Modulation of nickel pyridinedicarboxamidate complexes to explore the properties of high-valent oxidants

Paolo Pirovano,[a,b] Brendan Twamley[a] and Aidan R. McDonald*[a,b]

Abstract: High-valent Ni oxidants have been implicated in hydrocarbon oxidation catalysis, however, little is understood about the properties of these oxidant. Herein, a family of NiII complexes supported by a pyridinedicarboxamidate ligand and different ancillary ligands was synthesized. The series spans coordination numbers 4, 5, and 6, and contains neutral, mono- and di-anionic donor types. X-ray crystallography and magnetic measurements showed that the 4-coordinate complexes were square planar and low spin (S = 0) and the 5- and 6-coordinate were high spin (S = 1). The NiIII complexes could be oxidized by one electron to form a series of metastable NiII species. EPR analysis confirmed their description as S = ½ NiIII compounds with signal shape and hyperfine coupling dependent on the coordination environment. The oxidation of phenols by the NiII compounds with signal shape and hyperfine coupling dependent on species. EPR analysis confirmed that the pyridinedicarboxamidate ligand could be oxidized by one electron to form a series of metastable NiII species. EPR analysis confirmed their description as S = ½ NiIII compounds with signal shape and hyperfine coupling dependent on the coordination environment. The oxidation of phenols by the NiII species was probed, providing evidence for a correlation between oxidizing power and electron-donating properties of the supporting ligands. Critically, we found that the pyridinedicarboxamidate ligand may be a non-innocent proton acceptor in the oxidation reactions.

Introduction

High-valent transition metal species are important intermediates in a multitude of biological and synthetic oxidations. Numerous homogeneous and heterogeneous oxidation catalysts based on Ni have been developed for reactions such as alkene epoxidation,[1] alkane[2] and aren[3] hydroxylation and chlorination,[4] and water oxidation.[5] Terminal NiII=O and NiIII=O are frequently invoked as intermediates in these reactions, and their existence is supported by mechanistic experiments[6] and computational studies,[7] as well as by model complexes.[8]

While terminal M=O species have attracted the most focus, a slew of other nickel oxidants have been proposed, and in some cases demonstrated to be effective oxidants.[9] These include NiII(=O)2[10], NiIII(=O)3[11], NiII(OOR)[12], NiII=O=O[13], NiII–OOCOR[14], NiII=OCl[15], [NiII(μ-O)2]2[16,17] and [NiII(μ-O)2Cu][18]. NiII=O species have been shown to mediate the formation of highly reactive, metal-free C=O radicals in chlorination reactions.[4] Complexes with imides, NiII=NR, also constitute powerful oxidants.[19] This large family of nickel-based oxidants display a variety of coordination numbers and geometries, without any clear understanding of their structure/function relationships.

In light of this structural variety of nickel-centered oxidants, we aimed to explore the systematic variation of the coordination environment around the metal center. Pyridinedicarboxamidate ligands constitute a versatile support, which is effective in the stabilization of high valent nickel: hexacoordinate [NiIII(pyN2)2]2+ complexes have been reported (pyN2= H2/N,N-diphenyl-2,6-pyridinedicarboxamidate).[18] We have previously prepared square planar [NiII(=O)pyN2] complexes (OX = OCO2H, O2CCH2, ONO2; pyN2= N,N'-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate)[19] and demonstrated their reactivity as hydrogen atom transfer (HAT) oxidants towards O=H and C–H bonds. As a means of exploring structure/function relationships, we were interested in the role the ancillary ligands play in modulating the HAT reactivity of the high-valent Ni species. Furthermore, we were interested to understand the role the pyridinedicarboxamidate ligand plays in oxidation reactions. As the ligand has multiple potential proton-acceptor sites, we want to understand its role in HAT reactivity. We report here the preparation of an extended and unique family of NiII and NiIII complexes derived from the [Ni(pyN2)] core and explore the reactivity of the NiII entity (with varying neutral and anionic donors, in different coordination environs) in phenol oxidation.

Results and Discussion

Scheme 1. Synthetic routes to the NiII complexes 2a-8a. L* = N,N'-bis(2,6-dimethylphenyl)-2,6-pyridinedicarboxamidate.

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A family of [NiII(L)(pyN2)] complexes (1a-8a, Scheme 1) was prepared (see supporting information for details). To form previously reported 2a,[20] substitution of the neutral CH3CN ligand in the previously reported 1a (Scheme 1) was performed.
using Et$_3$NCl. For 3a-5a, 2a was initially generated in a reaction vessel without being isolated, and subsequently reacted with KO$_2$CH$_2$ (1.2 equiv.), NaOCC$_2$H$_5$ (1.2 equiv.), or Na(acac) (1.05 equiv., acac = acetylacetonate), respectively. Yields of 76% (3a), 68% (4a), and 55% (5a) were obtained after work-up and re-crystallization. These synthetic methods improved the previously reported synthesis of 5a, whose preparation from [Ni(OH)($\text{pyN}_2^{\text{Me}_2}$)]Et$_3$N required longer reactions time and displayed modest yield.

