A structure and reactivity analysis of monomeric Ni(II)–hydroxo complexes prepared from water†

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The nickel(II) chemistry with the tridentate ligands bis[(*N*′-R-ureido)-*N*-ethyl]-*N*-methylamine ($H_4\mathbf{1}^R$, R = isopropyl, *tert*-butyl) is described. The Ni(II)–OH complexes, $[Ni^{II}H_2\mathbf{1}^R(OH)]^-$ were generated using water as the source of the hydroxo ligand. These complexes are pseudo-square planar, in which the primary coordination sphere contains three nitrogen donors from $[H_2\mathbf{1}^R]^{2-}$ and the oxygen atom from the hydroxide (Ni–O(H), 1.857(1) Å). The Ni(II)–OH unit also is involved in two intramolecular hydrogen bonds between the urea groups of the $[H_2\mathbf{1}^R]^{2-}$ and the hydroxo oxygen atom. Attempts to deprotonate the Ni(II)–OH unit to produce Ni(II)–oxo complexes were unsuccessful. A variety of bases with pK_a of less than 15 (in DMSO) were unable to deprotonate the hydroxo ligand. Treating the Ni(II)–OH complexes with $KOBu^t$ ($pK_a \sim 29$) afforded the ligand substitution product, $[Ni^{II}H_2\mathbf{1}^R(OBu^t)]^-$. Ni(II)–siloxide complexes were isolated when the $[Ni^{II}H_2\mathbf{1}^R(OH)]^-$ complexes were allowed to react with $K[N(TMS)_2]$.

Introduction

Monomeric metal complexes of the middle and late 3d transition metals with terminal hydroxo ligands are rare because the OH^- ligand tends to bridge between metal centers.[1] In contrast, the active sites of many metalloproteins contain M–OH units, which are essential for function.[2] These sites are often distant from the protein surface, preventing interactions between M–OH centers. A similar "site isolation" design has been used to make synthetic M–OH complexes, in which bulky ancillary ligands are employed to prevent formation multi-nuclear species.

Our group[3] and others[4] have been exploring the chemistry of monomeric M–OH complexes using tripodal ligands containing hydrogen bond (H-bond) donors. We use ligands containing an apical nitrogen donor and three ethyleneureayl groups that form intramolecular H-bond networks between the NH groups and the M–OH units. One outcome of the H-bond networks is that stable cavities are formed around the metal centers, which aid in averting bridged species from occurring. We recently reported[5] the synthesis of the $[H_2\mathbf{1}^{tBu}]^{2-}$ ligand that has one of the tripodal arms replaced with a methyl group (Fig. 1). $[H_2\mathbf{1}^{tBu}]^{2-}$ coordinates in a facial manner to Fe(II), Mn(II), and Co(II) centers, producing more open structures that can lead to dimeric species.[6]

Herein we report the preparation of Ni(II)–OH complexes with $[H_2\mathbf{1}^R]^{2-}$ (R = iPr, *t*Bu). We reasoned that $[H_2\mathbf{1}^R]^{2-}$ would coordinate in a meridional fashion to a d^8 metal center, leaving one site available to bind a hydroxo ligand. There are only four examples of structurally-characterized mononeric Ni(II) complexes with terminal hydroxo ligands. Riordan has isolated a five-coordinate Ni(II)–OH complex for the oxidation of $[Ni^Icyclam]^-$ with dioxygen.[7] Cámpora has reported two square planar Ni(II)–OH complexes prepared with hydroxide salts (*e.g.* KOH and LiOH)[8] and Mindiola has shown that a Ni(I) complex can reductively split water, forming four-coordinate Ni(II)–OH species.[9] Our investigations showed that $[Ni^{II}H_2\mathbf{1}^R(OH)]^-$ is formed from water and is stabilized *via* an intramolecular H-bonding network. In addition, our efforts to deprotonate the hydroxo ligand are described.

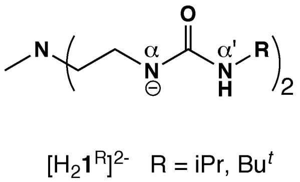

Fig. 1 Ligand $[H_2\mathbf{1}^R]^{2-}$ used in this investigation.

Experimental section

Preparative methods

All reagents were purchased from commercial sources and used as received, unless otherwise noted. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieve. Anhydrous solvents were purchased from Aldrich (Milwaukee, WI). Potassium hydride (KH) as a 30% dispersion in mineral oil was filtered with a medium porosity glass frit, washed five times each with pentane and Et_2O, dried under vacuum, and stored under an inert atmosphere. The syntheses of all metal complexes were conducted in a Vacuum Atmospheres, Co. (Hawthorne, CA) drybox under an argon atmosphere. Elemental analyses were accomplished at Robertson Microlit (Madison, NJ). Compound $H_4\mathbf{1}^{tBu}$ was prepared following the literature procedure.[5]

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† Electronic supplementary information (ESI) available: Crystallographic data for $K[Ni^{II}H_2\mathbf{1}^{Bu^t}(OH)]$ and $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OH)]$, and selected metrical parameters for the $K[Ni^{II}H_2\mathbf{1}^{Bu^t}(OH)]$, $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OH)]$, and $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$. CCDC reference numbers 708859–708863. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b820209e

Ligand synthesis

Bis[(*N*′-isopropylureido)-*N*-ethyl]-*N*-methylamine (H$_4$1^{iPr}). Freshly distilled *N*′-methyl-2,2′-diaminodiethylamine (2.0 g, 0.017 mmol) was dissolved in 50 mL of anhydrous THF under a N$_2$ atmosphere, cooled to 0 °C, and treated with isopropyl isocyanate (3.1 g, 0.36 mmol) *via* dropwise addition. The mixture was allowed to warm to room temperature and was stirred overnight. The solid that was formed was filtered, washed with 10 mL of diethyl ether three times, dried under vacuum overnight, and stored under an argon atmosphere. The yield of H$_4$1^{iPr} was 3.8 g (78%). δ_H (400 MHz; solvent DMSO-d$_6$): 5.78 (2 H, s, CO-NH-iPr), 5.66 (2 H, t, CH$_2$-NH-CO), 3.05 (4 H, q, CH$_2$–C*H*$_2$-NH), 2.32 (4 H, t, N–C*H*$_2$-CH$_2$), 2.16 (3 H, s, Me*H*), 3.65 (2 H, m, NH–C*H*-Me$_2$), 1.02 (12 H, s, iPr*H*); δ_C (400 MHz; solvent DMSO-d$_6$): 158.09, 57.71, 42.72, 41.48, 37.74, 23.93. FT-IR (Nujol, cm^{-1}) ν(NH) = 3329, ν(CO) = 1567, 1621; Mp 118–120 °C; HRMS (ES+): Exact mass calcd for $C_{13}H_{30}N_5O_2$ [M + H], 288.2400. Found 288.2405.

