Synthesis of Binucleating Macrocycles and their Nickel(II) Hydroxo- and Cyano-Bridged Complexes with Divalent Ions: Anatomical Variation of Ligand Features

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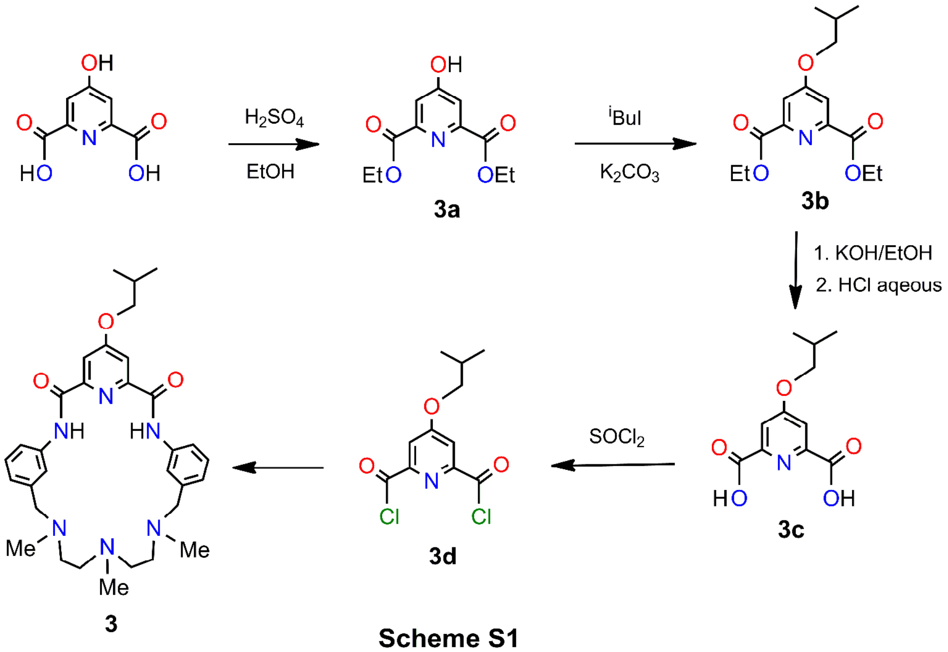


Scheme S1

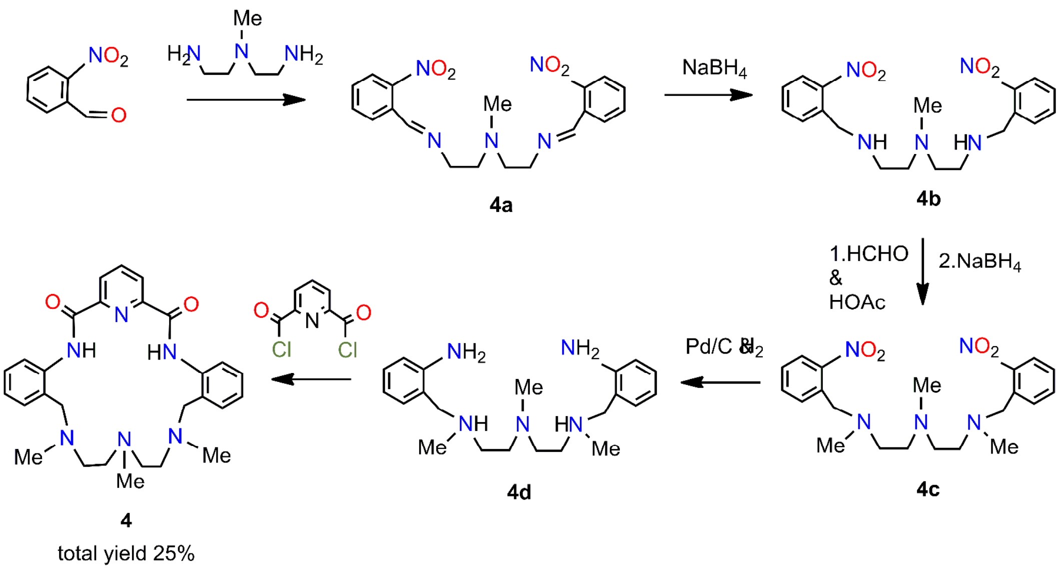
Intermediate (3a). Chelidamic acid (2.0g, 11 mmol) and concentrated sulfuric acid (H_2SO_4, 20 drops) in ethanol (75 mL) were refluxed at 80ºC for 4 h. The solvent was removed in vacuo to leave some white oily residue. Water (30 mL) and ethyl acetate (100 mL) were added to extract the product in organic layer and the aqueous layer was washed with ethyl acetate (2 ×100 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and solvent removed to give **3a** as a white powder (2.37 g, 90%). ^{1}H NMR ($CDCl_3$): δ 7.76 (s, 2), 4.45 (q, 4), 3.38 (d, 2), 2.13 (m, 1), 1.45 (t, 6), 1.06 (d, 6).