It is important to note that the synthesis of 5a was conducted under strictly anhydrous conditions. Early synthesis attempts under an air atmosphere yielded an impure product, which after re-crystallization was identified, by $^1$H NMR, to contain the acetate complex [Ni($\text{pyN}_2^{\text{Me}_2}$)]$_2$ (19a) and 5a. Furthermore, the XRD measurement on crystals obtained from these impure reaction conditions showed the presence of 1:1 co-crystals of 5a and [Ni($\text{pyN}_2^{\text{Me}_2}$)]$_2$ (Figure S1). We believe [Ni($\text{pyN}_2^{\text{Me}_2}$)]$_2$ originated either from the oxidation of the acac ligand by atmospheric O$_2$, or through its hydrolysis, through a retro-Claisen mechanism (Scheme S1). Previous reports on Ni$^2+$ complexes supported by $\beta$-diketonate ligands were spontaneously oxidized, on exposure to O$_2$, to yield two carboxylates and CO.$^2$ Furthermore, Ni-dependent acicredonate dioxygenase.$^2$ promotes the oxidation of its $\beta$-diketonate substrate in the same manner. However, we noted that a [D$_2$]DMSO solution of pure 5a did not appreciably decay over the course of two days, when exposed to oxygen. In contrast, 12 hours after the addition of 0.1 mL of D$_2$O to the same solution, [Ni($\text{pyN}_2^{\text{Me}_2}$)]$_2$ was identified by $^1$H NMR spectroscopy. For this reason, we propose hydrolysis of 5a via the retro-Claisen mechanism yields acetonate and acetate (Scheme S1).

Bipyridine (6a, bpy = 2,2’-bipyridine) and terpyridine (7a, terpy = 2,2’,6’,2”-terpyridine) complexes were prepared by a simple exchange reaction of bpy or terpy (1 equiv.) with 1a in CH$_3$CN (for 6a) or CH$_3$OH (for 7a), in 78% and 75% yields, respectively. Finally, the 2,6-pyridinedicarboxylate (2,6-dipic) complex 8a was generated by the reaction of 1a with Li$_2$(2,6-dipic) (1.2 equiv.) in CH$_3$OH, giving the complex in 64% yield.

Electrospray ionization mass spectrometry (ESI-MS) confirmed the elemental composition of 2a-8a. Ions corresponding to the Ni-containing fragment of the compounds were identified (in negative mode for the anionic 2a-5a and 8a, and in positive mode for the neutral 6a-7a). 4a-8a were further characterized via single crystal X-Ray diffraction (XRD) measurements, nuclear magnetic resonance (NMR), electronic absorption, Fourier transform infrared (FT-IR) spectroscopies, and cyclic voltammetry, as described in detail below.

Solid-state structures of previously reported compounds 2a,$^{21}$ 3a,$^{20}$ and [Ni($\text{pyN}_2^{\text{Me}_2}$)]$_2$ (OX = OH, OCH$_3$, OCO$_2$H, O$_2$CC$_3$H$_7$, ONO$_2$)$_{2a,21}$ were all four coordinate species with a square planar geometry. The XRD crystal structure of 4a displayed a similar square planar geometry (Figure 1), with the geometry index$^{20}$ $t_4 = 0.14$, in line with the previously reported square planar [Ni(L)]($\text{pyN}_2^{\text{Me}_2}$)] complexes.$^{19a,21}$