Preparation of metal salts

K[Ni^{II}H$_2$1^{iPr}(OH)]·DMA.

Method A. A solution of H$_4$**1**^{iPr} (100 mg, 0.348 mmol) in 3 mL of DMA was treated with solid KH (44 mg, 1.1 mmol). After gas evolution ceased, Ni(OAc)$_2$ (62 mg, 0.35 mmol) was added slowly as a solid. The solution was dark red and was stirred for 45 min, after which H$_2$O (6.3 uL, 0.35 mmol) was added *via* syringe, causing the solution to turn purple. The solution was stirred for an additional 20 min and then filtered through a medium glass frit to remove KOAc (67 mg, 98%). Purple crystals were obtained by 1 : 1 diethyl ether–pentane vapor diffusion into a DMA solution of K[Ni^{II}H$_2$1^{iPr}(OH)] (88 mg, 64%). Found: C, 41.76; H, 7.32; N, 17.09%. K[Ni^{II}H$_2$**1**^{iPr}(OH)]·DMA ($C_{17}H_{37}N_6KNiO_4$) requires C, 41.90; H, 7.65; N, 17.25%. FT-IR/cm^{-1} (Nujol): ν(NH) = 3157, ν(CO) = 1572, 1518; λ_{max} (DMA, nm (ε, M^{-1} cm^{-1})) 500 (158). Note that the peak associated with the ν(OH) was not present in FTIR spectra of the potassium salt of the complex. However, this peak was observed at ν(OH) = 3612 cm^{-1} in the tetramethyammonium salt, prepared by metathesis with [NMe$_4$][OAc] (see below for similar method of metathesis).

Method B. A solution of H$_4$**1**^{iPr} (100 mg, 0.348 mmol) in 3 mL of DMA was treated with solid KH (29 mg, 0.73 mmol). After gas evolution ceased, Ni(OAc)$_2$ (62 mg, 0.35 mmol) was added slowly as a solid. The dark red solution was then filtered to remove KOAc (61 mg, 99%) and characterized: FT-IR/cm^{-1} (Nujol): ν(NH) = 3355; λ_{max} (DMA, nm) 350. The solution was further treated with one equivalent of KH (14 mg, 0.35 mmol). After gas evolution ceased, H$_2$O (6.3 µL, 0.35 mmol) was added *via* syringe, causing the solution to turn purple. Volatiles were removed under reduced pressure and the resulting purple oil was triturated with diethyl ether to afford a purple powder. The spectroscopic properties of the purple powder prepared by this method are the same as those obtained for K[Ni^{II}H$_2$1^{iPr}(OH)] prepared by Method A.

K[Ni^{II}H$_2$1^{tBu}(OH)]·DMA. This was prepared following the procedure as outlined above for K[Ni^{II}H$_2$1^{iPr}(OH)] (Method A) with H$_4$**1**^{tBu} (100 mg, 0.317 mmol), KH (39 mg, 0.98 mmol), Ni(OAc)$_2$ (56 mg, 0.32 mmol), and H$_2$O (5.7 µL, 0.32 mmol). The solution was filtered to remove KOAc (52 mg, 0.53 mmol, 84%). Purple crystals of the salt were obtained by diffusing a 1 : 1 diethyl ether–pentane mixture into a DMA solution of K[Ni^{II}H$_2$1^{tBu}(OH)] (118 mg, 87%). Found: C, 44.28; H, 8.19; N, 16.08%. K[Ni^{II}H$_2$**1**^{tBu}(OH)]·DMA ($C_{19}H_{41}N_5KNiO_4$) requires C, 44.28; H, 8.02; N, 16.31%. FT-IR/cm^{-1} (Nujol): ν(OH) = 3612, ν(NH) = 3157, ν(CO) = 1638, 1584, 1542; λ_{max} (DMA, nm (ε, M^{-1} cm^{-1})) 500 (130).

K[Ni^{II}H$_2$1^{tBu}(^{18}OH)]. This was prepared using Method A and H$_2$^{18}O—the quantities of reagents were identical to those described above. The spectroscopic for this complex were identical to those of [Ni^{II}H$_2$**1**^{tBu}(^{16}OH)]$^-$ with the following exception: FT-IR/cm^{-1} (Nujol): ν(^{18}OH) = 3601.

[NMe$_4$][Ni^{II}H$_2$1^{iPr}(O^{t}Bu)].

Method C. A solution of H$_4$**1**^{iPr} (100 mg, 0.348 mmol) in 3 mL of DMA was treated with solid KH (29 mg, 0.73 mmol). After gas evolution ceased, solid Ni(OAc)$_2$ (61 mg, 0.35 mmol) was added slowly. The solution turned dark red and was stirred for 45 min. Solid KOtBu (39 mg, 0.35 mmol) was added and the solution turned blue-purple. [NMe$_4$][OAc] (51 mg, 0.38 mmol) was added, the mixture was allowed to stir for 1 h, and then filtered to remove KOAc (91 mg, 89%). Volatiles were removed under reduced pressure and the resulting blue-purple oil was triturated with diethyl ether to afford a blue-purple powder (156 mg, 91%). Found: C, 51.42; H, 10.23; N, 17.30%. [NMe$_4$][Ni^{II}H$_2$1^{iPr}(O^{t}Bu)] ($C_{21}H_{48}N_6NiO_3$) requires C, 51.33; H, 9.85; N, 17.10%. FT-IR (Nujol, cm^{-1}): ν(NH) = 3157, ν(CO) = 1665, 1575, 1520. λ_{max} (DMA, nm (ε, M^{-1} cm^{-1})) 495 (210).

[NMe$_4$][Ni^{II}H$_2$1^{iPr}(O^{t}Bu)].