Intermediate (3b). To a solution of **3a** (2.19 g, 9.15 mmol, 1 equiv) in DMF (45 mL) was added K_2CO_3 (3.79 g, 27.45 mmol, 3 equiv) under a nitrogen atmosphere. The reaction mixture was stirred at 120ºC for 1.5 h and cooled down to 70ºC. ^{i}BuI (1.59 mL, 13.73 mmol, 1.5 equiv) was added and the reaction mixture was stirred at 70ºC for 3 h. After that, the mixture was cooled down to room temperature and the volume of solution was reduced to *ca*. 5 mL. The residue was diluted with 50 mL of toluene and 20 mL of H_2O. The aqueous layer was extracted with toluene (3 ×50 mL). The organic layers were combined and washed with H_2O (2 × 50 mL), dried with anhydrous Na_2SO_4. Solvent was removed to give **3b** as a light yellow oil (1.82 g, 67%). ^{1}H NMR (DMSO-d_6): δ 7.57 (s, 2), 4.35 (q, 4), 1.32 (t, 6).

Intermediate (3c). A solution of KOH (1.38 g, 24.6 mmol) in ethanol (15 mL) was added to **3b** (1.8 g, 6.1 mmol) in ethanol (30 mL). The mixture was stirred at room temperature for 2 h. Solvent was removed and the white residue was dissolved in 50 mL of H_2O. The aqueous solution was washed with ether (2×50 mL), acidified pH to *ca*. 2.0 with 10% of HCl. The precipitate was collected and dried in vacuo to give **3c** as a white powder (1.38 g, 95%). ^{1}H NMR (DMSO-d_6): δ 7.65 (s, 2), 4.01 (d, 2), 2.04 (m, 1), 0.98 (d, 6).

Intermediate (3d). Compound **3c** (1.35g, 5.64 mmol), thionyl chloride (15 mL), and anhydrous DMF (15 drops) were mixed and stirred for 5 h at 75ºC under N_2 atmosphere. The crude product after removing of excess thionyl chloride was treated with dry THF and solvent removed in vacuo to leave **3d** as a white solid (1.26 g, 81%).

Macrocyclic ligand (3). To a solution of Et_3N (14 mL) in THF (350 mL) was added simultaneously solution of 3,3'-dien^{Me3}-dianiline (1.62 g, 4.56 mmol, the compound **12** in literature[1]) and **3d** (1.26g, 4.56 mmol), each in THF (50 mL), by syringe pump over 24 h. The reaction mixture was stirred for 3 h and filtered. The filtrate was evaporated to leave a yellow sticky solid. The residue was stirred in CH_3CN (250 mL) overnight and filtered. Solvent was removed to leave crude product as some light yellow solid, which was purified on a silica column eluted with CH_2Cl_2/MeOH/NH_4OH to give **3** as a white solid (0.90, 35%). ^{1}H NMR (DMSO-d_6): δ 1.02 (d, 6) 2.11(s, 6), 2.28 (s, 3), 2.54 (t, 4), 2.63 (t, 4), 3.50 (s, 4), 4.03(d, 2), 7.01 (d, 2), 7.33 (t, 2), 7.63 (s, 2), 7.83 (s, 2), 8.37 (d, 2), 11.16 (s, 2). *m/z* (ES) 559 $[M+H]^+$.