### Table 1. Spectral, magnetic, electrochemical and reactivity properties of 2a/b-8a/b.

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\mu_{\text{eff}}$ (µs)</th>
<th>$E_{\text{g}}$ vs FC/Fc (V)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$g_0$, $g_\perp$, $g_\parallel$ (av.)</th>
<th>$t_4$</th>
<th>$K_f$(M$^{-1}$s$^{-1}$)</th>
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<tr>
<td>3a</td>
<td>455 (1200)</td>
<td>0</td>
<td>0.48</td>
<td>3b</td>
<td>530, 830</td>
<td>2.25, 2.02 (2.17)</td>
<td>8 h $^{10,11}$ at -80 °C</td>
<td>na</td>
</tr>
<tr>
<td>4a</td>
<td>390 (4400), 460sh (850), 530sh (380)</td>
<td>0</td>
<td>0.26</td>
<td>5b</td>
<td>530, 720sh</td>
<td>2.32, 2.23, 2.01 (2.19)</td>
<td>8 h $^{10,11}$ at -40 °C; 3 h at 25 °C</td>
<td>no reaction</td>
</tr>
<tr>
<td>5a</td>
<td>380sh (1800), 770 (110), 980 (130)</td>
<td>2.99</td>
<td>-0.14</td>
<td>6b</td>
<td>580, 790sh</td>
<td>2.19, 2.16, 2.02 (2.12)</td>
<td>½ h at -40 °C</td>
<td>0.067</td>
</tr>
<tr>
<td>6a</td>
<td>380sh (2400), 470sh (450), 850 (40)</td>
<td>2.50</td>
<td>0.26</td>
<td>7b</td>
<td>420, 500, 680</td>
<td>2.17, 2.14, 2.02 (2.11)</td>
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<td>1.29</td>
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<tr>
<td>7a</td>
<td>400sh (70), 860 (100)</td>
<td>3.07</td>
<td>0.33</td>
<td>8b</td>
<td>560, 700sh</td>
<td>2.22, 2.19, 2.01 (2.14)</td>
<td>8 h $^{10,11}$ at -40 °C; 260 s at 25 °C</td>
<td>no reaction</td>
</tr>
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[a] Reaction with 2,6-DTBP at -40 °C [b] 2b prepared from 2a + CAN in acetone. [c] 6b prepared from 6a plus 2 eq. CAN in 9/1 acetone/CH$_3$CN. [d] 7b prepared from 7a plus 2 eq. CAN in CH$_3$OH. [e] 8 h was the maximum allowable measurement time, lifetimes likely to be considerably longer.

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Figure 1. ORTEP plots (at 50% probability level) of the X-ray structures of 4a-8a. Hydrogen atoms, the counterions Et$_3$N$^+$ for 4a-5a and Li$^+$ for 8a, and solvents of crystallization have been omitted for clarity; disorder is not shown.
The metal-ligand bond distances in the \([\text{Ni}^{II}(\text{pyN}_2^{\text{Me}_2})]\) core were essentially unvaried in the square planar complexes 2a-4a and \([\text{Ni}^{II}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]\)\(^{19a,21}\) whereas for 5a-8a, with higher coordination numbers, there was an average elongation of 0.1-0.2 Å of both the Ni–Namine and the Ni–Npyridine bonds (Table S3). In the square pyramidal structures, the apical ligands showed significantly longer Ni–O/N bonds than the equatorial bond lengths. Even in the pseudo-octahedral compounds 7a and 8a, there was a marked lengthening of the axial (apical) bond distances of the ligands above and below the \([\text{Ni}(\text{pyN}_2^{\text{Me}_2})]\) plane. Compounds 5a and 6a displayed a square pyramidal geometry in the solid state (Figure 1), with the three N donors from the \(\text{pyN}_2^{\text{Me}_2}\) ligand and one N/O donor from the acac or bpy ligands in the basal plane, and the other binding apically. \(\tau\) values of 0.22 and 0.35 respectively,\(^{26}\) demonstrated the environment to be closer to square pyramidal rather than trigonal bipyramidal. In one of the two independent molecules of 6a in the asymmetric unit cell, the molecule was refined with a CH$_3$CN ligand bound in the sixth coordination position, with 10% occupancy. 7a and 8a both displayed distorted octahedral geometries (Figure 1), with double axial bending,\(^{27}\) i.e. two of the L–Ni–L axes had angles smaller than 180°. This distortion was caused by the tridentate, meridional ligands \(\text{pyN}_2^{\text{Me}_2}\), terpy, and 2,6-dipic having bite angles smaller than 90° for each cis pair of donor atoms. In 8a there was an interaction between one of the carboxylic acid C=O groups and one of the lithium counterions, whose coordination is completed by H$_2$O and CH$_3$OH molecules.

The $^1$H NMR spectrum of 4a was comparable to those of previously reported square planar 2a, 3a, and \([\text{Ni}(\text{OX})(\text{pyN}_2^{\text{Me}_2})]\) complexes,\(^{19a,21}\) and indicative of a diamagnetic, low-spin (\(S = 0\)) \(d^8\) electronic structure (Figures S2-S5). The C–H resonances attributed to the phenoxide group of 4a displayed 5 distinct signals (one of which is masked by the aniline resonances), indicating that they are neither exchanged by symmetry (consistent with the solid state structure, Figure 1), nor by rotation about the Ni–O/C$_6$H$_5$ bond on the NMR timescale. In contrast, the five- and six-coordinate complexes 5a-8a displayed peak broadening and peak shifts typical of paramagnetic species (Figure 2). With the exception of 7a (Figure S10), the peaks were sufficiently sharp and well-resolved, that integration and cross-correlation allowed for the partial assignments of the peaks. This is expected among high-spin \(\text{Ni}^{II}\) complexes - four-coordinate tetrahedral and five-coordinate complexes have relaxation times that are short enough for reasonable $^1$H NMR data acquisition, while this is more difficult for the six-coordinate octahedral geometry.\(^{28}\)

