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Decorating the Second Coordination Sphere in Pyrazolate-Based Dinickel(II) Complexes with H-Bond Donors

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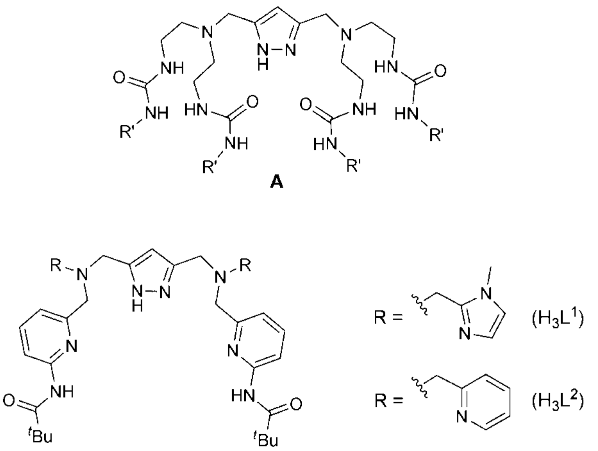
Compartmental pyrazolate-based ligands with bis(2-pyridinylmethyl)aminomethyl or (2-pyridinylmethyl)[2-(1-methylimidazolyl)methyl]aminomethyl chelate arms have been further elaborated by attaching pivaloylamido groups to the outer pyridine rings, giving the new ligands H_3L^1 and H_3L^2. The peripheral pivaloylamido groups may serve as potential H-bond donor or acceptor sites towards substrates in the bimetallic cavity. Protonation constants of the new ligand H_3L^1 as well as its nickel(II) speciation in solution have been studied by pH potentiometry, revealing $pK_a = 8.9$ for the metal-bound water. Based on the X-ray crystallographic structure of $[Ni_2(H_2L^1)(H_3O_2)(MeCN)_2](ClO_4)_2$ (**3**) this pK_a is rationalized in terms of two balancing effects, namely involvement of the pivaloylamido O atom in metal coordination and H-bonding between the pivaloylamido NH group and the resulting nickel-bound hydroxide. Complex **3** features a pyrazolate-bridged dinickel(II) core and a bridging HO···H···OH unit within the bimetallic cavity, which is involved in multiple H-bonding interactions.

Introduction

Compartmental dinucleating ligands based on a central pyrazolate bridge are valuable scaffolds for creating bimetallic complexes that exhibit metal–metal cooperativity with respect to their physicochemical properties and their chemical reactivities.[1] These types of ligands have been successfully used to emulate structural and functional aspects of dinuclear metalloprotein active centers such as the dinickel(II) site of urease,[2] dizinc metallohydrolases,[3] and type 3 dicopper sites.[4] Characteristics of the bimetallic core, including the metal–metal distance and the individual metal ion coordination spheres, can be tuned by variation of the chelate arms that are attached to the 3- and 5-positions of the central pyrazole.[5,6] Further elaboration towards reproducing metalloprotein reactivity would require placing functional groups such as H-bond donors or acceptors close to the bimetallic pocket, as H-bonding interactions in the second coordination sphere are known to contribute significantly to the binding or transformation of substrate molecules in metalloproteins[7] as well as in bioinspired systems.[8,9] Although dangling ligand side arms of multidentate pyrazolate-derived ligands can in principle engage in H-bonding,[4a,10] Borovik and coworkers have reported a dinucleating ligand **A** providing four terminal urea groups that specifically serve as intramolecular H-bond donors to exogeneous ligands such as chloride or acetate in the cavity of some dicobalt(II) complexes of **A** (Scheme 1).[11] Peripheral H-bond donors have previously proven beneficial for enhancing the hydrolytic efficiency of phenolate-bridged dinuclear zinc complexes, illustrating the importance of the secondary coordination sphere in sophisticated metallohydrolase models.[12] We introduce two new ligands H_3L^1 and H_3L^2 with pyridyl or mixed imidazolyl/pyridyl donors in the chelate arms, which bear two appended pivaloylamido groups. It should be noted that the pivaloylamido group is flexidentate, since it may potentially serve as a H-bond donor in its common protonated form and also as a H-bond acceptor or even as an O ligand after deprotonation.[13]



Scheme 1.

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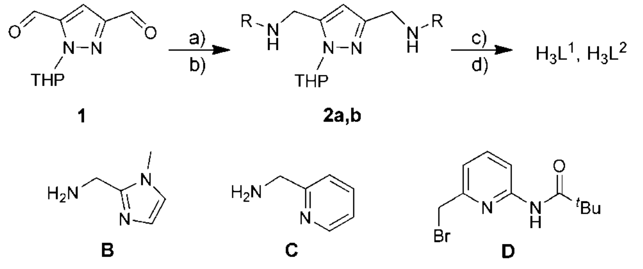
In this report we include a speciation study of H_3L^1 with nickel(II) in solution and the first crystallographic structure of a dinickel(II) complex of H_3L^1.

Results and Discussion

Our synthesis of H_3L^1 and H_3L^2 starts from 1-(tetrahydropyran-2-yl)-1*H*-pyrazole-3,5-dicarbaldehyde (**1**), which is accessible from 3,5-dimethylpyrazole in five steps.[14] Reductive amination of **1** with **B** or **C** produces secondary amines **2a** and **2b**, respectively (Scheme 2). The side arms with pivalamido groups are then introduced by reaction with 2.05 equiv. of **D** (prepared in two steps from 2-amino-6-methylpyridine),[15] and finally the acid-labile THP protecting group is removed to give the new dinucleating ligands in reasonable yield. Both H_3L^1 and H_3L^2 provide two tetradentate {N_4} binding compartments decorated with one peripheral pivaloylamido group per compartment.



Scheme 2. H_3L^1 and H_3L^2. Reagents and conditions: (a) **B** or **C**, MeOH, 1 h, reflux; (b) $NaBH_4$, 0 °C, then room temp., 12 h, 44/54%; (c) 2.05 equiv. **D**, Cs_2CO_3, CH_3CN, 1 d, reflux, 72/80%; (d) EtOH/HCl, 2 h, room temp., then NH_3/DCM, 2 h, room temp., 99/98%.