Method D. K[Ni^{II}H$_2$1^{iPr}(OH)] (0.35 mmol), prepared by Method A, in 3 mL of DMA was treated with solid KOtBu (39 mg, 0.35 mmol) and stirred for 30 min, causing a subtle change in color from purple to bluish-purple. [NMe$_4$][OAc] (46 mg, 0.35 mmol) was added and, after 1 h of stirring, the reaction mixture was filtered to remove the KOAc (91 mg, 89%). Volatiles were removed under reduced pressure, producing a blue-purple oil that was triturated with diethyl ether to give a blue-purple powder. The product was obtained in pure form *via* recrystallization by diffusing a 1 : 1 diethyl ether–pentane mixture into a DMA solution of [NMe$_4$][Ni^{II}H$_2$1^{iPr}(O^{t}Bu)] to give 156 mg (91%) of the salt. Spectroscopic properties of the blue-purple powder prepared by this method are the same as those of the blue-purple powder prepared in Method C.

[NMe$_4$][Ni^{II}H$_2$1^{tBu}(O^{t}Bu)]. This was prepared following Method D using K[Ni^{II}H$_2$**1**^{tBu}(OH)] (0.32 mmol), KO^{t}Bu (36 mg, 0.32 mmol), and NMe$_4$OAc (63 mg, 0.48 mmol). The amount of KOAc isolated was 147 mg (96%). The salt was recrystallized by diethyl ether diffusion in to a DMA solution of crude product, resulting in blue-purple crystals (128 mg, 78%). FT-IR/cm^{-1} (Nujol): ν(N–H) = 3157. λ_{max} (DMA, nm (ε, M^{-1} cm^{-1})) 495 (166). Repeated elemental analysis gave consistently low values.

[NMe$_4$]$_{0.5}$K$_{0.5}$[Ni^{II}H$_2$1^{iPr}(OSiMe$_3$)]·DMA. This was prepared following Method D using K[Ni^{II}H$_2$**1**^{iPr}(OH)] (0.35 mmol), solid KN(SiMe$_3$)$_2$ (70 mg, 0.35 mmol), and NMe$_4$OAc (55 mg, 0.42 mmol). The amount of KOAc isolated was 106 mg (98%). The solution was set up for recrystallization *via* 1 : 1 diethyl ether–pentane vapor diffusion into a DMA solution and purple crystals

Table 1 Crystallographic data for $K[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]\cdot DMA$, $[NMe_4]_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)]\cdot DMA$, and $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$

Salt	$K[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]\cdot DMA$	$[NMe_4]_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)]\cdot DMA$	$[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$
Molecular formula	$C_{13}H_{28}KN_5NiO_3$	$C_{24}H_{55}K_{1/2}N_{6.5}NiO_4Si$	$C_{23}H_{52}N_6NiO_3$
Formula weight/g mol^{-1}	400.12	603.83	519.39
T/K	163(2)	158(2)	148(2)
Space group	$P\bar{1}$	$I\bar{4}2d$	$P4_32_12$
a/Å	9.6492(9)	24.6663(11)	17.6716(10)
b/Å	9.8057(9)	24.6663(11)	17.6716(10)
c/Å	10.2370(9)	17.6314(16)	21.525(3)
α/°	86.824(2)	90	90
β/°	88.467(2)	90	90
γ/°	74.471(2)	90	90
Z	2	16	8
V/Å^3	931.73(15)	10727.4(12)	6722.1(9)
δ_{calcd}/Mg m^{-3}	1.427	1.213	0.971
$R_1{}^a$	0.0286	0.0258	0.0996
$wR_2{}^b$	0.716	0.0610	0.3029
GOF^c	1.050	1.120	1.471

[a] $R_1 = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $wR_2 = [\sum[\omega(F_o{}^2 - F_c{}^2)^2]/\sum[\omega(F_o{}^2)^2]]^{1/2}$. [c] $GOF = [\sum[\omega(F_o{}^2 - F_c{}^2)^2]/(n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

resulted (161 mg, 94%). Found: C, 45.72; H, 8.95; N, 17.34%. $[NMe_4]_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)]\cdot DMA$, ($C_{22}H_{51}K_{0.5}N_{6.5}NiO_4Si$) requires C, 45.79; H, 8.91; N, 17.78%. FT-IR/cm^{-1} (Nujol): ν(N–H) = 3157. λ_{max} (DMA, nm (ε, M^{-1} cm^{-1})) 495 (166).

$[NMe_4][Ni^{II}H_2\mathbf{1}^{tBu}(OSiMe_3)]$. This was prepared as described above for $[NMe_4]_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)$ with $K[Ni^{II}H_2\mathbf{1}^{tBu}(OH)]$ (0.32 mmol), solid $KN(SiMe_3)_2$ (63 mg, 0.32 mmol), and NMe_4OAc (63 mg, 0.48 mmol). The solution was then filtered to remove the insoluble KOAc (110 mg, 1.1 mmol) and recrystallization *via* 1 : 1 diethyl ether–pentane vapor diffusion into a DMA solution and purple crystals resulted (161 mg, 95%). FT-IR/cm^{-1} (Nujol): ν(N–H) = 3157. λ_{max} (DMA, nm (ε, M^{-1} cm^{-1})) 495 (158). Repeated elemental analysis gave consistently low values.

Physical methods

NMR spectra were obtained on either Bruker DRX-400 MHz or Bruker Avance 500 MHz spectrometers. NMR solvents were purchased in ampules and stored over molecular sieves. Electronic spectra were recorded with a Cary 50 spectrophotometer or an Agilent 8453 spectrophotometer. FT-IR spectra were collected on a Mattson Genesis series FT-IR spectrometer or Varian 800 Scimitar series FT-IR spectrophotometer and are reported in wavenumbers. Mass spectra were recorded on a Termo Trace MS+ GC-MS operated in EI mode.

X-Ray crystallographic data collection and refinement of the structures

Intensity data for $K[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]\cdot DMA$, $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$, and $(NMe_4)_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)]\cdot DMA$ were collected using a Bruker CCD platform diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The SMART[10] program package was used to determine the unit-cell parameters and for data collection (25 s/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT[11] and SADABS[12] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[13] program. Partial crystal data, data collection and refinement parameters for $K[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]$, $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$ and $(NMe_4)_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)]\cdot DMA$ are listed in Table 1.