Assignment of the signals was facilitated by analysis of the spectrum of \([\text{Ni}(2,6\text{-dipic})]\)\(_2\)\(\text{Li}_2\) \((9)^{30}\), a few crystals of which were serendipitously obtained from a failed synthesis of 8a (the solid state structure was also investigated - see suppl. info.). 9 had a simple two-resonance $^1$H NMR spectrum. On the basis of signal intensity and integration (Figure 2), the peak at 63 ppm was assigned to the meta protons of the pyridine ring, and the peak at 22 ppm was assigned to the para protons in 9. Similar resonances were identified in 8a (which contains the 2,6-dipic ligand, Figure 2). A signal at -60-80 ppm was present in complexes 5a, 6a, and 8a, which we assigned to the meta-pyridine protons of the \(\text{pyN}_2^{\text{Me}_2}\) ligand. The para-proton signal of the \(\text{pyN}_2^{\text{Me}_2}\) ligand was more mobile, at 7 ppm in 4a, 10 ppm in 6a, and 20 ppm in 8a. Integration of the signals at ~−6 to −10, −10 to 14, and −6 to 10 ppm assisted in identifying the aniline carboxamide para- and meta-phenyl, and 12 -CH$_3$ signals, respectively, for all complexes.

The number of signals in the spectra of 5a and 6a suggested a high symmetry. For 5a one additional resonance, integrating to one proton, at -20 ppm can be assigned to the methine proton of acac, and a broad signal at 1.7 ppm, corresponding to six protons, is attributed to the methyl protons of the acac ligand. Four additional signals that integrated to two protons each were present in the spectrum of 6a, corresponding to the bpy ligand. In the solid state XRD structures of 5a and 6a a square pyramidal geometry was observed, which would suggest that the CH$_3$ resonances of acac, and the pyridine ring $^1$H NMR signals of bpy would be non-equivalent as a result of apical and equatorial coordination. Even at lower temperatures, similarly
symmetric $^1$H NMR spectra were obtained (Figures S6b-S8b). The solution $^1$H NMR spectra were indicative of either a change to trigonal bipyramidal coordination, or fast dynamic exchange between the two alternative square pyramidal conformations.

The magnetic moments of 5a-8a in solution were measured via the Evans method (Table 1, see supporting info).\cite{30} The $\mu_B$ values (5a: 2.99, 6a: 2.50, 7a: 3.07, 8a: 3.04 $\mu_B$) were within the typical range for five- and six-coordinate $S = 1$ Ni$^{II}$ complexes,\cite{31} with the exception of 6a, which was slightly lower but nevertheless indicative of a high spin $d^6$ ion, possessing two unpaired electrons. The different magnetic properties of the square planar four-coordinate Ni$^{II}$ complexes and their five- and six-coordinate counterparts are a consequence of their different ligand fields. A second effect was evident in their electronic absorption spectra (Table 1, Figures S27-S33). The square planar 1a-4a and [Ni$^{II}$((OX)(pyN$_{2}$)$_{2}$)][\cite{19a,21}] all displayed orange or red bands arising from moderately intense ($\varepsilon = 100$ M$^{-1}$cm$^{-1}$) bands at 450-550 nm, as is common for Ni$^{II}$ complexes of this geometry.\cite{32} 5a-8a, conversely, displayed weak d-d bands ($\varepsilon \leq 100$) at lower energy (800-1000 nm), which is again typical for five- and six-coordinate Ni$^{II}$.\cite{32a}