Potentiometric titrations were carried out in order to determine the pK_a values of the new ligands and to probe their nickel(II) coordination chemistry in solution. For the Ni^{2+}/H_3L^2 system precipitation occurred in a wide pH range and prevented potentiometric studies.

Ligand Protonation Constants

Titrations were performed starting at acidic pH using a potassium hydroxide titrant. The deprotonation steps can be derived from the titration curves (Figure S1 and Table 1). Overall, ten N atoms are available in H_3L^1 that may potentially participate in protonation/deprotonation events (four protons per side arm and two protons on the pyrazole ring). Six protonation constants have been determined in the pH range 2–11. The three protons of the neutral ligand H_3L^1, namely the central pyrazole NH and the two peripheral amide NH protons are nondissociable in the studied pH range. Furthermore, protonation of the pyrazole to the corresponding $[H_{10}L^1]^{7+}$ occurs below pH 2, hence this event was not detected. The six observed events are thus assigned to protonation/deprotonation of the six N atoms in the ligand's side arms, i.e. the imidazole N, the pyridine N, and the tertiary N atoms in the hinge positions. Only in case of $[H_8L^1]^{5+}/[H_7L^1]^{4+}$ is the difference between sequential pK_a values much higher (2.29) than expected for statistical reasons, which indicates some interactions between the individual protonation sites in this particular event. This is in accordance with a sequence where $[H_8L^1]^{5+}$ and $[H_9L^1]^{6+}$ correspond to the protonation of the third N atom in each side arm. For the remaining steps the differences are smaller (0.27–0.88), suggesting that the protonation sites are relatively far apart and independent, likely the outer imidazole N and pyridine N atoms. Protonation of the latter may include H-bonding to the proximate pivaloylamido O atom.

Table 1. Overall protonation constants (logβ) and sequential dissociation constants (pK_a) of the ligand H_3L^1 at 25 °C; I = 0.1 M KCl.[a]

	$[H_9L^1]^{6+}$	$[H_8L^1]^{5+}$	$[H_7L^1]^{4+}$	$[H_6L^1]^{3+}$	$[H_5L^1]^{2+}$	$[H_4L^1]^{+}$
logβ	31.78(2)	29.21(2)	25.98(1)	20.46(1)	14.06(1)	7.39(1)
pK_a	2.57	3.23	5.52	6.40	6.67	7.39

[a] S = 1.23. Number of points 326. Standard deviations are given in parenthesis.

Species Distribution of Nickel(II) Complexes

Titrations of H_3L^1 in the presence of various equivalents of Ni^{2+} were analyzed in batch calculations in which all titration curves were fitted at the same time with one model (Figure 1 and S1; Table 2). Evaluation of the titration curves shows that H_3L^1 has quite high Ni^{2+}-chelating capabilities. Coordination begins below pH 2 with the formation of dinuclear species; no significant amount of mononuclear species was detected. Starting from a $[Ni_2H_4L^1]^{5+}$ complex formed under acidic conditions, sequential deprotonations occur and lead to the presence of several dimeric species $[Ni_2H_3L^1]^{4+}$, $[Ni_2H_2L^1]^{3+}$, $[Ni_2HL^1]^{2+}$, and $[Ni_2H_{-1}L^1]$ over the entire pH range. Calculated stability constants are given in Table 2.

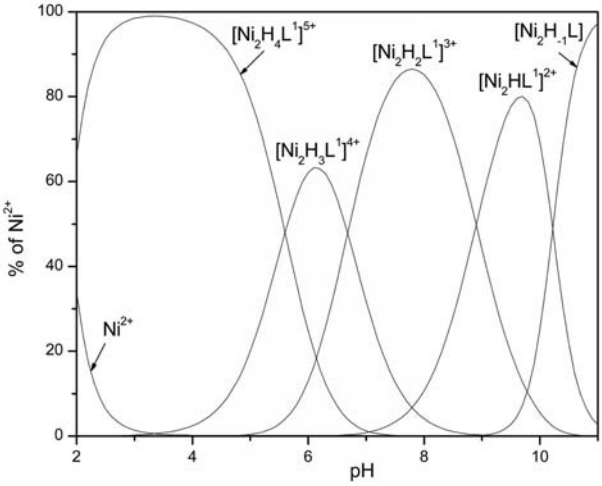


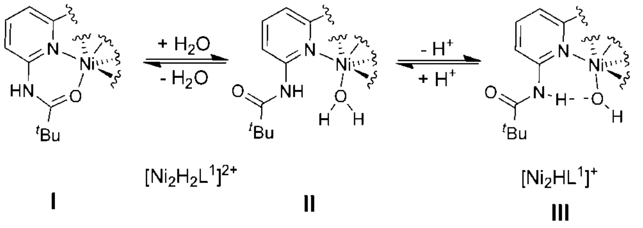
Figure 1. Species distribution profile for Ni^{2+} complexes of H_3L^1 at 25 °C and I = 0.1 M KCl, M/L molar ratio 2:1, $c_L = 4 \times 10^{-4}$ M.

Table 2. Overall stability constants (log*β*) and some dissociation constants (pK_a) for the complexes formed with Ni^{2+} at 25 °C; I = 0.1 м KCl.[a]

	$[Ni_2H_4L^1]^{5+}$	$[Ni_2H_3L^1]^{4+}$	$[Ni_2H_2L^1]^{3+}$	$[Ni_2HL^1]^{2+}$	$[Ni_2H_{-1}L^1]$
log β	27.32(6)	21.72(7)	15.04(7)	6.14(9)	–14.30(8)
pK_a	5.60	6.68	8.90		

[a] S = 0.77. Number of points 385. Standard deviations are given in parenthesis.