Scheme S2

Intermediate (4a). 2-Nitrobenzaldehyde (7.56 g, 50 mmol) and 3-*N*-methylaminopentane-1,5-diamine (2.93 g, 25 mmol) were reacted in ethanol (150 mL) for 24 h. The orange solution was pumped to leave product as some orange-red oil (9.58 g, 100%). ^{1}H NMR ($CDCl_3$): δ 2.39 (s, 3), 2.82 (t, 4), 3.79 (t, 4), 7.49 (t, 2), 7.58 (t, 2), 7.92 (d, 2), 7.97 (d, 2), 8.64 (s, 2).

Intermediate (4b). $NaBH_4$ (3.78 g, 100 mmol) was added slowly to a solution of **4a** (9.58 g, 25.0 mmol) in methanol (160 mL) at 50ºC and stirred for 2h. The solution was cooled to room temperature, solvent was removed, and the orange solid was extracted with dichloromethane/water (200 mL/120 mL). The organic layer was washed with saturated NaCl aqueous solution (4 × 80 mL), dried over $MgSO_4$, and filtered. Removal of solvent gave product as a yellow-orange oil (8.96 g, 92.5%). ^{1}H NMR ($CDCl_3$): δ 2.05 (s, br, 2), 2.15 (s, 3), 2.48 (t, 4), 2.68 (t, 4), 4.02 (s. 4), 7.36 (t, 2), 7.53 (t, 2), 7.61 (d, 2), 7.89 (d, 2).

Intermediate (4c). To a solution of **4b** (8.96 g, 23.1 mmol) in acetonitrile (600 mL) and acetic acid (70 mL) was added an aqueous solution of formaldehyde (35 mL, 37%). The mixture was stirred for 1 h, cooled to 0ºC, and $NaBH_4$ (4.37 g, 115.5 mmol) was slowly added. Stirring was continued for 2 h and for 40 h at room temperature. After filtration, solvent was removed from the filtrate to give a light yellow oily residue, which was stirred in dichloromethane (200 mL). A solution of 2 M NaOH was added until pH was *ca*. 14. The aqueous layer was extracted with dichloromethane (2 × 50 mL) and the combined organic layers were washed with saturated NaCl aqueous solution (2 × 100 mL), dried over $MgSO_4$ and filtered. Removal of solvent from the filtrate gave product as a light yellow-orange oil (9.00 g, 94%). ^{1}H NMR ($CDCl_3$): δ 2.16 (s, 6), 2.18 (s, 3), 2.46 (s, 8), 3.77 (s, 4), 7.34 (t, 2), 7.50 (t, 2), 7.63 (d, 2), 7.78 (s, 2).

Intermediate (4d). A mixture of **4c** (2.49 g, 6.0 mmol) and Pd/C (90 mg) in anhydrous ethanol was attached a H_2 balloon under dihydrogen atmosphere. The mixture was stirred vigorously for 6 h at room temperature and filtered. Volume reduction of the filtrate gave a light orange oil. The crude product was purified in the air on a silica column eluted with dichloromethane/methanol/NH_4OH to give a yellow oil (1.55 g, 73%). ^{1}H NMR ($CDCl_3$): δ 2.17 (s, 6), 2.21 (s, 3), 2.51 (m, 8), 3.47 (s, 4), 4.79 (s, br, 4), 6.61 (d, 2), 6.67 (t, 4), 6.98 (d, 2), 7.10 (t, 2).