A purple crystal of $K[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]\cdot DMA$ of approximate dimensions 0.14 × 0.19 × 0.26 mm was mounted on a glass fiber and transferred the diffractometer. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group $P\bar{1}$ was assigned and later determined to be correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[14] for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}). At convergence, $wR_2 = 0.0757$ and GOF = 1.050 for 320 variables refined against 4501 data (0.75 Å), $R_1 = 0.0286$ for those 3931 data with $I > 2.0(I)$.

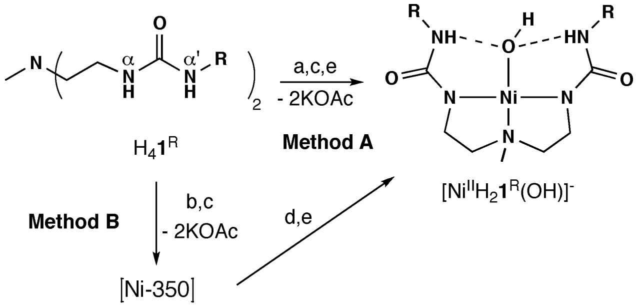
A red crystal of $[NMe_4]_{0.5}K_{0.5}[Ni^{II}H_2\mathbf{1}^{iPr}(OSiMe_3)]\cdot DMA$ of approximate dimensions 0.24 × 0.32 × 0.37 mm was mounted on a glass fiber and transferred to the diffractometer. The diffraction symmetry was $4/mmm$ and the systematic absences were consistent with the tetragonal space groups $I\bar{4}2d$ and $I4_1md$. It was determined that space group $I\bar{4}2d$ was correct. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[14] for neutral atoms were used throughout the analysis. Hydrogen atoms H4 and H5 were located from a difference-Fourier map and refined (x,y,z and U_{iso}); all other hydrogen atoms were included using a riding model. The potassium and tetramethylammonium ions were each assigned a site-occupancy value of one-half. Carbon atoms C(11) and C(12) were disordered and included using multiple components, partial site-occupancy factors (50%) and isotropic thermal parameters. At convergence, $wR_2 = 0.0647$ and GOF = 1.120 for 289 variables refined against 6158 data (0.77 Å), $R_1 = 0.0258$ for those 5709 data with $I > 2.0(I)$. The absolute structure was assigned by refinement of the Flack[15] parameter.

An orange crystal of $[NMe_4][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$ of approximate dimensions 0.38 × 0.39 × 0.41 mm was mounted on a glass fiber and transferred to the diffractometer. The diffraction symmetry was 4/*mmm* and the systematic absences were consistent with the tetragonal space groups $P4_32_12$ and $P4_12_12$. Unfortunately, it was not possible to determine which space group was correct. The structure was solved and refined in both of the above space groups. The quality of the refinement was the same for both space groups—the results reported here were based on refinement under space group $P4_32_12$. Attempts to refine the structure as a racemic twin did not improve the refinements. In addition, there was an undetermined solvent molecule present that was not included in the refinement. Because of these difficulties in refinement, only a brief description of structure is included.

Results and discussion

Preparation of $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}(\mathrm{OH})]^-$

Scheme 1 outlines the two methods that have been developed for the isolation of the $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}(\mathrm{OH})]^-$ complexes. Method A follows from procedures we have used previously in synthesizing M–OH complexes with our tripodal ureayl ligands. Three equiv. of base are used to deprotonate $\mathrm{H_4}\mathbf{1}^{\mathrm{R}}$, which deprotonates both αNH groups and one of the α′NH groups. Treating this salt with one equiv. of both $\mathrm{Ni(OAc)_2}$ and $\mathrm{H_2O}$ affords purple solution of $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}(\mathrm{OH})]^-$, from which crystalline product was obtained in yields of greater than 60%. In addition, we recover KOAc, which precipitates from the reaction mixture in nearly quantitative amounts.



^{a}Conditions: (a) 3 equiv KH, DMA, rt, Ar; (b) 2 equiv KH, DMA, rt, Ar (c) $\mathrm{Ni^{II}(OAc)_2}$, DMA, rt, Ar; (d) KH, DMA, rt, Ar; (e) $\mathrm{H_2O}$.

Scheme 1 Preparative routes to Ni(II)–OH complexes.

Method B began with the preparation of a new nickel complex, denoted Ni-350, that was obtained from treating $[\mathrm{H_2}\mathbf{1}^{\mathrm{R}}]^{2-}$ with one equiv. of $\mathrm{Ni(OAc)_2}$. This red species has a characteristic absorbance band at $\lambda_{\max} = 350$ nm and was stable in solution for approximately 6 h. We were not able to determine either its formula or structure—removal of solvent produced a red powder that formed a purple solution (*i.e.* $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}(\mathrm{OH})]^-$) when dissolved. Note that we obtained greater than 95% of the expected KOAc precipitated from the reaction mixture after addition of $\mathrm{Ni(OAc)_2}$, suggesting that acetate ions were not coordinated. We found that Ni-350 was a good synthon to produce isolatable four-coordinate complexes. For instance, treating *in situ* generated Ni-350 with one equiv. of KH and $\mathrm{H_2O}$ produced $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}(\mathrm{OH})]^-$ in yields that are comparable to those obtained with Method A. This method was also used prepare alkoxide complexes (see below). Both $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]^-$ and $[\mathrm{Ni^{II}H_2}\mathbf{1}^{t\mathrm{Bu}}(\mathrm{OH})]^-$ were stable solid-state for weeks under a dry, inert atmosphere.

