) UV-vis monitoring of the deprotonation study of $[1](\text{ClO}_4)_4$ in the presence of air and NaOH in acetonitrile solution. (b) Schematic representation of $[1](\text{ClO}_4)_4 \leftrightarrow 2$ interconversion.

findings indicate that for the conversion of $[1]^{2+}$ to **2**, both base and oxygen are required for simultaneous deprotonation and oxidation of the coordinated ligands. To get further insight of the mechanism of the electron transfer process associated with ligand oxidation, EPR studies were carried out immediately after the addition of NaOH to $[1]^{2+}$ in air. The EPR spectrum obtained at 10 K reveals a sharp, single-line signal centered around $g = 2.013$, strongly suggestive for a ligand centered radical (Figure 7). Interestingly, the same solution, when exposed to air in the presence of NaOH for several hours, produces complex **2**. Notably, the blue-colored complex obtained by oxidation of $[1]^{2+}$ with Fc^+ in the absence of base also showed an EPR signal characteristic for a ligand radical complex (SI, S9), but reveals a different signal. The EPR spectrum is clean and shows clearly resolved hyperfine interactions when measured at RT. A satisfactory simulation could be obtained assuming an isotropic g -value of 2.0033 and hyperfine coupling with one unique nitrogen atom (21 MHz) and two equivalent ones (16 MHz). As such the spectrum is suggestive for formation of a square planar $[(\kappa^3\text{-L}^{\bullet 2-})\text{-Ni}^{\text{II}}(\text{NCMe})]$ complex. This would imply ligand dissociation (e.g., $[\text{H}_3\text{L}]^{2+}$ formation from H_3L acting as a base) occurs upon oxidation of $[1]^{2+}$ in the absence of added base, thus explaining why the presence of base is important in the conversion of $[1]^{2+}$ to **2**.

To check the reversibility of this interconversion, complex **2** was also subjected to reduction and reprotonation. Chemical reduction of complex **2** by cobaltocene in absolutely inert atmosphere in alcoholic solvents yielded complex $[1]^{2+}$. The complex $[1]^{2+}$ thus obtained via chemical reduction of **2** was isolated, and its electronic spectral data indeed matches exactly with that of pure $[1]^{2+}$. This chemical reduction is quite fast (nearly instantaneous).

Alcohol Oxidation Catalysis. We were curious to check how the control of fluxional coordination upon exposure to

external stimuli like base and oxygen might affect the activity of the complexes in catalytic reactions. Although complex $[1](\text{ClO}_4)_2$, in its native state, is coordinatively saturated, we still decided to test its activity in catalytic alcohol oxidation reactions. Interestingly, and counterintuitively, complex $[1](\text{ClO}_4)_2$ actually proved to be an efficient catalyst for the catalytic oxidation of both primary and secondary alcohols under aerobic conditions.

Initial experiments were focused on the evaluation of the optimal reaction conditions for the catalytic alcohol oxidation under aerobic conditions using benzyl alcohol as the model substrate at 70 °C using $[1](\text{ClO}_4)_2$ as the catalyst. Optimization of the reaction conditions revealed that the reaction proceeded most efficiently in nonpolar solvents like toluene, whereas reactions in solvents of high polarities such as MeCN, dioxane, methanol, and DMF afforded poor yields (Table 5, entries 10–14). Among the series of bases tested such as K_3PO_4 , K_2CO_3 , Cs_2CO_3 , LiO^tBu , NaO^tBu , KO^tBu , NaOMe, NaOH, and NaH, the best results were obtained with NaOH and NaH (Table 5, entries 1–9). In further studies we focused on the use of NaOH as the base. Lowering the reaction temperature decreased the yield slightly; however, the same yield can be achieved using longer reaction times. Lowering the catalyst loading below 6 mol % leads to poor conversion of the alcohols to the corresponding aldehydes or ketones. The reaction conditions were also investigated to check the stability of the catalytic system in air and the effect of open and closed systems. Excellent conversion of alcohol to aldehyde or ketone was achieved in the presence of oxygen. In a closed system with limited oxygen present only poor conversion of alcohol to aldehyde was observed.