Macrocyclic ligand (4). To a solution of Et_3N (12 mL) in THF (350 mL) was added simultaneously solutions of **4d** (1.55 g, 4.37 mmol) and pyridine-2,6-dicarbonylchloride (1.03 g, 5.03 mmol), each in THF (50 mL), by syringe pump over 24 h. The reaction mixture was stirred for 2 h, filtered, and the filtrate was evaporated to leave a oily yellow solid. This residue was stirred with acetonitrile (150 mL, 3 h) and the solution was filtered. Solvent of filtrate was removed and the crude product was purified on a silica column eluted with dichloromethane/methanol/NH_4OH to afford product as a white solid (0.85 g, 40%). ^{1}H NMR ($CDCl_3$): δ 1.59 (s, 3), 2.19 (s, 6), 2.29 (s, 8), 3.35 (s, 4), 7.09 (m, 4), 7.34 (t, 2), 7.94 (d, 2), 8.02 (t, 1), 8.32 (d, 2), 11.23 (s, 2). *Anal.* Calcd. for $C_{28}H_{34}N_6O_2$: C, 69.11; H, 7.04; N, 17.27. Found: C, 69.25; H, 6.97; N, 17.18.

Anomalous Scattering.[2-3] Crystals suitable for X-ray diffraction were mounted on glass fibers affixed to a copper pin for each. Data were collected at ChemMatCARS at the Advanced Photon Source at Argonne National Laboratory (CAR Center for Advanced Radiation Sources). The data set was collected at 95 K using a diamond (111) crystal monochromator and a Bruker CCD detector. The incident X-ray wavelengths used were following: the Cu edge: 1.38082×10^{-10} m, the Ni edge: 1.48787×10^{-10} m, the Fe edge: 1.74331×10^{-10} m. The diffraction data for overall structure determination were collected on a Bruker CCD area detector at 0.71073×10^{-10} m (100 K). All the structures were solved using the SHELX program package.[4]

References

1. Huang, D; Holm, R. H. *J. Am. Chem. Soc.* **2010**, *132*, 4693-4701.
2. Coppens, P. Synchrotron Radiation Crystallography ; Academic Press Limited : London, **1992**.
3. Wu, G.; Zhang, Y.; Ribaud, L.; Coppens, P. *Inorg. Chem.* **1998**, *37*, 6078-6083.
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Table S1. Crystallographic Data[a] for Compounds **4-8**.

compounds	[**4**]	[**5**]·HOTf ·MeCN	[**6**]·2H_2O ·0.5EtOAc	(Et_4N)[**7**]	(Et_4N)[**8**]
formula	$C_{28}H_{34}N_6O_2$	$C_{33}H_{40}F_3N_7O_5S_2$	$C_{35}H_{51}N_7O_5$	$C_{31}H_{42}N_4CuO_3$	$C_{32}H_{42}N_4CuO_5$
M	486.61	735.83	649.83	582.23	626.24
crystal system	triclinic	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	*P-1*	*Pna2(1)*	*C2/c*	*Cmc2(1)*	*P2(1)/n*
a, Å	11.0491(5)	16.7365(19)	15.9011(10)	14.6152(12)	11.8393(15)
b, Å	11.2919(5)	12.7588(15)	19.9913(12)	14.0240(11)	17.340(2)
c, Å	11.6718(5)	32.639(4)	21.7382(14)	14.7774(12)	15.206(2)
α, deg	65.896(2)	90	90	90	90
β, deg	70.060(2)	90	95.5310(10)	90	93.708(5)
γ, deg	76.715(2)	90	90	90	90
V, $Å^3$	1242.60(9)	6969.7(14)	6878.0(7)	3028.8(4)	3115.2(7)
Z	2	8	8	4	4
μ, mm^{-1}	0.085	0.221	0.085	0.758	0.747
independent data	4851	11873	6550	3755	5636
refined parameters	325	1129	552	208	416
R_1[b], wR_2[c] (I >2σ(I))	0.0378, 0.0954	0.0653, 0.1407	0.0588, 0.1508	0.0391, 0.1057	0.0472, 0.1152
R_1, wR_2 (all data)	0.0442, 0.1002	0.1014, 0.1602	0.0737, 0.1639	0.0419, 0.1101	0.0683, 0.1278