Table 2 Selected metrical parameters for the $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{X})]^-$

X	$\mathrm{OH^-}$	$\mathrm{OTMS^-}$
Distances (Å)		
Ni–O1	1.857(1)	1.876(1)
Ni–N1	1.928(1)	1.925(2)
Ni–N2	1.917(1)	1.913(1)
Ni–N3	1.914(2)	1.913(2)
O1 ··· N4	2.649(2)	2.719(2)
O1 ··· N5	2.757(2)	2.760(2)
O1 ··· K1	3.251(2)	—
Angles (°)		
N1–Ni–O1	172.49(6)	171.27(6)
N1–Ni–N2	86.21(6)	85.84(7)
N1–Ni–N3	84.71(6)	84.24(7)
N2–Ni–N3	168.91(6)	169.18(2)
N2–Ni–O1	94.59(6)	96.01(6)
N3–Ni–O1	95.24(6)	94.44(6)

Isotopic labeling studies confirmed that water was the source of the hydroxo ligands in the $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{Bu}^t}(\mathrm{OH})]^-$ complexes. Solid-state FTIR spectra on isolated $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{Bu}^t}(^{16}\mathrm{OH})]^-$ complexes showed a prominent band at frequency of 3612 cm^{-1}, which is assigned ν(OH) from the terminal hydroxo ligand.[3] Preparing the complexes with $\mathrm{H_2{}^{18}O}$ afforded the corresponding $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{Bu}^t}(^{18}\mathrm{OH})]^-$ species, whose ν(OH) shifted to 3601 cm^{-1}. These observed shifts are expected based on a harmonic O–H oscillator model ($\nu(^{16}\mathrm{OH})/\nu(^{18}\mathrm{OH}) = 1.003$; calcd. 1.003).

Structural studies on $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]^-$

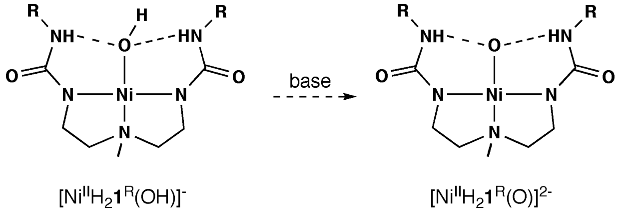
The solid-state structures of the $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}(\mathrm{OH})]^-$ were probed using single crystal X-ray diffraction methods. Selected data for $\mathrm{K}[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]$ are found in Tables 1 and 2; similar information for $[\mathrm{Me_4N}][\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]$ and $\mathrm{K}[\mathrm{Ni^{II}H_2}\mathbf{1}^{t\mathrm{Bu}}(\mathrm{OH})]$ is found in the ESI.† Because the molecular structures of anions in the three salts are nearly identical, only the properties of $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]^-$ will be discussed in detail. See the ESI for detail on the structures of the other Ni(II)–OH complexes.

The Ni(II) center in $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]^-$ has a distorted square planar coordination geometry (Fig. 2), in which three of the sites are occupied by nitrogen donors from $[\mathrm{H_2}\mathbf{1}^{\mathrm{R}}]^{2-}$. The ureayl αN atoms are nearly *trans* to each other with an average $\mathrm{Ni{-}N_{urea}}$ distance of 1.916(1) Å, whereas the Ni–N1 bond length is slightly longer at 1.928(1) Å. The Ni(II) ion is nearly in the plane formed by the three αN atoms (N1/N2/N3-plane), displaced out by 0.11 Å. The final coordination site is taken up by the hydroxo ligand, with a Ni–O1 distance of 1.857(1) Å and an O1–Ni–N1 angle of 172.49(6)°. The hydroxo ligand also interacts with the potassium cation within the lattice, with a K1 ··· O1 distance of 3.251(2) Å. It does not appear that this intermolecular interaction affects the coordination properties of the complex. We have also prepared and structurally characterized $[\mathrm{Me_4N}][\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]$ and $\mathrm{K}[\mathrm{Ni^{II}H_2}\mathbf{1}^{t\mathrm{Bu}}(\mathrm{OH})]$, salts in which there are no additional intermolecular interactions to the hydroxo ligand.[16] The molecular structures of the anions for the all salts are effectively the same: for instance, the Ni1–O1 distance of 1.862(3) Å in the tetramethylammonium salt is statistically identical to that observed with $\mathrm{K}[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}(\mathrm{OH})]$ (see above). The overall coordination geometry in $[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]^-$ is similar to that reported for $Ni^{II}(PCP)(OH)$ (PCP, 2,6-bis((diisopropylphosphino)methyl)phenyl);[8] this structure also has a short Ni–O(H) distance of 1.865(2) Å. These Ni–O(H) bond lengths in $[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]^-$ and $Ni^{II}(PCP)(OH)$ are significantly shorter than the 1.955(2) Å distance found in the five-coordinate $[Ni^{II}cyclam(OH)]^+$.[7]

One distinguishing feature in the molecular structure of $[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]^-$ is the H-bonding network surrounding the hydroxo ligand. Two intramolecular H-bonds are formed between the α′NH groups and O1, as indicated by the N···O1 distances of 2.649(2) and 2.757(2) Å. This assignment is support by FTIR studies that showed a broadening of the peaks associated with the N–H vibrations, which is a common occurrence for H-bonded systems. Notice the placement of the urea groups of the $[H_2\mathbf{1}^{iPr}]^{2-}$ relative to the N1/N2/N3-plane: both urea arms are tilted from the plane, positioned on the same side such that the α′N–H vectors are directed toward the O1. However, their relative displacements from the N1/N2/N3-plane are not equivalent; for instance, the differences in the distances of N4 and N5 to the plane differ by more than 0.7 Å (0.306 Å for N4 and 1.07 Å for N5). An unsymmetrical H-bonding network is observed, with N···O1 distances that differ by greater than 0.1 Å. Note also that O1 is displaced from the N1/N2/N3-plane by 0.467 Å, on the side opposite to that of the urea arms.

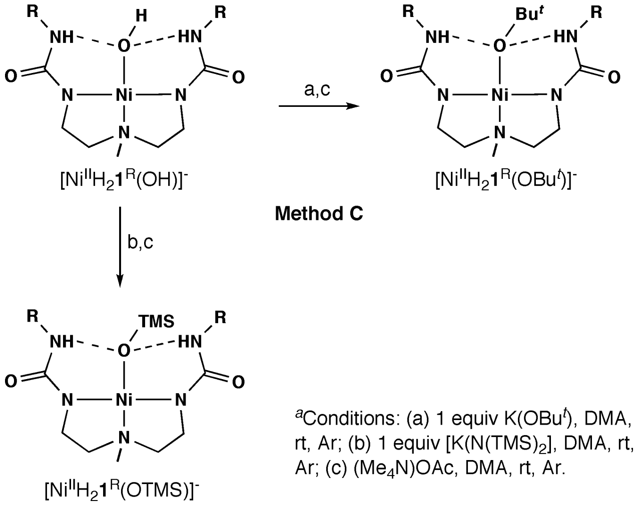
Reactivity of $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ with bases

The isolation of the $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ complexes allowed us to explore the formation of a Ni(II)–oxo species *via* deprotonation of the hydroxo ligand (eqn (1)). We have used this method previously in preparing M(III)–O complexes (M(III) = Fe, Mn). Initial studies involved treating $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ with alkali hyrides. The product(s) of these reactions did not contain the characteristic *ν*(NiO–H) peak at 3612 cm^{-1}, yet these findings alone are not proof of formation of the desired N(II)–O complexes. For instance, there were no changes in the absorbance spectra of these produces compared to those of the starting Ni(II)–OH complexes. Unfortunately, several attempts to isolate single crystals of these species were unsuccessful.