Several control experiments were carried out to gain more insight into the catalytic reactions. No product was obtained in the presence of only ligand and base. Interestingly, no product

Table 5. Optimization of Reaction Conditions Using $[1](\text{ClO}_4)_2$ and **2** as the Catalyst^{a,b,c}

entry	solvent	base	time	yield (isolated)
1	toluene	K_3PO_4	24	50
2	toluene	K_2CO_3	24	30
3	toluene	Cs_2CO_3	24	35
4	toluene	LiO^tBu	24	20
5	toluene	NaO^tBu	24	30
6	toluene	KO^tBu	24	35
7	toluene	NaOMe	24	40
8	toluene	NaOH	24	95
9	toluene	NaH	24	95
10	THF	NaOH	24	trace
11	acetonitrile	NaOH	24	trace
12	dioxane	NaOH	24	trace
13	methanol	NaOH	24	NR
14	DMF	NaOH	24	NR
15	DCM	NaOH	24	NR
16 ^d	toluene	NaOH	16	95

^aStoichiometry: benzyl alcohol (0.3 mmol); catalyst (0.02 mmol); base (0.45 mmol, 1.5 equiv). ^bIsolated yields after column chromatography. ^cReaction temperature: 70 °C. ^dComplex **2** was used as the catalyst.

was obtained in the presence of a radical scavenger like TEMPO.

Complex $[1](\text{ClO}_4)_2$, under the catalytic reaction conditions (in the presence of base and oxygen), is believed to be converted to the corresponding square planar complex **2** (see above) which then acts as the actual catalyst in the catalytic alcohol oxidation reactions. The catalytic activity of complex **2** was also investigated under the same optimized reaction conditions as described above, and indeed complex **2** catalyzes alcohol oxidation and is even a bit faster than complex $[1](\text{ClO}_4)_2$ (see Table 5, entry 16).

To explore the substrate scope and the versatility of the catalytic methodology developed above, several alcohols with different electronic properties and functional groups were tested. Excellent yields were obtained with alcohols containing both electron donating as well as electron withdrawing groups. Secondary alcohols are also suitable for oxidation to the corresponding ketones. Reactions of methyl phenyl alcohol or diphenyl alcohol produced acetophenone and benzophenone in high yields (Table 6, entry 5, 6) under the same optimized reaction condition with both $[1](\text{ClO}_4)_2$ and **2** as the catalyst. It is noteworthy to mention that catalytic reactions with complex **2** is comparatively faster, and almost identical yields were obtained in shorter reaction times.

CONCLUSION

The present report represents an unprecedented redox-induced interconversion of two Ni^{II} -complexes supported by a redox noninnocent tridentate ligand H_3L . The ligand N^1 -(2-aminophenyl)benzene-1,2-diamine complex **1** shows fluxional coordination behavior upon exposure to oxygen and base. The coordinated ligands in complex $[1]^{2+}$, in the presence of base and oxygen, undergoes simultaneous deprotonation and oxidation to produce the square planar neutral complex **2**, where two of the amine arms of the ligand become pendant.

Table 6. Oxidation of Primary and Secondary Alcohols to Aldehydes and Ketones Catalyzed by $[1](\text{ClO}_4)_2$ and **2**^{a-e}

Entry	Alcohol	Product	Yield ^d
1.			85 (87) (3a)
2.			95 (95) (3b)
3.			90 (95) (3c)
4.			87 (85) (3d)
5.			95 (98) (3e)
6.			93 (95) (3f)
7.			90 (95) (3g)

^aStoichiometry: alcohol (0.3 mmol); catalyst (0.02 mmol) base (NaOH) (0.45 mmol, 1.5 equiv). ^bIsolated yields after column chromatography. ^cReaction temperature: 70 °C. ^dFor catalyst $[1]^{2+}$, reaction time = 24 h; for catalyst **2**, reaction time = 16 h. ^eIsolated yields with catalyst **2** is reported in the parentheses “()”.

Complex **2** converts to six-coordinate $[1]^{2+}$ upon chemical reduction with cobaltocene in alcohol solvents. The fluxional coordination of H_3L was used to carry out catalytic alcohol oxidation reactions using complex $[1]^{2+}$, where the coordination sites were originally masked in its ground state structure. Both the complexes $[1]^{2+}$ and **2** were found to act as efficient catalysts in alcohol oxidation reactions. Both primary and secondary alcohols were found to be converted to the corresponding aldehydes and ketones in excellent yields. Mechanistic investigations and catalytic oxidations reactions involving other non benzylic alcohols are in progress and will be reported in due course.

EXPERIMENTAL SECTION

Materials. $\text{Ni}(\text{ClO}_4)_2$ and all alcohols were purchased from Sigma-Aldrich. All other reagents and chemicals were purchased from commercial sources and used without further purifications. Tetrabutylammonium perchlorate was prepared and recrystallized as reported before.¹⁶ **Caution!** Perchlorates have to be handled with care and appropriate safety precautions.