[a] T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å). [b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

Table S2. Crystallographic Data[a] for Compounds **11, 14** and **16-18**.

compounds	(Et_4N)$_2$[**11**]	[**14**]	[**16**][b]	(Me_4N) [**17**] · toluene	[**18**] ·DMF
formula	$C_{62}H_{82}N_8CoO_4$	$C_{28}H_{33}ClMnN_6NiO_3$	$C_{28}H_{33}ClCuN_6NiO_3$	$C_{43}H_{61}N_7NiO_4$	$C_{35}H_{48}ClCuN_7NiO_5$
M	1062.29	650.70	659.30	798.70	804.50
crystal system	orthorhombic	monoclinic	monoclinic	orthorhombic	monoclinic
space group	*Pbcn*	*P2(1)/c*	*P2(1)/c*	*P2(1)2(1)2(1)*	*P2(1)/n*
a, Å	12.7121(8)	8.727(3)	7.8719(16)	12.2953(10)	8.2255(5)
b, Å	28.3291(18)	17.896(6)	19.078(4)	12.6618(10)	24.8410(16)
c, Å	15.4425(9)	17.134(5)	17.542(4)	26.974(2)	18.1320(12)
α, deg	90	90	90	90	90
β, deg	90	100.227(6)	95.97(3)	90	102.2800(10)
γ, deg	90	90	90	90	90
V, $Å^3$	5561.2(6)	2633.4(15)	2620.1(9)	4199.4(6)	3620.1(4)
Z	4	4	4	4	4
μ, mm^{-1}	0.364	1.341	0.883	0.511	1.233
independent data	5228	5099	4670	8537	7410
refined parameters	638	365	393	496	483
R_1[c], wR_2[d] (I >2σ(I))	0.0624, 0.1640	0.0514, 0.0973	0.0514, 0.1002	0.0403, 0.1022	0.0453, 0.1091
R_1, wR_2 (all data)	0.0929, 0.1888	0.1007, 0.1174	0.0910, 0.1140	0.0459, 0.1053	0.0573, 0.1166

[a] T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å). [b] T = 15(2) K, synthrotron radiation (λ = 0.41328 Å).
[c] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{1/2}$.

Table S3. Crystallographic Data[a] for Compounds **19-23**.

compounds	[**19**]·0.5Et$_2$O	(Et$_4$N)[**20**] ·(HOTf)·DMF	(Me$_4$N)[**21**]	[**22**][b]	[**23**]·DMF
formula	$C_{35}H_{45}ClFeN_7NiO_{3.5}$	$C_{40}H_{59}F_3N_8NiO_6S$	$C_{34}H_{47}N_7NiO_3S$	$C_{30}H_{36}N_6NiO_3S$	$C_{33}H_{41}Cl_2FeN_7NiO_3S$
M	769.79	895.72	692.56	619.42	801.25
crystal system	monoclinic	triclinic	Triclinic	monoclinic	monoclinic
space group	*P2(1)/c*	*P-1*	*P1*	*P2(1)/n*	*P2(1)/c*
a, Å	11.2981(11)	12.4478(19)	8.9626(16)	19.5761(5)	10.9069(17)
b, Å	15.9375(16)	13.120(2)	8.9597(16)	7.8176(2)	17.413(3)
c, Å	20.206(2)	15.302(2)	10.890(2)	22.1213(6)	18.504(3)
α, deg	90	76.443(2)	99.410(3)	90	90
β, deg	105.165(2)	80.907(2)	99.424(3)	108.7690(10)	103.226(2)
γ, deg	90	61.410(2)	91.889(3)	90	90
V, Å^3	3511.6(6)	2130.0(6)	849.5(3)	3205.38(14)	3421.1(9)
Z	4	2	1	4	4
μ, mm^{-1}	1.073	0.573	0.678	0.377	1.238
independent data	8372	8821	5976	16952	6472
refined parameters	461	597	542	405	469
R_1^c, wR_2^d (I >2σ(I))	0.0433, 0.1048	0.0646, 0.1780	0.0581, 0.1388	0.0678, 0.2069	0.0573, 0.1424
R_1, wR_2 (all data)	0.0565, 0.1143	0.0774, 0.1899	0.0669, 0.1454	0.1011, 0.2483	0.0917, 0.1651