The formation of only dinuclear complexes suggests that the pyrazole adopts a bridging position already at acidic pH, with its proton captured by a dangling side arm,[10] possibly stabilized by a H-bonding interaction with a peripheral pivaloylamido group. These protons in the side arms dissociate at higher pH to sequentially form $[Ni_2H_3L^1]^{4+}$ and $[Ni_2H_2L^1]^{3+}$. Such a scenario is in accordance with the results of a UV/Vis titration, where no major absorption changes are observed up to around pH 8 (see Figure S3). In the pyrazolate-bridged species $[Ni_2H_4L^1]^{5+}$, $[Ni_2H_3L^1]^{4+}$, and $[Ni_2H_2L^1]^{3+}$ either intramolecular coordination of the pivaloylamido O atom or binding of water may occur (**I** and **II**, Scheme 3). Bidentate *N*,*O*-coordination of *N*-(2-pyridyl)-amido ligands akin to the situation in **I** has been observed previously in nickel(II) chemistry.[16] Further deprotonation (pK_a = 8.90) then leads to a metal bound hydroxide in $[Ni_2HL^1]^{2+}$, which is better described as $[Ni_2H_2L^1(OH)]^{2+}$ or $[Ni_2H_2L^1(O_2H_3)]^{2+}$ (see below). The pK_a value for $[Ni_2H_2L^1]^{3+}$ (8.90) likely reflects the balancing of two effects of the appended pivaloylamido groups: stabilization of $[Ni_2H_2L^1]^{3+}$ by intramolecular coordination (**I**, Scheme 3) and stabilization of the metal-bound hydroxide by H-bonding (**III**, Scheme 3).



Scheme 3.

Structure of $[Ni_2(H_2L^1)(\mu\text{-}H_3O_2)(MeCN)_2](ClO_4)_2$ (3)

Single crystals of the nickel(II) complex $[Ni_2(H_2L^1)(H_3O_2)(MeCN)_2](ClO_4)_2$ (**3**) were obtained by vapor diffusion of diethyl ether into a MeCN solution of the complex. Its molecular structure is shown in Figure 2, together with selected bond distances and angles. Complex **3** features the expected dinickel(II) core where the two metal ions are spanned by the pyrazolate and are nested within the $\{N_4\}$ compartments of the dinucleating ligand scaffold. As has been seen in related pyrazolate-based complexes that lack the peripheral pivaloylamido groups, the short length of the chelate arms in H_3L^1 enforces metal···metal distances >4 Å (4.33 Å in **3**), which is too large to accommodate a small coligand such as hydroxide in the resulting bimetallic cavity.[5d,5e,17] Instead, an additional water molecule is incorporated to generate a H_3O_2 unit with a short (and likely strong) intramolecular O···H···O hydrogen bond. The donor–acceptor distance *d*(O···O) is 2.44 Å, and the central H4A atom was located and refined freely in the crystallographic analysis of **3**. Such a bridging motif has previously been observed for some dinickel(II) complexes of related bis(tetradentate) pyrazolate-based ligands, with O···O distances ranging from 2.41 to 2.43 Å.[18]

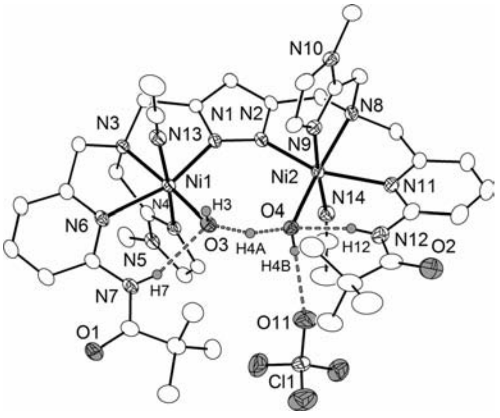


Figure 2. ORTEP plot (30% probability thermal ellipsoids) of the molecular structure of **3** emphasizing the hydrogen bonding (dashed lines). For the sake of clarity most hydrogen atoms (not involved in hydrogen bonding) and one of the perchlorate ions are omitted. Selected bond lengths [Å] and angles [°]: Ni1–O3 2.0221(19), Ni1–N1 2.0352(19), Ni1–N4 2.052(2), Ni1–N3 2.140(2), Ni1–N13 2.142(2), Ni1–N6 2.188(2), Ni2–O4 2.0224(18), Ni2–N2 2.038(2), Ni2–N9 2.039(2), Ni2–N14 2.121(2), Ni2–N8 2.146(2), Ni2–N11 2.198(2), O4···O3 2.444(3), Ni1···Ni2 4.3252(4), O4···O11 2.955(3), N7···O3 2.865(3), N12···O4 2.881(3); O3–Ni1–N1 103.42(8), O3–Ni1–N4 98.16(8), N1–Ni1–N4 89.38(8), O3–Ni1–N3 176.22(7), N1–Ni1–N3 80.18(8), N4–Ni1–N3 82.92(8), O3–Ni1–N13 87.79(9), N1–Ni1–N13 89.97(8), N4–Ni1–N13 174.00(9), N3–Ni1–N13 91.09(9), O3–Ni1–N6 97.34(8), N1–Ni1–N6 159.17(8), N4–Ni1–N6 89.36(8), N3–Ni1–N6 79.03(8), N13–Ni1–N6 89.12(8), O4–Ni2–N2 103.96(7), O4–Ni2–N9 95.53(8), N2–Ni2–N9 89.48(8), O4–Ni2–N14 89.00(8), N2–Ni2–N14 91.16(8), N9–Ni2–N14 175.13(9), O4–Ni2–N8 175.32(7), N2–Ni2–N8 80.51(8), N9–Ni2–N8 83.02(8), N14–Ni2–N8 92.32(8), O4–Ni2–N11 97.52(8), N2–Ni2–N11 158.47(8), N9–Ni2–N11 89.87(8), N14–Ni2–N11 87.76(9), N8–Ni2–N11 78.05(8), O4–H4A···O3 160(3), O4–H4B···O11 169(4), N7–H7···O3 158(3), N12–H12···O4 155(4).