Cyclic voltammetry (CV) measurements were performed on 1a-8a in order to gain insight into their redox behaviors. All CV experiments were done in acetone (with 20% CH$_3$CN for 6a and 50% CH$_3$OH for 7a-8a, in order to improve solubility), with 0.1 M Bu$_4$NPF$_6$ and scan rates of 0.05 V s$^{-1}$. Almost all compounds displayed one (quasi-)reversible redox wave at relatively low potentials vs. Fc$^+$/Fc (Table 1, Figure 3), with peak separations of 0.08-0.10 V, which we attributed to the Ni$^{II/III}$ couple. The exceptions were 1a, with no redox events at $E < 1$ V, and 4a, which only had an irreversible oxidation wave at 0.26 V vs. Fc$^+$/Fc. The redox behavior of 4a was most likely complicated by the redox-active nature of the phenoxy ligand. The variation in $E^{\infty}_{\text{Ni}^{II/III}}$, can be explained on the basis of the charge of the complex, and the electron-donation from the ligands, estimated from their basicity (pK$_a$ of their conjugate acids). The lowest values belonged to 5a ($E^{\infty}_{\text{Ni}^{II/III}} = -0.14$ V), which is an anionic molecule and has the most basic donor ligand (acac, aqueous scale pK$_a$ of Hacac = 9), and 8a ($E^{\infty}_{\text{Ni}^{II/III}} = 0.07$ V), which has three donor atoms in its ancillary ligand, two of which are anionic carboxylates. The highest $E^{\infty}_{\text{Ni}^{II/III}}$ values corresponded to chloride complex 2a (0.43 V) and formate complex 3a (0.48 V). It is interesting to compare the three neutral compounds 1a and 6a-7a. Clearly, the lack of a negative charge makes oxidation more arduous, as demonstrated by 1a, which was only oxidised (irreversible wave) at 1.03 V. The bpy and terpy complexes 6a-7a, however, had relatively low $E^{\infty}_{\text{Ni}^{II/III}}$ of 0.26 and 0.33 V respectively, having multiple pyridine donors which are more electron-rich than CH$_3$CN; nevertheless, the six-coordinate, dianionic 8a had a potential that was lower by 0.4 V than the terpy containing 7a.

2a-8a all displayed further oxidation waves beginning at $E$ = 0.8 V (Figures S34-41), however these were all irreversible and likely involve ligand oxidation processes. In conclusion, 2a-8a constitute a range of compounds, based on the same [Ni$^{II}$((pyN)$_2$)$_2$] core, with varied structural and electrochemical properties, suitable as starting materials for the study of Ni$^{III}$ species; the presence of reversible redox behavior was encouraging in suggesting that a simple one-electron oxidation without successive reaction is plausible.

Preparation of Ni$^{III}$ complexes: We attempted to generate Ni$^{III}$ species by the chemical oxidation of the 1a-8a precursors (see supporting information for details). The Ni$^{III}$ complexes were oxidized with the one-electron oxidants tris(4-bromophenyl)ammonium hexachloroantimonite (magic blue) and cerium ammonium nitrate, ([NH$_4$]$_2$[Ce$^{IV}$(NO$_3$)$_7$]). The reactions were performed in thermostated cuvettes and monitored by electronic absorption spectroscopy. For the acetonitrile complex 1a and the phenoxy 4a, we could not find suitable conditions to generate a stable oxidized species. The preparation, characterization, and reactivity properties of 2b, are described in a separate report.\cite{33} 3a and 5a (0.4 mM acetone solutions) reacted with one equivalent of magic blue at -80 °C. New species with intense visible absorption bands (3b: 530 and 830 nm, 5b: 530 and 720 nm, Figure 4) that were comparable to previously reported [Ni$^{III}$((OX)(pyN$_{2}$)$_2$)] complexes,\cite{39} were obtained. Because of solubility limitations associated with 6a-8a, the latter three Ni$^{III}$ compounds could not be prepared in pure acetone solutions: 6a was dissolved in a 9/1 acetone/acetonitrile mixture; 7a in pure CH$_3$OH; and 8a in 1/1 acetone/CH$_3$OH. For 6a-8a, the addition of 2 equivalents of CAN (as an acetonitrile solution) yielded the maximum yields of the corresponding Ni$^{III}$ species 6b-8b.

The products showed bands at $\lambda_{\text{max}}$ = 580 and 790 nm (6b), 680 nm (7b), and 560 and 700 nm (8b). High yields for 6b could only be obtained at -80 °C, resulting in long preparation times (50 minutes), while 7b-8b were stable and prepared in high yields at higher temperature (-40 °C). We have previously observed that, in oxidation reactions mediated by CAN, the ONO$_2$ anion can compete with the ancillary ligand for binding to

Figure 3. Cyclic voltammograms of 2a-8a vs. Fc$^+$/Fc (orange trace: 2a, solid blue: 3a, dashed blue: 4a, purple: 5a, pink: 6a, green: 7a, red: 8a); conditions: 0.1 mM, 0.1 Bu$_4$NPF$_6$ ([Bu = C$_4$H$_9$]), scan rate 0.05 V s$^{-1}$, room temperature. Cyclic voltammetry experiments were conducted with a CH Instruments 600E electrochemical analyser, using a glassy carbon working electrode, a platinum wire counter electrode and an Ag/AgNO$_3$ 0.01 M reference electrode.
Indeed, reacting more than 2 equiv. of CAN with 6a caused the formation of [Ni\(\text{III(OX)}\)(pyN\(\text{Me}_{2}\))] as evident from its absorption bands at \(\lambda_{\text{max}} = 560\) and 890 nm.\(^{10}\) We did not encounter this problem with 7a-8a. Complexes 5b-8b represent the first examples of non-square planar high-valent oxidants supported by the 2.6-pyridinecarboxamidate ligand. Furthermore, complexes 6b and 7b are the only cationic Ni\(\text{III}\) species supported by the 2.6-pyridinedicarboxamidate ligand (in contrast to the previously described neutral (2b, 3b, [Ni\(\text{III(OX)}\)(pyN\(\text{Me}_{2}\))]) and anionic (8b) complexes).