Physical Measurements. UV-vis spectra were recorded in a Jasco spectrometer. ^1H NMR spectra were recorded on a Bruker Avance 400/500 MHz spectrometer, and SiMe_4 was used as the internal standard. A PerkinElmer 240C elemental analyzer was used to collect microanalytical data (C, H, N). ESI mass spectra were recorded

Table 7. Crystal Data and Structure Refinement Parameters of Complexes $[1](\text{ClO}_4)_2$ and **2**

	1	2 (no disorder)
empirical formula	$\text{C}_{24}\text{H}_{26}\text{Cl}_2\text{N}_6\text{NiO}_8$	$\text{C}_{24}\text{H}_{22}\text{N}_6\text{Ni}$
formula weight	656.12	453.18
crystal system	tetragonal	monoclinic
space group	$P-42_1/c$	$P21/c$
<i>a</i> (Å)	13.6483(5)	8.8868(7)
<i>b</i> (Å)	13.6483(5)	9.1899(6)
<i>c</i> (Å)	14.6410(8)	13.2495(11)
β (deg)	90	98.474(3)
volume	2727.3(2)	1070.26(14)
<i>Z</i>	4	2
<i>D_c</i> (Mg m^{-3})	1.598	1.406
$\mu/(\text{mm}^{-1})$	0.967	0.930
<i>F</i> (000)	1352	472
theta min–max (deg)	2.110–29.172	2.317–27.935
index ranges	$-18 < h < 18, -18 < k < 18, -20 < l < 20$	$-11 < h < 11, -12 < k < 9, -17 < l < 17$
reflections collected	46739	9735
unique reflections, [<i>R</i> _{int}]	3693[0.0490]	2554[0.0322]
data/restraints/parameters	3693/5/206	2554/0/156
goodness-of-fit on <i>F</i> ²	1.037	1.098
final <i>R</i> indices		
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ <i>I</i>]	0.0292, 0.0621 [3289]	0.0535, 0.1490 [2021]
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0380, 0.0655	0.0687, 0.1582
largest diff. peak and hole	0.56/−0.26	1.50/−0.66

on a micromass Q-TOF mass spectrometer (serial no. YA 263). All electrochemical measurements were performed using a PC-controlled PAR model 273A electrochemistry system. Cyclic voltammetric experiments were performed under nitrogen atmosphere using a Ag/AgCl reference electrode, with a Pt disk working electrode and a Pt wire auxiliary electrode, in acetonitrile or dichloromethane containing supporting electrolyte, 0.1 M Et_4NClO_4 or 0.1 M Bu_4NClO_4 , respectively. A Pt wire gauge working electrode was used for exhaustive electrolyses. Room temperature magnetic moment measurements for $[1]^{2+}$ were carried out with Gouy balance (Sherwood Scientific, Cambridge, U.K.). EPR spectra in the X-band were recorded with a Bruker EMX plus spectrometer.

Syntheses. The ligand H_3L was prepared by following the reported procedure.⁸ All other chemicals were of reagent grade and used as received. Solvents were purified and dried prior to use. Synthesis and handling of air-sensitive materials were carried out under an inert atmosphere by using standard Schlenk technique.

Synthesis of $[1](\text{ClO}_4)_2$. Under a argon atmosphere, $\text{Ni}(\text{ClO}_4)_2$ (100 mg, 0.387 mmol) and the ligand H_3L (154 mg, 0.774 mmol) were added to a flame-dried Schlenk tube. The tube was capped with a Teflon screw cap, evacuated, and backfilled with argon. The screw cap was replaced with a condenser fitted with a argon balloon. Twenty milliliters of deoxygenated methanol was added to the Schlenk tube already containing $\text{Ni}(\text{ClO}_4)_2$ and H_3L . The Schlenk tube was then placed in an oil bath and heated to reflux for 4 h under argon atmosphere. During this time the solution turned dull violet, and colorless crystalline compound was formed. The solvent was decanted and the complex $[1](\text{ClO}_4)_2$ was crystallized by slow evaporation of its dichloromethane/methanol solution under inert atmosphere. Its yield and characterization data are as follows: Yield 90%. UV/vis: 494(5969, b), 293 (17450, s), 230(38224), IR (KBr cm^{-1}): 3317, 3294, 3251 [$\nu(\text{NH}/\text{NH}_2)$]. Anal. Calcd for $\text{C}_{24}\text{H}_{26}\text{N}_6\text{NiCl}_2\text{O}_8$: C 43.94, H 3.99, N 12.81; Found: 43.91, H 4.03, N: 12.85. ESI-MS, *m/z* 455[1 - H]⁺.