A unique feature in **3** is the additional stabilization of the H_3O_2 unit within the bimetallic cavity by two further intramolecular H-bonds involving the N–H of the appended pivaloylamido groups of $[H_2L^1]^-$, albeit these are somewhat weaker than the O···H···O bridge with *d*(N···O) = 2.86/2.88 Å. Participation of the amide groups in H-bonding is reflected by changes in the C=O vibration with respect to the free ligand (see Experimental Section). This situation forces the two pyridyl rings that carry the pivaloylamido groups into equatorial positions *trans* to the pyrazolate, while the imidazole groups of the ligand scaffold and MeCN solvent molecules complete the nickel(II) coordination sphere in axial positions. The H_3O_2 unit finally serves as a weak H-bond donor towards a perchlorate counterion

[d(O4···O11) = 2.95 Å]. Overall the two nickel-bound hydroxides in **3**, i.e. the proximate Ni–OH subunits, are involved in an extensive network of H-bonds.

Regarding its overall protonation status, **3** corresponds to the species $[\mathrm{Ni_2HL^1}]^{2+}$ in solution, which is the dominant species in the range pH 9–10. This species should be described as $[\mathrm{Ni_2(H_2L^1)(H_3O_2)}]^{2+}$. Intramolecular H-bonding of the pivaloylamido groups as observed in the solid-state structure of **3** presumably facilitates deprotonation of nickel-bound water, i.e., generation of the nickel-bound hydroxide (or $\mathrm{H_3O_2}$ bridge), as discussed above. ESI mass spectrometry of **3** in MeCN solution shows signals for $[\mathrm{Ni_2(H_2L^1)(ClO_4)_3H}]^+$ at m/z = 1107, $[\mathrm{Ni_2(H_2L^1)(ClO_4)_2}]^+$ at m/z = 1007, and $[\mathrm{Ni_2(HL^1)(ClO_4)}]^+$ at m/z = 907, besides major signals for $[\mathrm{Ni_2(HL)}]_2^{2+}$ at m/z = 404 and some fragments of $[\mathrm{Ni_2(H_2L^1)}]^{x+}$ (Figure S4). This indicates that the $\mathrm{H_3O_2}$ bridge may be lost under ESI-MS conditions.

Conclusions

We have developed new pyrazolate-based dinucleating ligands that provide two $\{\mathrm{N_4}\}$ binding sites, each decorated with a pivaloylamido group that may engage in H-bonding interactions if substrates are hosted between the two metal ions. Potentiometric titrations confirm the high propensity of these ligand scaffolds to form dinuclear complexes over a wide pH range, and the molecular structure of $[\mathrm{Ni_2(H_2L^1)(H_3O_2)(MeCN)_2}](\mathrm{ClO_4})_2$ (**3**) reveals that the appended pivaloylamido groups serve as H-bond donors to support an HO···H···OH moiety within the bimetallic pocket. These systems might be useful for studying effects of the secondary coordination sphere in biomimetic and bioinspired substrate transformations.

Experimental Section

General: All solvents were purified by distillation before use. If necessary, solvents were dried according to established procedures.

TLC plates: MACHERY NAGEL POLYGRAM® ALOX N/ $\mathrm{UV_{254}}$, POLYGRAM® SIL G/ $\mathrm{UV_{254}}$. NMR spectra: BRUKER Avance 200, BRUKER Avance 300, BRUKER Avance 500. IR spectra: DIGILAB Excalibur Series FTS 3000, recorded as KBr pellets. MS spectra: FINNIGAN MAT 8200 (EI MS), APPLIED BIOSYSTEMS API 2000 and FINNIGAN MAT 95 (ESI MS), FINNIGAN MAT 95 (HRMS). UV/Vis spectra: VARIAN Cary 5000, recorded as KBr pellets, ANALYTIK JENA Specord S100 as solutions. Microanalyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry at the University of Göttingen.

CAUTION: Although no problems were encountered in this work, transition metal perchlorate complexes are potentially explosive and should be handled with appropriate precautions.[19]

3,5-Bis[{2-(1-methylimidazolyl)methyl}aminomethyl]-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (2a): A solution of dialdehyde **1** (1.50 g, 7.20 mmol) and amine **B** (1.60 g, 14.4 mmol) in dry methanol (200 mL) was charged with molecular sieves under an atmosphere of dry nitrogen and heated to reflux for 1 h. After cooling to 0 °C sodium borohydride (5.5 g, 14.4 mmol) was added in small portions. The reaction mixture was warmed to room temperature overnight. After filtration the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane (200 mL) and washed with water (3 × 200 mL). After drying over $\mathrm{Na_2SO_4}$ all volatile material was removed. Purification was achieved by filtration through aluminium oxide; impurities were first eluted with ethyl acetate, then the product was eluted with methanol. The solvent was removed and the residue was dissolved in dichloromethane. After filtration the volatiles were removed under reduced pressure to afford **2a** as a yellow resin (1.27 g, 3.19 mmol, 44%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 1.45–1.65 (m, 3 H, C$H_2^{\mathrm{THP4,5}}$), 1.83 (dd, $^3J_{\mathrm{ae}}$ = 2.4, ^2J = 13.3 Hz, 1 H, CH_2^{THP4}), 1.95–2.00 (m, 1 H, CH_2^{THP3}), 2.26–2.39 (m, 1 H, CH_2^{THP6}), 2.79 ($\mathrm{s_{br}}$, 2 H, NH), 3.47–3.54 (m, 1 H, CH_2^{THP6}), 3.55 (s, 3 H, CH_3), 3.58 (s, 3 H, CH_3), 3.75–3.80 (m, 8 H, CH_2), 3.89–3.96 (m, 1 H, CH_2^{THP6}), 5.29 (dd, $^3J_{\mathrm{ae}}$ = 2.4, $^3J_{\mathrm{aa}}$ = 10.5 Hz, 1 H, CH_2^{THP2}), 6.14 (s, 1 H, CH^{Pz}), 6.75 (dd, ^3J = 9.7, $^2J_{\mathrm{C\text{-}H}}$ = 1.0 Hz, 1 H, CH^{Im}), 6.85 (dd, ^3J = 7.1, $^2J_{\mathrm{C\text{-}H}}$ = 1.2 Hz, 1 H, CH^{Im}) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ = 22.7 ($C\mathrm{H_2}^{\mathrm{THP4}}$), 24.7 ($C\mathrm{H_2}^{\mathrm{THP5}}$), 29.5 ($C\mathrm{H_2}^{\mathrm{THP3}}$), 32.5 ($C\mathrm{H_3}$), 32.7 ($C\mathrm{H_3}$), 43.1 ($C\mathrm{H_2}$), 44.61 ($C\mathrm{H_2}$), 44.62 ($C\mathrm{H_2}$), 46.5 ($C\mathrm{H_2}$), 67.7 ($C\mathrm{H_2}^{\mathrm{THP6}}$), 84.4 ($C\mathrm{H}^{\mathrm{THP2}}$), 105.7 ($C\mathrm{H}^{\mathrm{Pz}}$), 121.1 ($C\mathrm{H}^{\mathrm{Im}}$), 121.2 ($C\mathrm{H}^{\mathrm{Im}}$), 126.8 ($C\mathrm{H}^{\mathrm{Im}}$), 126.9 ($C\mathrm{H}^{\mathrm{Im}}$), 141.7 ($\mathrm{C_q}^{\mathrm{Pz5}}$), 145.8 ($\mathrm{C_q}^{\mathrm{Pz3}}$), 146.1 ($\mathrm{C_q}^{\mathrm{Im}}$), 150.1 ($\mathrm{C_q}^{\mathrm{Im}}$) ppm. IR (KBr): $\tilde{\nu}$ = 3314 (w), 2936 (vs), 2852 (s), 1462 (s), 1083 (s), 735 (m). MS (ESI$^+$): m/z (%) = 421.3 (100) [M + Na]$^+$, 399.3 (13) [M + H]$^+$.