The solutions of 2b-8b generated through the aforementioned methods were analyzed by EPR spectroscopy (Figure 5). All showed the presence of \(S = \frac{1}{2}\) species, with average \(g\)-values of 2.11-2.22, which are consistent with the unpaired spin density localized mainly on a low-spin, \(d^1\), Ni\(\text{III}\) ion.\(^{20}\) Spin quantification against a standard (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)) provided the following yields of Ni\(\text{III}\) species: 3b = 90 \(\pm\) 20%, 5b = 80 \(\pm\) 20% = 80; 6b = 70 \(\pm\) 20%, 7b = 80 \(\pm\) 20%, 8b = 80 \(\pm\) 20%.

The formate complex, 3b, displayed an axial signal (\(g_x = 2.25, g_y = 2.02\)), and was very similar to previously reported square planar bicarbonate, acetate, and nitrate [Ni\(\text{III(OX)}\)(pyN\(\text{Me}_{2}\))] complexes. However, the broadness of the features in 3b showed it was either not entirely pure or there was some fluxional behavior of the potentially bidentate ligand.

The spectrum of the \(^{14}\)Cl complex (2b) was considerably more rhombic, with \(g = 2.32; 2.23\) and 2.00, and hyperfine coupling to the \(^{35/37}\)Cl nucleus (I = 3/2), evident from the four-line splitting of the \(z\) component of the signal (\(A_{zz} = 110\) MHz).\(^{20}\)

The spectrum of the acac complex, 5b, displayed a mixture of a major, markedly rhombic (\(g = 2.32, 2.23, 2.01\)) species, plus a relatively small contamination of a second species (\(g_x = 2.21, g_y = 2.02; \approx\) 15% of total Ni\(\text{III}\), evaluated on the basis of the height of the signals at \(g = 2\) and of simulation of the spectrum). The contamination appears similar to 3b and previously prepared [Ni\(\text{III(OX)}\)(pyN\(\text{Me}_{2}\))] complexes. We identified that 5a was readily converted to [Ni\(\text{II(O}_{2}\text{CCH}_3)(\text{pyN}_{2}\text{Me}_{2})\)]\(^-\) and thus surmise the contaminant is [Ni\(\text{II(O}_{2}\text{CCH}_3)(\text{pyN}_{2}\text{Me}_{2})\)]. The remaining three compounds, 6b-8b, displayed EPR spectra with \(g_x > g_y > g_z\). Interestingly, 6b showed a three-line signal shape corresponding to hyperfine coupling to one I = 1, \(^{14}\)N nucleus in the \(z\) direction (\(A_{zz} = 65\) MHz), whereas 7b had coupling to two \(^{14}\)N nuclei (five-line splitting, \(A_{zz} = 55\) MHz), whereas 8b had no visible hyperfine coupling.

In principle, a complex with unpaired spin density will give rise to an axial EPR signal if it has a fourfold symmetry axis, at least locally around the unpaired spin density. Hence, in the putative square planar complexes (2b-3b and [Ni\(\text{III(OX)}\)(pyN\(\text{Me}_{2}\))])\(^+\) by virtue of having a pseudo-\(D_{4h}\) symmetry, we expect an axial signal, as we indeed observed for 3b and [Ni\(\text{III(OX)}\)(pyN\(\text{Me}_{2}\))].\(^{19}\)

For 2b, because chlorine is considerably larger and has different donor properties than the O-atoms of the other complexes, we suggest the markedly different first coordination sphere induces a more rhombic EPR signal. Similar arguments are valid for the
square pyramidal structures, which 5b and 6b potentially are, that is, there would be a plane with four similar N/O ligands, plus one apical ligand, to give a pseudo-C₂ᵥ symmetry, and hence an axial EPR signal would be expected. The alternative for 5b and 6b, is a trigonal bipyramidal geometry, which we postulate is more likely to give a more rhombic EPR spectrum. For 6b by virtue of the fact that gₓ = gᵧ, suggesting a near-axial symmetry of the compound, a square pyramidal geometry is more likely than trigonal bipyramidal. In contrast, 5b’s greater separation between gₓ and gᵧ was suggestive of either a trigonal bipyramidal geometry, or a bigger distortion in the coordination plane. Finally, the pseudo-octahedral complexes 7b-8b were comparable to the square planar complexes, with approximate fourfold rotational symmetry in at least one direction, and thus more axial EPR signals.