(1)

The reactivity of $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ with weaker bases than hydrides has also be examined. No reactions were observed between $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ and quinuclidine, 1,8-diazabicyclo(5.4.0)-undec-7-ene (DBU), 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), and triethylamine, bases with pK_a values of less than 13 in DMSO. We were able to isolate pure products for the reaction of $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ with KOBu^t, a base with a pK_a ~ 29 in DMSO (Scheme 2). These complexes lacked the *ν*(NiO–H) peaks in their FTIR spectra and showed ~5 nm blue shifts in their visible absorbance features. Analytical and X-ray diffraction data confirmed that rather than deprotonation, a ligand substitution reaction occurred, whereby the *tert*-butoxide anion replaced the hydroxo ligand. These alkoxide complexes, $[Ni^{II}H_2\mathbf{1}^{R}(OBu^t)]^-$ were also prepared independently by treating Ni-350 with 1 equiv. of KOBu^t in DMA.



^{a}Conditions: (a) 1 equiv K(OBu^t), DMA, rt, Ar; (b) 1 equiv [K(N(TMS)$_2$], DMA, rt, Ar; (c) (Me$_4$N)OAc, DMA, rt, Ar.

Scheme 2 Reaction of Ni(II)–OH complexes with bases.

The molecular structure of $[Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]^-$ (Fig. 3A) determined by X-ray diffraction closely resembled that found for $[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]^-$ (Fig. 2). The X-ray data collected for $[Me_4N][Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]$ was of insufficient quality to obtain a complete description of the lattice, yet the connectivity of the anion was clearly resolved. The Ni(II) center in $[Ni^{II}H_2\mathbf{1}^{iPr}(OBu^t)]^-$ is coordinated by three nitrogen atoms and the oxygen atom from the OBu^t ligand, producing a nearly square planar geometry. The complex can accommodate the bulky *tert*-butyl group by placing it out of the equatorial plane, away from the H-bonding pocket that surrounds the alkoxy oxygen, O1. In addition, the *tert*-butyl group is arranged *anti* to the methyl group containing C13, presumably to avoid unfavorable steric interactions.

The deprotonation of $[Ni^{II}H_2\mathbf{1}^{R}(OH)]^-$ was further investigated with $[N(TMS)_2]^-$ because we thought this base would not displace the hydroxo ligand as seen with alkoxides. Our previous work on related complexes showed that external species containing nitrogen-donors are unable to displace oxo or hydroxo ligands, results attributed to oxygen atoms being significantly better H-bond acceptors. Thus treating the Ni(II)–OH complexes with $[N(TMS)_2]^-$ in DMA produced spectroscopic changes consistent with loss of the hydroxo ligand. However, the desired Ni(II)–oxo complexes were not isolated; instead complexes were produced in which the hydroxo ligand was converted into a siloxyl group.

Results from X-ray diffraction experiments confirmed the formation of the siloxide (Fig. 3B, Table 2). The primary coordination sphere in $[Ni^{II}H_2\mathbf{1}^{iPr}(OTMS)]^-$ includes a relatively short Ni–O1 bond of 1.876(1) Å with Ni–N distances that are nearly identical to those observed in $[Ni^{II}H_2\mathbf{1}^{iPr}(OH)]^-$. The Ni center and O1 are positioned out of the N1/N2/N3 plane by 0.079 and 0.434 Å respectively. Short N4···O1 and N5···O1 distances of 2.719(2) and 2.760(2) Å suggest the presence of intramolecular H-bonds in $[Ni^{II}H_2\mathbf{1}^{iPr}(OTMS)]^-$. The TMS group of the siloxide is pointed away from the square plane in an analogous manner to that *tert*-butyl group in Ni(II)–OBu^t complex.

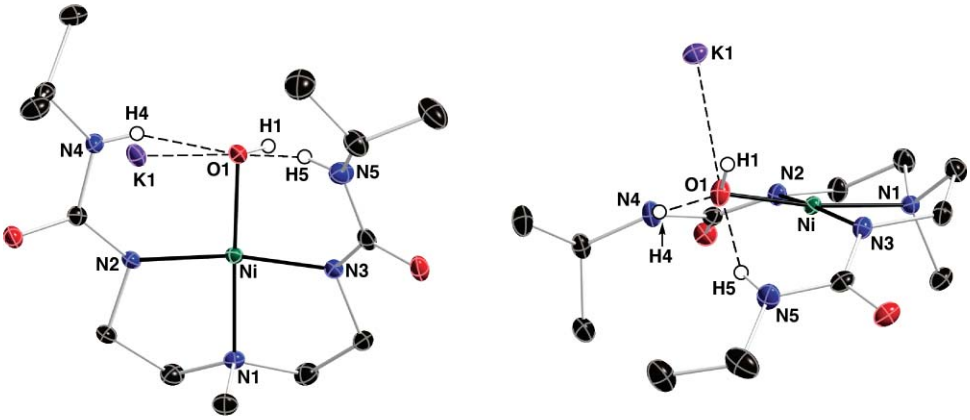


Fig. 2 Thermal ellipsoid plots illustrating two views of the molecular structure of $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}\mathrm{(OH)}]^-$. Thermal ellipsoids are drawn at the 50% level and for clarity only urea and hydroxo hydrogen atoms are shown.