3,5-Bis[2-pyridinylmethyl]aminomethyl-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (2b): The same conditions were used as described for **2a**. The product was isolated as a yellow resin (54%). ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 1.40–1.65 (m, 3 H, C$H_2^{\mathrm{THP4,5}}$), 1.82–2.23 (m, 3 H, C$H_2^{\mathrm{THP3,4}}$), 2.37 (m, 1 H, CH_2^{THP6}), 2.82 ($\mathrm{s_{br}}$, 2 H, NH), 3.52 (m, 1 H, CH_2^{THP6}), 3.80 (m, 8 H, CH_2), 3.93 (m, 1 H, CH_2^{THP6}), 5.30 (m, 1 H, CH_2^{THP2}), 6.23 (s, 1 H, CH^{Pz}), 7.23 (m, 2 H, CH^{Py}), 7.27 (m, 2 H, CH^{Py}), 7.63 (m, 2 H, CH^{Py}), 8.51 (m, 2 H, CH^{Py}) ppm. ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): δ = 22.7 ($C\mathrm{H_2}^{\mathrm{THP4}}$), 24.9 ($C\mathrm{H_2}^{\mathrm{THP5}}$), 29.6 ($C\mathrm{H_2}^{\mathrm{THP3}}$), 43.5 ($C\mathrm{H_2}$), 46.8 ($C\mathrm{H_2}$), 54.2 ($C\mathrm{H_2}$), 54.7 ($C\mathrm{H_2}$), 67.8 ($C\mathrm{H_2}^{\mathrm{THP6}}$), 84.6 ($C\mathrm{H}^{\mathrm{THP2}}$), 105.8 ($C\mathrm{H}^{\mathrm{Pz}}$), 121.8 ($C\mathrm{H}^{\mathrm{Py}}$), 122.3 ($C\mathrm{H}^{\mathrm{Py}}$), 136.3 ($C\mathrm{H}^{\mathrm{Py}}$), 142.0 ($\mathrm{C_q}^{\mathrm{Pz5}}$), 149.2 ($C\mathrm{H}^{\mathrm{Py}}$), 150.4 ($\mathrm{C_q}^{\mathrm{Pz3}}$), 159.4 ($\mathrm{C_q}^{\mathrm{Py}}$) ppm. IR (KBr): $\tilde{\nu}$ = 2936 (s), 2851 (m), 1686 (s), 1591 (s), 1470 (s), 1042 (s), 760 (m) cm^{-1}. MS (ESI$^+$): m/z (%) = 393.3 (100) [M + H]$^+$, 309.3 (75) [M – THP]$^+$.