We observed resolved hyperfine coupling in the three complexes 2b and 6b-7b, in all cases only in the gₓ component. Coupling in the other directions cannot be excluded, as the gᵧ/zy parts of the signal display considerably larger line broadening that could mask a fine structure. The bpy and terpy compounds 6b-7b coupled to one and two (equivalent) ¹⁴N nuclei, respectively. In the 2,6-dipic complex 8b, which still contains a pyridine donor, no coupling was visible. The three complexes have respectively 5, 6, and 4 N donor ligands. We can infer that, as a result of the particular electronic structure of the complexes, only donor atoms above and below the molecular plane formed by the [Ni(pyN₂Me₂)] core have large hyperfine coupling. On the basis of this hypothesis, we can further deduce that the two N donors of bpy in 6b are non-equivalent, and support the conclusion that a symmetrical trigonal bipyramidal structure is not present in solution.

The thermal stability of 3b-8b was quite varied (Table 1), however, all Ni(III) species were reasonably stable at -40 to -80 °C. Generally, the complexes supported by more electron-rich ancillary ligands displayed longer lifetimes. 2b and [Ni(II)(OX)(pyN₂Me₂)] complexes were stable at -40 °C, whereas 3b, conversely, could only be prepared and remained stable at -80 °C. 5b, with the particularly basic bidentate acac ligand, was the most stable of the prepared complexes, being stable at -40 °C, and even displaying a t₁/₂ = 3 h at 25 °C. 6b, was prepared in highest yield at -80 °C, and had a t₁/₂ = 30 minutes after warming to -40 °C. 7b and 8b were indefinitely stable at -40 °C, and were even moderately stable (t₁/₂ = 30 s and 260 s respectively) after warming to 25 °C. A general trend in stability was that the complexes supported by multiple donors (e.g. 8b), or single highly basic anionic donors (e.g. 5b) were the most stable, while those with low coordination numbers and/or single anionic donors were less stable. This would suggest that by simply tuning the donor strength of the ancillary ligand one could prepare highly stable (less reactive) high-valent oxidants.

In order to understand the oxidation reactivity properties of 5b-8b, and the role the supporting ligands play in modulating the reactivity of these high-valent oxidants; we reacted 5b-8b with phenols. 3b was insufficiently stable to explore its reactivity. We explored the reactivity of 5b-8b towards 2,6-di-tert-butylphenol (2,6-DTBP). At -40 °C, neither 5b nor 8b reacted with a large excess of 2,6-DTBP (100 eq.), while both 6b and 7b reacted readily, as evidenced by the disappearance of their characteristic visible absorption bands (Figures S55-S56). Mass spectrometric analysis of the post-reaction mixtures showed the formation of 3,3′,5,5′-tetra-tert-butyl-[1,1'-bi(cyclohexyldiene)]-2,2′,5,5′-tetraene-4,4′-dione (Figures S59-S60), a homo-coupling product likely derived from the phenoxyl radical (from HAT). These observations correlate well with the thermal stability observations that the complexes supported by highly basic ancillary donors are unreactive oxidants, whereas those with neutral donors are reactive towards phenols.

The reactions of 6b and 7b with 2,6-DTBP were pseudo-first order in the presence of excess 2,6-DTBP, and we measured their rate constants (kobs) by exponential fitting of the decay plot. Second order rate constants (kₛ) were determined by plotting kobs (determined at varying substrate concentrations) against substrate concentration and calculating the slope of the resulting linear plots (Figures S57-S58). 6b reacted with a kₛ = 0.087 M⁻¹s⁻¹ in a solvent mixture of 9/1 acetone/acetonitrile. 7b (Eᵥ(ox/rej) = 0.33 V) reacted an order of magnitude faster, with kₛ = 1.29 M⁻¹s⁻¹, however in pure CH₂OH. Importantly, none of 5b-8b reacted with hydrocarbons containing weak C–H bonds (xanthene and 9,10-dihydroanthracene). These rate constants compare favourably with those determined for [Ni(II)(OX)(pyN₂Me₂)] suggesting these cationic complexes (6b and 7b) with neutral ancillary ligands are active HAT oxidants. Unfortunately, we cannot draw much insight into structural effects on reactivity from these studies, because only 6b and 7b displayed reactivity towards 2,6-DTBP. Given that these 5- and 6-coordinate complexes reacted at rates similar to 4-coordinate [Ni(II)(OX)(pyN₂Me₂)] complexes, we surmise that the geometry and coordination number of these oxidants has minimal effect on the reactivity properties, and that the charge on the metal ion appears to govern its relative reactivity in phenol oxidation.