[a] T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å). [b] T = 95(2) K, synthrotron radiation (λ = 0.39364 Å).
[c] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [d] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{½}$.

Table S4. Crystallographic Data[a] for Compounds **24-28**.

compounds	[**24**]·DMSO	[**25**](ClO$_4$)· 0.5DMF	(Me$_4$N)[**26**] ·0.5Et$_2$O	[**27**]·ClO$_4$	[**28**]·ClO$_4$
formula	$C_{35}H_{40}ClFeN_7NiO_3S_2$	$C_{31.5}H_{38.5}ClCuN_{6.5}NiO_{7.5}S$	$C_{39}H_{59}N_8NiO_{3.5}$	$C_{39}H_{56}ClCuN_9NiO_9$	$C_{36}H_{49}ClCuN_8NiO_8$
M	796.85	817.95	754.65	952.63	879.53
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
space group	*P2(1)/n*	*P2(1)/n*	*C2*	*P2(1)/n*	*P2(1)/c*
a, Å	14.8812(14)	11.1284(12)	13.1014(8)	18.272(2)	12.586(4)
b, Å	14.8236(14)	19.205(2)	12.8847(8)	11.5911(13)	12.796(5)
c, Å	15.4676(15)	15.8027(16)	23.4563(15)	20.991(2)	23.054(7)
α, deg	90	90	90	90	90
β, deg	93.701(2)	94.954(2)	94.8400(10)	108.935(2)	94.040(6)
γ, deg	90	90	90	90	90
V, Å^3	3404.9(6)	3364.8(6)	3945.5(4)	4205.1(8)	3704(2)
Z	4	4	4	4	4
μ, mm^{-1}	1.227	1.393	0.540	1.083	1.219
independent data	6949	6891	8102	7945	6924
refined parameters	461	546	653	545	496
R_1^b, wR_2^c (I >2σ(I))	0.0402, 0.0973	0.0502, 0.1158	0.0701, 0.1837	0.0605, 0.1399	0.0571, 0.1254
R_1, wR_2 (all data)	0.0489, 0.1026	0.0553, 0.1183	0.0882, 0.2033	0.1095, 0.1668	0.0955, 0.1444

[a] T = 100(2) K, Mo Kα radiation (λ = 0.71073 Å). [b] $R_1 = \sum||F_o| - |F_c|| / \sum|F_o|$. [c] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2/(F_o^2)^2]\}^{½}$.