3,5-Bis[{2-(1-methylimidazolyl)methyl}{2-(6-pivaloylamidopyridinyl)-methyl}aminomethyl]-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (3a): To a solution of **2a** (531 mg, 1.33 mmol) in acetonitrile (125 mL) three equivalents of dry $\mathrm{Cs_2CO_3}$ (1.30 g, 4.00 mmol) were added and the mixture heated to reflux. A solution of **D** (746 mg, 2.73 mmol) in acetonitrile (10 mL) was added dropwise. The reaction mixture was heated to reflux for further 24 h. After cooling to room temp. all salts were filtered off and the solvent was removed. The residue was dissolved in dichloromethane (50 mL) and washed with water (3 × 50 mL). The combined organic phase was dried with $\mathrm{Na_2SO_4}$. After removing the solvent the raw material was purified by column chromatography ($\mathrm{ALOX_{neutral}}$, ethyl acetate/methanol, 10:1). The product **3a** was isolated as a yellow solid (795 mg, 0.96 mmol, 72%). R_{f} (ethyl acetate:methanol, 10:1) = 0.78. ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): δ = 1.28 (s, 18 H, CH_3), 1.37–1.48 (m, 3 H, C$H_2^{\mathrm{THP4,5}}$), 1.53–1.71 (m, 2 H, C$H_2^{\mathrm{THP3,4}}$), 1.94–1.99 (m, 1 H, CH_2^{THP3}), 2.27–2.39 (m, 1 H, CH_2^{THP6}), 3.34 (s, 3 H, CH_3^{Im}), 3.49 (s, 3 H, CH_3^{Im}), 3.55–3.78 (m, 12 H, CH_2), 3.82–3.88 (m, 1 H, CH_2^{THP6}), 4.98 (dd, $^3J_{\mathrm{ae}}$ = 2.4, $^3J_{\mathrm{aa}}$ = 10.5 Hz, 1 H, CH_2^{THP2}), 6.23 (s, 1 H, CH^{Pz}), 6.71 (dd, $^2J_{\mathrm{C\text{-}H}}$ = 1.2 Hz, 1 H, CH^{Im}), 6.77 (dd, $^2J_{\mathrm{C\text{-}H}}$ = 1.2 Hz, 1 H, CH^{Im}), 6.82 (dd, $^2J_{\mathrm{C\text{-}H}}$ = 1.2 Hz, 1 H, CH^{Im}), 6.90 (dd, $^2J_{\mathrm{C\text{-}H}}$ = 1.2 Hz, 1 H, CH^{Im}), 6.94 (d, J_{o} = 7.5 Hz, 1 H, CH^{Py}), 7.05 (d, J_o = 7.5 Hz, 1 H, CH^{Py}), 7.56 (t, J_o = 8.3 Hz, 1 H, CH^{Py}), 7.60 (t, J_o = 7.7 Hz, 1 H, CH^{Py}), 8.03 (d, J_o = 8.3 Hz, 1 H, CH^{Py}), 8.10 (d, J_o = 8.3 Hz, 1 H, CH^{Py}), 8.14 (s, 1 H, NH), 8.19 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.8 (CH_2^{THP4}), 24.7 (CH_2^{THP5}), 27.4 (CH_3), 29.7 (CH_2^{THP3}), 39.7 ($C_q^{t\mathrm{Bu}}$), 39.8 ($C_q^{t\mathrm{Bu}}$), 48.2 (CH_2), 50.0 (CH_2), 50.1 (CH_2), 51.5 (CH_2), 59.1 (CH_2), 59.5 (CH_2), 67.7 (CH_2^{THP6}), 83.7 (CH^{THP2}), 108.4 (CH^{Pz}), 111.8 (CH^{Py}), 112.3 (CH^{Py}), 118.9 (CH^{Py}), 119.4 (CH^{Py}), 121.46 (CH^{Im}), 121.54 (CH^{Im}), 126.9 (CH^{Im}), 127.3 (CH^{Im}), 138.5 (CH^{Py}), 138.7 (CH^{Py}), 140.1 (C_q^{Pz5}), 144.7 (C_q^{Py}), 145.1 (C_q^{Py}), 148.8 (C_q^{Pz3}), 150.9 (C_q^{Im}), 151.1 (C_q^{Im}), 156.9 (C_q^{Py}), 157.5 (C_q^{Py}), 177.2 (C = O) ppm. MS (ESI$^+$): m/z (%) = 801.5 (70) [M + Na]$^+$, 779.4 (100) [M + H]$^+$, 695.5 (63) [M – THP + 2 H]$^+$. MS (ESI-): m/z (%) = 777.5 (100) [M – H]$^-$. HRMS (ESI +): m/z (%) calcd. for $C_{42}H_{60}N_{12}O_3$ [M + 2 H]$^{2+}$: 390.24502; found 390.24498.

3,5-Bis[{2-(6-pivaloylamidopyridinyl)methyl}{2-pyridinylmethyl}-aminomethyl]-1-(tetrahydropyran-2-yl)-1*H*-pyrazole (3b): To a solution of **2b** (1 g, 2.55 mmol) in acetonitrile (125 mL) four equivalents of dry Cs_2CO_3 (3.32 g, 10.2 mmol) were added and the mixture heated to reflux. A solution of **D** (1.392 mg, 5.10 mmol) in acetonitrile (20 mL) was added dropwise. The reaction mixture was heated to reflux for a further 24 h. All salts were filtered off and the solvent was removed. The residue was dissolved in dichloromethane (100 mL) and washed with water (3 × 100 mL). The combined organic phase was dried with Na_2SO_4. After removing the solvent the raw material was purified by column chromatography (ALOX$_{\mathrm{neutral}}$). R_f (dichloromethane/ethyl acetate, 2:1) = 0.59. The product **3b** was isolated as a yellow solid (1.575 g, 2.04 mmol, 80%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 18 H, CH_3), 1.40–1.55 (m, 3 H, C$H_2^{\mathrm{THP4,5}}$), 1.57–1.77 (m, 2 H, C$H_2^{\mathrm{THP3,4}}$), 1.96–2.09 (m, 1 H, CH_2^{THP3}), 2.27–2.40 (m, 1 H, CH_2^{THP6}), 3.55–3.76 (m, 12 H, CH_2), 3.77–3.92 (m, 1 H, CH_2^{THP6}), 5.25 (d, $^3J_{aa}$ = 10.5 Hz, 1 H, CH_2^{THP2}), 6.33 (s, 1 H, CH^{Pz}), 7.07 (m, 2 H, CH^{Py}), 7.13 (m, 2 H, CH^{Py}), 7.36 (d, J_o = 8.3 Hz, 2 H, CH^{Py}), 7.59 (m, 4 H, CH^{Py}), 8.05 (m, 4 H, CH^{Py}), 8.48 (m, 4 H, CH^{Py}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.9 (CH_2^{THP4}), 24.8 (CH_2^{THP5}), 27.4 (CH_3), 29.8 (CH_2^{THP3}), 39.7 ($C_q^{t\mathrm{Bu}}$), 48.7 (CH_2), 51.7 (CH_2), 59.7 (CH_2), 60.2 (CH_2), 67.7 (CH_2^{THP6}), 83.8 (CH^{THP2}), 106.9 (CH^{Pz}), 111.8 (CH^{Py}), 112.1 (CH^{Py}), 118.9 (CH^{Py}), 122.2 (CH^{Py}), 123.2 (CH^{Py}), 136.4 (CH^{Py}), 138.6 (CH^{Py}), 140.3 (C_q^{Pz5}), 148.8 (C_q^{Pz3}), 150.9 (C_q^{Py}), 157.3 (C_q^{Py}), 159.0 (C_q^{Py}), 177.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2962 (s), 2866 (m), 1688 (s), 1579 (s), 1519 (s), 1452 (vs), 1304 (m), 1152 (m) cm^{-1}. MS (ESI$^+$): m/z (%) = 795 (60) [M + Na]$^+$, 773 (100) [M + H]$^+$, 689 (27) [M – THP + 2 H]$^+$. HRMS (ESI +): m/z (%) calcd. for $C_{44}H_{57}N_{10}O_3$ [M + H]$^+$: 773.46096; found 773.46077, calcd. for $C_{44}H_{56}N_{10}O_3Na$ [M + Na]$^+$: 795.44291; found 795.44263.