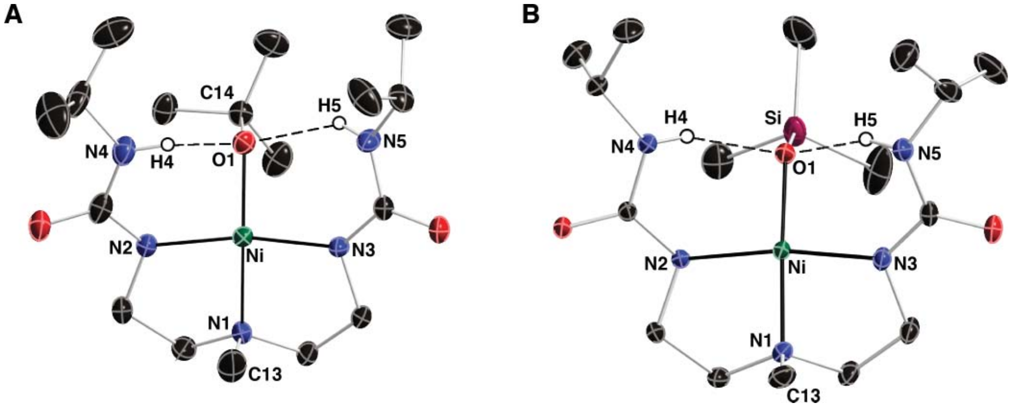


Fig. 3 Thermal ellipsoid plots illustrating the molecular structure of $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}\mathrm{(OBu^{\it t})}]^-$ (A) and $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{iPr}}\mathrm{(OTMS)}]^-$ (B). Thermal ellipsoids are drawn at the 50% level and for clarity only urea atoms are shown. Only one of the disorder fragments of the isopropyl group appended from N5 is shown for the structure in B.

Summary

We have described the preparation of monomeric Ni(II) complexes with terminal hydroxo ligands. The isolation of such complexes is rare and was achieved using $[\mathrm{H_2}\mathbf{1}^{\mathrm{R}}]^{2-}$, a tridentate ligand containing two ureayl groups. This chelating ligand provided three nitrogen donors to the Ni(II) center, leaving one coordination site available to bind an external ligand. Water was used as the source of hydroxide, which was produced *via* deprotonation by $[\mathrm{H}\mathbf{1}^{\mathrm{R}}]^{3-}$ as shown in Fig. 4. The $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}\mathrm{(OH)}]^-$ complexes have intramolecular H-bonding networks surrounding the Ni(II)–OH unit, involving the hydroxo oxygen atom and the ureayl groups of $[\mathrm{H_2}\mathbf{1}^{\mathrm{R}}]^{2-}$. The H-bonds help stabilize the complexes and undoubtedly prevent formation of the more common Ni(II)–μ-(OH)–Ni(II) species through placement of bulky R groups proximal to the hydroxide.

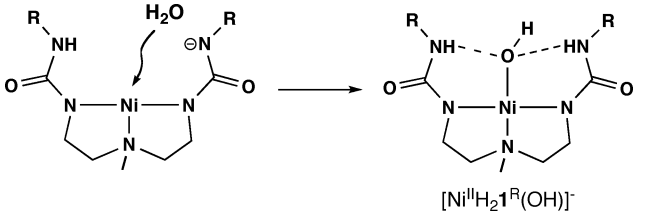


Fig. 4 Proposed interaction of water with the H-bonding ligand $[\mathrm{H}\mathbf{1}^{\mathrm{R}}]^{3-}$.

Attempts to deprotonate the hydoxo ligand were undertaken with a variety of bases but definitive evidence for the formation of a Ni(II)–oxo complex was not obtained. This type of oxometal complex has yet to be observed—orbital arguments involving the inability of the Ni(II) center to form π-bonds are often used to rationalize the lack of examples. However, we have found that H-bonds can, in some systems, replace π-bonds in stabilizing with M–oxo unit, leading to the isolation of late 3d oxometal complexes. Our failure to detect a Ni(II)–oxo complex is most likely because of their strong basicity and nucleophilicity. We did observed ligand substitution reactions with KOBu^t to prepare Ni(II)–OBu^t complexes and the formation of Ni(II)–siloxyl complexes when $[\mathrm{Ni^{II}H_2}\mathbf{1}^{\mathrm{R}}\mathrm{(OH)}]^-$ was treated with $\mathrm{K[N(TMS)_2]}$.

Acknowledgements

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References

1 (*a*) J. Du Bois, T. J. Mizoguchi and S. J. Lippard, *Coord. Chem. Rev.*, 2000, **200–202**, 443–485; (*b*) M. Merkx, D. A. Kopp, M. H. Sazinsky, J. L. Blazyk, J. Müller and S. J. Lippard, *Angew. Chem.*, 2001, **113**,

2860–2888, (*Angew. Chem., Int. Ed.*, 2001, **40**, 2782); (*c*) L. Que, Jr. and W. B. Tolman, *Angew. Chem.*, 2002, **114**, 1160–1185, (*Angew. Chem., Int. Ed.*, 2002, **41**, 1114); (*d*) S. Hikichi, M. Yoshizawa, Y. Sasakura, M. Akita and Y. Moro-oka, *J. Am. Chem. Soc.*, 1998, **120**, 10567–10568; (*e*) K. Shiren, S. Ogo, S. Fujinami, H. Hayashi, M. Suzuki, A. Uehara, Y. Wantanabe and Y. Moro-oko, *J. Am. Chem. Soc.*, 2000, **122**, 254–262; (*f*) S. Itoh, H. Bandoh, M. Nakagawa, S. Nagatomo, T. Kitagawa, K. D. Karlin and S. Fukusumi, *J. Am. Chem. Soc.*, 2001, **123**, 11168–11178; (*g*) B. S. Mandimutsira, J. L. Yamarik, T. C. Brunold, W. Gu, S. P. Cramer and C. G. Riordan, *J. Am. Chem. Soc.*, 2001, **123**, 9194–9195; (*h*) K. H. Theopold, O. M. Reinaud, D. Doren, R. Konecny, in *3rd World Congress on Oxidation Catalysis*, (Eds.: R. K. Grasselli, S. T. Oyama, A. M. Gaffney, J. E. Lyons), Elsevier Science, New York, 1997, pp. 1081–1088; (*i*) S. Hikichi, M. Morooka and M. Akita, *Chem.–Eur. J.*, 2001, **7**, 5012–5028; (*j*) D. E. Benson, A. E. Haddy and H. W. Hellinga, *Biochemistry*, 2002, **41**, 3262–3269.