Synthesis of $[\text{Ni}(\text{L}^*)_2]$ (2**).** Under an aerobic atmosphere, $\text{Ni}(\text{ClO}_4)_2$ (100 mg, 0.387 mmol), the ligand H_3L (154 mg, 0.774 mmol), and NaOH (32 mg, 0.8 mmol) were added to a flame-dried Schlenk tube. Subsequently 20 mL of dry methanol was added to the Schlenk tube already containing $\text{Ni}(\text{ClO}_4)_2$ and H_3L . The Schlenk tube was then placed in an oil bath and heated to reflux for 4 h under air. The initial yellow color of the solution gradually changes to bluish

green, and a green colored precipitate was obtained. The crude mass, obtained by evaporation of solvent in vacuum, was purified by fractional crystallization from dichloromethane and hexane solvent mixture. The precipitate was crystallized by slow evaporation of a dichloromethane solution of the compound into hexane. Its yield and characterization data are as follows: Yield: 90%, ESI-MS, *m/z* 452 [2]⁺, UV/vis: 240(18841), 276 (10938, s), 325 (5969, s), 845 (22724), IR (KBr cm^{-1}) 3438, 3317, 3053, Anal. Calcd for $\text{C}_{24}\text{H}_{22}\text{N}_6\text{Ni}$: C 63.61, H 4.89, N 18.55; Found: C 63.65; H 4.93; N 18.51. ¹H NMR (500 MHz, CDCl_3): 7.46 (d, 2H, *J* = 9.5 Hz); 7.32 (t, 2H, *J* = 9.5 Hz); 6.93 (m, 4H), 6.45 (m, 6H); 6.46 (d, 2H, *J* = 10 Hz); 6.37 (s (b), 2H (−NH)); 3.91 (s(b), 4H (−NH₂)).

EPR Spectral Studies. The one-electron reduced complex $[2]^-$ was generated by exhaustive electrolysis of **2** at −0.9 V in $\text{CH}_2\text{Cl}_2/0.1$ M TBAP and was immediately dipped into liquid nitrogen, and the resulting frozen solution was used for the EPR measurements at 77 K. During deprotonation studies, EPR spectral measurements were carried out immediately after the addition of NaOH to an acetonitrile solution of $[1]^{2+}$ in air at 10 K.

Catalytic Alcohol Oxidation. Under aerobic conditions, the catalyst $[1](\text{ClO}_4)_2$ (8 mol %) and the respective alcohols (0.3 mmol) were added to a flame-dried Schlenk tube. Subsequently NaOH (0.45 mmol, 1.5 equiv) and 10 mL of dry toluene was added, and the Schlenk tube was placed in an oil bath and heated to 70 °C for 24 h. After the reaction was completed, the resulting mixture was concentrated, and the residue was purified by column chromatography to get the products (**3a–g**). For catalyst **2**, using the same procedure described above, reactions were found to be completed in 16 h. The pure products were identified by ¹H NMR.

X-ray Crystallography. Suitable X-ray quality crystals of complexes $[1](\text{ClO}_4)_2$ and **2** were obtained by the slow evaporation of a dichloromethane/methanol and dichloromethane/hexane solution of the complexes, respectively. The X-ray single crystal data of both complexes $[1](\text{ClO}_4)_2$ and **2** were collected with monochromated Mo- $\text{K}\alpha$ radiation (λ = 0.71073 Å) on a Bruker SMART Apex II diffractometer equipped with a CCD area detector at 150(2) K. The crystals were positioned at 40 mm from the CCD, and the spots were measured using 5 s and 10 s counting time, respectively. Data reduction was carried out using the SAINT-NT software package.¹⁷ Multiscan absorption correction was applied to all intensity data using

the SADABS program.¹⁸ The structure was solved by a combination of direct methods with subsequent difference Fourier syntheses and refined by full matrix least-squares on F^2 using the SHELX-2013 suite.¹⁹ All non-hydrogen atoms were refined with anisotropic thermal displacements. The N15 atom in complex **2** was refined over two positions with refined occupancies of x (connected to C14) and $1 - x$ (connected to C10), x being equal to 0.717. The C–H hydrogen atoms were included at calculated positions and refined with isotropic parameters equivalent 1.2 times those of the atom to which they are attached. Furthermore, the hydrogen atoms bound to nitrogen atoms (except for disordered N15 in NP4 compound) were unequivocally located from the last calculated difference Fourier maps. Molecular diagram were drawn with the Olex2²⁰ and platon²¹ software package. The crystal data together with refinement details are given in Table 7.

Computational Details. All DFT calculations presented herein were carried out using the Gaussian 09 program package.²² Geometry optimizations were performed without imposing geometric constraints. The vibrational frequency calculations were performed to ensure that the optimized geometries represent the local minima and that there are only positive Eigen values. All calculations utilized the B3LYP hybrid functional in conjunction with the LANL2DZ on Ni; and 6-31G* on C, H, N atoms.²³ Mulliken spin densities were used for analysis of spin populations on ligand and metal centers.²⁴

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.6b00646.

Experimental and characterization details, NMR spectral data (PDF)

X-ray crystallographic files (CIF1 and CIF2)

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Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Sreebrata Goswami on the occasion of his 60th birthday.

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