3,5-Bis[{2-(1-methylimidazolyl)methyl}{2-(6-pivaloylamidopyridinyl)-methyl}aminomethyl]-1*H*-pyrazole (H_3L^1): The ligand precursor **3a** (724 mg, 0.93 mmol) was dissolved in ethanol (30 mL) and ethanolic HCl (20 mL) was added. After stirring overnight all volatile material was removed and ammoniacal dichloromethane (30 mL) was added. The reaction mixture was left stirring for 2 h. After extraction with water (3 × 30 mL), the combined water phases were re-extracted with dichloromethane (30 mL). The combined organic phase was dried with Na_2SO_4. If applicable, remaining ammonium chloride was filtered off. The solvent was evaporated and the residue was dried under vacuum to give H_3L^1 as a light yellow solid (638 mg, 0.92 mmol, 99%). If necessary the product can be purified by column chromatography using ALOX$_{\mathrm{basic}}$. Potential impurities can be eluted with ethyl acetate and the product can be obtained by elution with methanol. The solvent was evaporated and the residue was dissolved in dichloromethane. After filtration the filtrate was evaporated to dryness and dried under reduced pressure to give the product H_3L^1. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 18 H, C$H_3^{t\mathrm{Bu}}$), 3.56 (s, 6 H, CH_3^{Im}), 3.64 (s, 12 H, CH_2), 6.13 (s, 1 H, CH^{Pz}), 6.77 (s, 2 H, CH^{Im}), 6.90 (s, 2 H, CH^{Im}), 7.10 (d, J_o = 7.5 Hz, 2 H, CH^{Py}), 7.62 (t, J_o = 7.5 Hz, 2 H, CH^{Py}), 8.09 (d, J_o = 8.3 Hz, 2 H, CH^{Py}), 8.24 (s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.4 ($CH_3^{t\mathrm{Bu}}$), 32.8 (CH_3^{Im}), 39.8 ($C_q^{t\mathrm{Bu}}$), 49.1 (CH_2), 59.4 (CH_2), 106.5 (CH^{Pz4}), 112.2 (CH^{Py}), 118.9 (CH^{Py}), 121.5 (CH^{Im}), 127.0 (CH^{Im}), 138.7 (CH^{Py}), 145.0 (C_q^{Py}), 151.2 (C_q^{Im}), 157.2 (C_q^{Py}),177.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2963 (s), 2930 (m), 2870 (w), 1686 (s), 1579 (s), 1452 (vs), 1302 (m) cm^{-1}. MS (ESI$^+$): m/z (%) = 717 (20) [M + Na]$^+$, 695.5 (100) [M + H]$^+$. MS (ESI-): m/z (%) = 693.5 (100) [M – H]$^-$. HRMS (ESI-): m/z (%) calcd. for $C_{37}H_{50}N_{12}O_2$ [M – H]$^-$: 693.4107; found 693.4115.

3,5-Bis[{2-(6-pivaloylamidopyridinyl)methyl}{2-pyridinylmethyl}-aminomethyl]-1*H*-pyrazole (H_3L^2): The same conditions were used as described for compound H_3L^1. The product was isolated as a yellow resin (98%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.29 (s, 18 H, C$H_3^{t\mathrm{Bu}}$), 2.06 (s$_{\mathrm{br}}$, 2 H, NH), 3.66 (s, 4 H, CH_2), 3.70 (s, 4 H, CH_2), 3.76 (s, 4 H, CH_2), 6.13 (s, 1 H, CH^{Pz}), 7.13 (ddd, J_o = 7.5, J_o = 4.8, J_m = 1.2 Hz, 2 H, CH^{Py}), 7.18 (d, J_o = 7.5 Hz, 2 H, CH^{Py}), 7.43 (d, J_o = 7.7 Hz, 2 H, CH^{Py}), 7.62 (dt, J_o = 7.7, J_m = 1.6 Hz, 4 H, CH^{Py}), 8.08 (d, J_o = 8.3, J_m = 0.8 Hz, 2 H, CH^{Py}), 8.33 (s, 1 H, NH), 8.53 (ddd, J_o = 5.6, J_m = 1.8, J_p = 0.8 Hz 2 H, CH^{Py}) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 27.4 ($CH_3^{t\mathrm{Bu}}$), 39.8 ($C_q^{t\mathrm{Bu}}$), 49.6 (CH_2), 59.35 (CH_2), 59.40 (CH_2), 105.0 (CH^{Pz4}), 112.5 (CH^{Py}), 118.9 (CH^{Py}), 122.2 (CH^{Py}), 123.4 (CH^{Py}), 136.7 (CH^{Py}), 138.8 (CH^{Py}), 144.7 (C_q^{Py}), 149.0 (CH^{Py}), 151.3 (C_q^{Pz}), 157.3 (C_q^{Py}), 158.9 (C_q^{Py}),177.3 (C=O) ppm. MS (ESI$^+$): m/z (%) = 711 (100) [M + Na]$^+$, 689 (84) [M + H]$^+$. HRMS (ESI$^+$): m/z (%) calcd. for $C_{39}H_{49}N_{10}O_2$ [M + H]$^+$: 689.40345; found 689.40333, calcd. for $C_{39}H_{48}N_{10}O_2Na$ [M + Na]$^+$: 711.38539; found 711.38563.