2 (*a*) N. E. Dixon, P. W. Riddles, C. Gazzola, R. L. Blakeley and B. Zerner, *Can. J. Biochem.*, 1980, **58**, 1335–1344; (*b*) E. Jabri, M. B. Carr, R. P. Hausinger and P. A. Karplus, *Science*, 1995, **268**, 998–1004; (*c*) W. N. Lipscomb and N. Sträter, *Chem. Rev.*, 1996, **96**, 2375–2433and references therein; (*d*) D. W. Christianson and J. D. Cox, *Annu. Rev. Biochem.*, 1999, **68**, 33–57; (*e*) D. W. Christianson and C. A. Fierke, *Acc. Chem. Res.*, 1996, **29**, 331–339.

3 (*a*) R. Gupta and A. S. Borovik, *J. Am. Chem. Soc.*, 2003, **125**, 13234–13242; (*b*) C. E. MacBeth, B. S. Hammes, V. G. Young, Jr. and A. S. Borovik, *Inorg. Chem.*, 2001, **40**, 4733–4741; (*c*) C. E. MacBeth, R. Gupta, K. R. Mitchell-Koch, V. G. Young, Jr., G. H. Lushington, W. H. Ward, M. P. Hendrich and A. S. Borovik, *J. Am. Chem. Soc.*, 2004, **126**, 2556–2567; (*d*) R. Gupta, C. E. MacBeth, V. G. Young, Jr and A. S. Borovik, *J. Am. Chem. Soc.*, 2002, **124**, 1136–1137; (*e*) Z. Shirin, V. G. Young, Jr. and A. S. Borovik, *J. Am. Chem. Soc.*, 2000, **122**, 1836–1837; (*f*) Z. Shirin, V. G. Young, Jr. and A. S. Borovik, *Chem. Commun.*, 1997, 1967–1968; (*g*) J. Mukherjee, R. L. Lucas, M. K. Zart, D. R. Powell, V. W. Day and A. S. Borovik, *Inorg. Chem.*, 2008, **47**, 5780–5786.

4 (*a*) Fe–OH complexes:S. Hikichi, T. Ogihara, K. Fujisawa, N. Kitajima, M. Akita and Y. Moro-oko, *Inorg. Chem.*, 1997, **36**, 4539–4547; (*b*) S. Ogo, S. Wada, Y. Watanabe, M. Iwase, A. Wada, M. Harata, K. Jitsukawa, H. Masuda and H. Einaga, *Angew. Chem., Int. Ed.*, 1998, **37**, 2102–2104; (*c*) C.-Y. Yeh, C. J. Chang and D. G. Nocera, *J. Am. Chem. Soc.*, 2001, **123**, 1513–1514; (*d*) A. Orlandini and L. Sacconi, *Inorg. Chem.*, 1976, **15**, 78–85; (*e*) S. E. Kucharski, B. W. Skelton and A. H. White, *Aust. J. Chem.*, 1978, **31**, 47–51; (*f*) R. Prabaharan, S. Parsons and J. C. Mareque-Rivas, *Dalton Trans.*, 2004, 1648–1655; (*g*) B. M. Bridgewater and G. Parkin, *Inorg. Chem. Commun.*, 2001, **4(3)**, 126–129; (*h*) M. M. Ibrahim, C. P. Olmo, T. Tekeste, J. Seebacher, G. He, J. A. Maldonado Calvo, K. Bohmerle, G. Steinfeld, H. Brombacher and H. Vahrenkamp, *Inorg. Chem.*, 2006, **45**, 7493–7502; (*i*) C. R. Goldsmith, A. P. Cole and T. D. P. Stack, *J. Am. Chem. Soc.*, 2005, **127**, 9904–9912; (*j*) G. Yin, J. M. McCormick, M. Buchalova, A. M. Danby, K. Rodgers, V. W. Day, K. Smith, C. M. Perkins, D. Kitko, J. D. Carter, W. M. Scheper and D. H. Busch, *Inorg. Chem.*, 2006, **45**, 8052–8061; (*k*) C. R. Goldsmith and T. D. P. Stack, *Inorg. Chem.*, 2006, **45**, 6048–6055.

5 M. K. Zart, T. N. Sorrell, D. Powell and A. S. Borovik, *Dalton Trans.*, 2003, 1986–1992.

6 M. K. Zart, D. Powell and A. S. Borovik, *Inorg. Chim. Acta*, 2007, **360**, 2397–2402.

7 M. T. Kieber-Emmons, R. Schenker, G. P. A. Yap, T. C. Brunold and C. G. Riordan, *Agnew. Chem., Int. Ed.*, 2004, **43**, 6716–6718.

8 (*a*) J. Campora, P. Palma, D. Del Rio and E. Alvarez, *Organometallics*, 2004, **23**, 1652–1655; (*b*) J. Campora, P. Palma, D. Del Rio and E. Alvarez, *Organometallics*, 2005, **24**, 2827–2830.

9 D. Adhikari, S. Mossin, F. Basuli, B. R. Dible, M. Chipara, H. Fan, J. C. Huffman, K. Meyer and D. J. Mindiola, *Inorg. Chem.*, 2008, **47**, 10479–10490.

10 Data collection: *SMART Software Reference Manual*Bruker-AXS, Madison, WI, 1994.

11 Data reduction: *SAINT Software Reference Manual*Bruker-AXS, Madison, WI, 1995.

12 G. M. Sheldrick, *SADABS*, Version 2.10, Bruker Analytical X-Ray Systems, Inc.Madison, WI 2002.

13 G. M. Sheldrick, *SHELXTL* Version 6.12, Bruker Analytical X-Ray Systems, Inc.Madison, WI 2001.

14 *International Tables for X-Ray Crystallography* 1992, Vol. C., Dordrecht, Kluwer Academic Publishers.

15 H. D. Flack, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 1983, **39**, 876–881.

16 In $K[Ni^{II}H_2\mathbf{1}^{tBu}(OH)]$ a K1 · · · O1 distance of greater than 3.9 Å is observed, which is beyond a bonding distance expected from van der Waals radii. Note that the Ni–O distance is 1.864(2) Å.