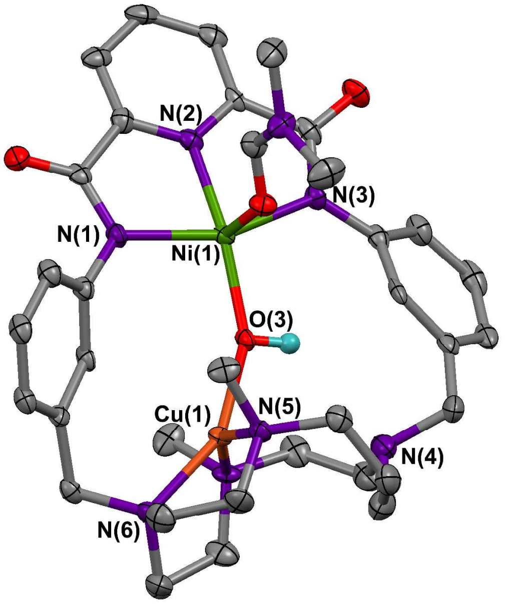

Figure S1. Structure of $(Me_4N)[Ni(\mu_2\text{-}OH)(DMF)Cu(\subset\text{-}pyN_2N_4^{Me2})]$ (**28**). Bond lengths (Å): Ni-N(1) 2.080(4), Ni-N(2) 1.993(4), Ni-N(3) 2.141(4), Ni-O(3) 2.008(4), Cu-O(3) 1.936(3), Cu-N(5) 2.074(4), Cu-N(6) 2.068(4), Cu-N(7) 2.086(4), Cu···N(4) 3.129(4), Ni···Cu 3.833 (2).

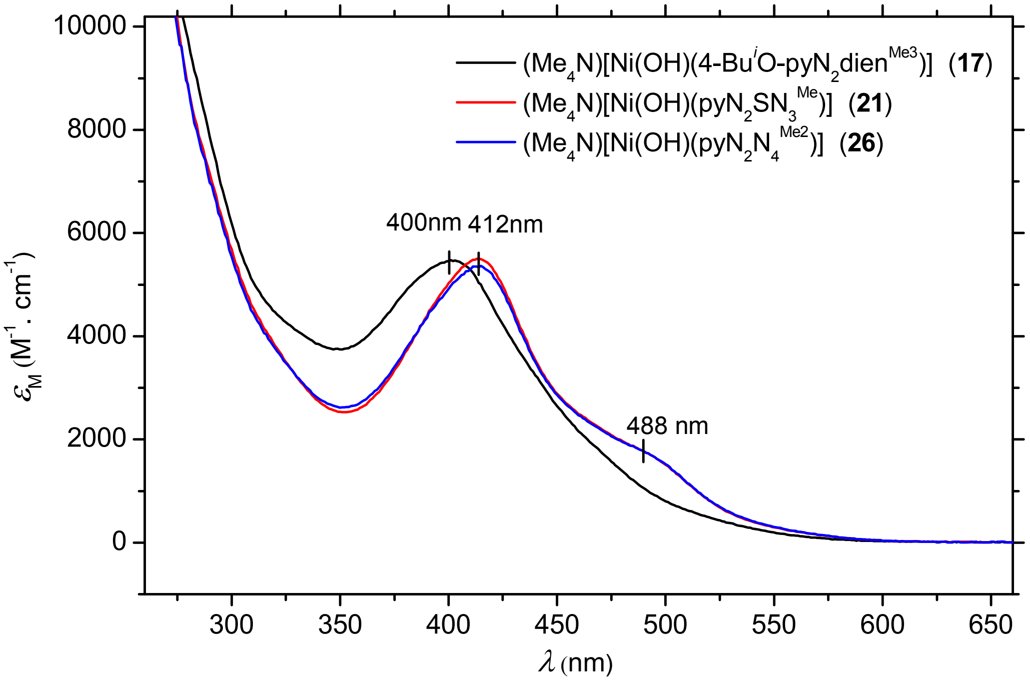

Figure S2. Absorption spectra of mononuclear $[Ni^{II}\text{-}OH]$ complexes $(Me_4N)[Ni(OH)(\subset_{22}\text{-}4\text{-}Bu^iO\text{-}pyN_2dien^{Me3})]$ (**17**), $(Me_4N)[Ni(OH)(\subset\text{-}pyN_2SN_3^{Me})]$ (**21**) and $(Me_4N)[Ni(OH)(\subset\text{-}pyN_2N_4^{Me2})]$ (**26**) in DMF at 298 K.