$[H_2L^1\{(MeCN)Ni\}_2(\mu\text{-}O_2H_3)](ClO_4)_2$ (3): KOtBu (157 mg, 1.40 mmol) was added to a solution of H_3L^1 (486 mg, 0.70 mmol) in methanol (25 mL). After stirring for 15 min at room temp., $Ni(ClO_4)_2 \cdot 6\,H_2O$ (512 mg, 1.40 mmol) was added. The reaction mixture was stirred for 2 h at room temp. All salts were filtered off, the solvent was removed, and the residue dried under reduced pressure, yielding a green powder. Dark blue X-ray quality crystals (225 mg, 0.20 mmol, 29%) were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of **3**. IR (KBr): $\tilde{\nu}$ = 2970 (s), 2935 (w), 2878 (w), 1660 (s), 1621 (s), 1531 (s), 1460 (s), 1302 (m), 1095 (vs), 625 (s) cm^{-1}. MS (ESI$^+$) in acetonitrile: m/z (%) = 1107 (3) $[H_2L^1Ni_2(ClO_4)_3H]^+$, 1007 (6) $[H_2L^1Ni_2(ClO_4)_2]^+$, 907 (7) $[HL^1Ni_2(ClO_4)]^+$, 404 (65) $[HL^1Ni_2]_2^{2+}$. UV/Vis (KBr): $\lambda_{\max}$ [nm] = 240, 291, 344 (sh), 593, 798, 972. UV/Vis (acetonitrile): $\lambda_{\max}$[nm] (ε [Mcm]$^{-1}$) = 238 (480), 288 (329), 328 (185, *sh*), 584 (19). $C_{37}H_{52}Cl_2N_{12}Ni_2O_{12} \cdot 2CH_3OH$ (1108.73): calcd. C 42.23, H 5.45, N 15.15; found C 42.87, H 5.52, N 15.10.

Potentiometric Measurements: The formation constants for proton and Ni^{2+} complexes were calculated from pH-metric titration curves, which were obtained at 25 °C using a total volume of 2.5–3.0 cm^3 under an atmosphere of N_2. The purity and exact concentration of the ligand were determined by Gran's method.[20] Titrations were performed in 30% DMSO–0.1 mol dm^{-3} KCl (v/v) with a Metrohm 809 Titrando system. HCl stock solutions were prepared from conc. HCl in the mentioned solvent mixture and their concentrations were determined by potentiometric titrations. The 0.05 M stock solution of Ni^{2+} was also prepared in the DMSO/aq. KCl solvent mixture. Alkali, 0.1 mol dm^{-3} KOH (in 30% DMSO), free of CO_2, standard solution was added from a Metrohm 800 Dosino auto burette, which was calibrated by both weight titration and titration of standard materials. The Metrohm semicombined electrode (type 6.0224.100) was calibrated in hydrogen concentrations using 30% (v/v) DMSO–HCl according to the procedure of Irving et al.[21] Before the measurements the electrode was conditioned for two days in the DMSO/water (30:70) solvent mixture. The determined value of pK_W in this solvent mixture used in all computations was 14.56 ± 0.02. The HYPERQUAD2008[22] computer program was used to calculate stability constants. The results were obtained in the form of concentration overall stability constants $\beta pqr = [MpHqLr]/[M]p[H]q[L]r$, where M is metal, H is proton, and L the deprotonated form of the ligand. The standard deviations quoted were computed by HYPERQUAD2008 and refer to random errors only. They are, however, a good indication of the importance of a particular species in the equilibrium. Each time about 140 titration points have been used for the calculations. In all cases triplicate titrations were carried out at metal to ligand ratios 0:1, 1:1, and 2:1. The ligand concentration was varied in a range $0.4–2 \times 10^{-3}$ mol dm^{-3} in all titrations. DMSO was added due to solubility reasons.

X-ray Crystallography: X-ray data for **3** were collected with a STOE IPDS II diffractometer (graphite monochromated Mo-K_α radiation, λ = 0.71073 Å) by use of ω scans at –140 °C (Table 3). The structures was solved by direct methods and refined on F^2 using all reflections with SHELX-97.[23] Non-hydrogen atoms were refined anisotropically. Most hydrogen atoms were placed in calculated positions and assigned to an isotropic displacement parameter of 0.08 Å^2. The positions of the hydrogen atoms H3, H4B, H7, and H12 were refined using DFIX restraints (d_{O-H} = 0.82 Å, d_{N-H} = 0.87 Å). H4A was refined freely. No satisfactory model for the disorder could be found for some disordered MeCN molecules. For further refinement, the contribution of the missing molecules was subtracted from the reflection data by the SQUEEZE[24] routine of the PLATON[25] program.

Table 3. Crystal data and refinement details for **3**.

	$[H_2L^1Ni_2(H_3O_2)(MeCN)_2](ClO_4)_2$
Empirical formula	$C_{43}H_{61}Cl_2N_{15}Ni_2O_{12}$
Formula weight	1168.39
Crystal size [mm^3]	0.48 × 0.41 × 0.36
Crystal system	triclinic
Space group	$P\bar{1}$ (No. 2)
a [Å], α [°]	12.6002(4), 73.342(2)
b [Å], β [°]	12.8363(4), 86.625(2)
c [Å], γ [°]	20.9609(6), 89.963(2)
V /Å^3	3241.84(17)
Z	2
ρ [g/cm^3]	1.197
F(000)	1220
μ [mm^{-1}]	0.723
θ range [°]	1.62–25.64
hkl range	–15–15, –15–15, –25–25
Measured reflections	42749
Unique reflections [R_{int}]	12219 [0.0413]
Observed reflections [$I > 2\sigma(I)$]	10106
Data/restraints/parameters	12219/4/698
Goodness-of-fit (F^2)	1.036
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0426, 0.1169
$R1$, $wR2$ (all data)	0.0518, 0.1219
Residual e$^-$ density [e/Å^3]	–0.639/0.629

CCDC-825614 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Titration curves. Species distribution curves for H_3L^1. ESI mass spectrum of **3**.

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