We previously found that 2b and [Ni(II)(OX)(pyN₂Me₂)] (OX = OCO₂H, O₂CCH₃, ONO₂ reacted with phenols through a HAT mechanism. Unfortunately, a consistent comparison with the extended series presented here is hampered by the different conditions necessary to prepare [Ni(II)(L)(pyN₂Me₂)] (L = Cl, OCO₂H, O₂CCH₃, ONO₂) and 5b-8b. We previously found that the most electron-poor [Ni(II)(ONO₂)(pyN₂Me₂)] complex reacted at the highest rates. The observations that only 6b and 7b were capable of oxidizing 2,6-DTBP is thus not surprising, because both are cationic complexes, with Ni(II) redox potentials in the same range as [Ni(II)(OX)(pyN₂Me₂)]. 7b constituted somewhat of an exception, being considerably more reactive than 6b in spite of there being little-to-no difference in their redox potentials. The presence of aprotic solvent medium (CH₂OH) for 7b likely influenced the reaction rate.

The oxidation of 2,6-DTBP by high-valent metal-based oxidants comes under the class of proton coupled electron transfer (PCET) reactions. We previously demonstrated that 2b and [Ni(II)(OX)(pyN₂Me₂)] complexes reacted with 2,6-DTBP and hydrocarbons through a HAT (concerted PCET) mechanism. We proposed the OX ligand acted as a proton acceptor in these reactions, yielding [Ni(II)(HX)] products. The discovery that the bpy and terpy complexes 6b and 7b can perform phenol oxidation suggests that the 2,6-pyridinedicarboxamidate ligand
and lower reactivity levels. The reactivity of the Ni complex is typically of metal carboxamidates (pyNMe2) ligand played a non-innocent role in the HAT reaction. This is because the bpy and terpy ligands are neutral donors, and thus in principle may not act as proton acceptors, whereas the pyNMe2 could potentially act as a proton acceptor on either the carboxamidate O- or N-atoms. The argument can also be made that a pyridine donor of the bpy and terpy ligands may act as a proton acceptor site in 6b and 7b.

Unfortunately, we cannot assume that the same PCT (thus HAT) mechanism is at play in the case of 6b-7b, particularly by virtue of the fact that they were analysed in different solvent media (7b could only be analysed in CH3OH). Indeed the use of a protic solvent can potentially have large effects on the mechanisms of PCT reactions. Work is underway in our laboratory to probe the mechanism of phenol oxidation by 6b-7b. That is, do they oxidise via HAT or by another non-concerted form of PCT? We also intend to identify conditions where a fair comparison of 6b-7b and [Ni(II)(O)](pyNMe2) complexes can be made. This will be a critical piece of future work, because the observation that these complexes will oxidise phenols with weak O–H bonds is critically important in the future development and studies of oxidants supported by carboxamidate ligands. Our results demonstrate that such functional groups may not be non-innocent proton acceptors in PCT reactivity.

Conclusions

We synthesised and characterised a series of NiII complexes based on the NiII(L)(pyNMe2) core, with different coordination numbers (4–6) and geometries, and ligands with a variety of donor groups. The binding mode of the supporting ligand pyNMe2 was essentially unvaried, as a meridional N3 ligand, with the exception of minor bond lengthening caused by increased coordination numbers. The other (ancillary) ligand determined the coordination geometry, with the mono-dentate -OH and -OC2H5 donors forming square planar complexes 3a–4a, the bidentate acac and bpy yielding square pyramidal complexes 5a–6a, and the tridentate terpy and 2,6-dipic forming pseudo-octahedral complexes 7a–8a. While the four-coordinate square planar complexes were low spin (S = 0), higher coordination numbers caused a switch to the high spin state (S = 1).

Most of the complexes could be oxidised at low temperature to generate putative NiIII species 3b–8b. Electronic absorption and EPR spectra typical of metal-centred spin density confirmed the formation of NiIII species. The oxidation reactivity of the NiIII species was examined by their reactivity towards 2,6-DTBP. Diverse reactivity properties were evident, with higher basicity of the ligands contributing to higher stability and lower reactivity levels. The major influence on reactivity derived from the relative charge at the Ni ion, and not from the geometry or coordination number. Fascinatingly, complexes with neutral ancillary donors were still capable of oxidizing 2,6-DTBP, suggesting the supporting 2,6-pyridinecarboxamidate ligand may not be innocent in PCT phenol oxidation reactions.

Experimental Section

See supporting information file for experimental details.

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Keywords: high-valent nickel • oxidation • EPR spectroscopy • mechanism elucidation • structure/function relationships


The synthesis of a family of NiII and NiIII complexes supported by a common 2,6-pyridinedicarboxamidate ligand is described. The complexes display coordination numbers of 4, 5, and 6 and different sets of N- and O-atom donors. The coordination environment allows for tuning of the magnetic and spectroscopic (UV-Vis, NMR, EPR) properties of the complexes and provides insights into the oxidising power of high-valent Ni.