Supporting Information for

Synthesis, magnetic and high-field EPR investigation of two tetranuclear Ni^{II}-based complexes

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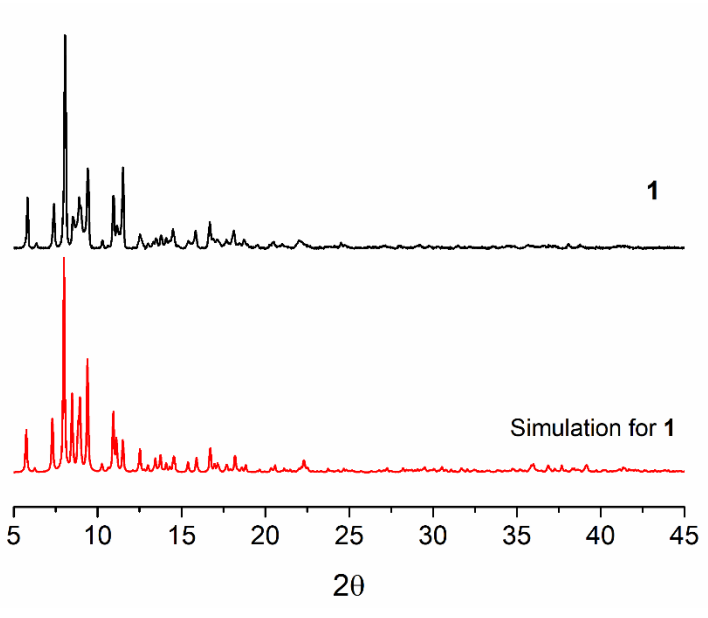
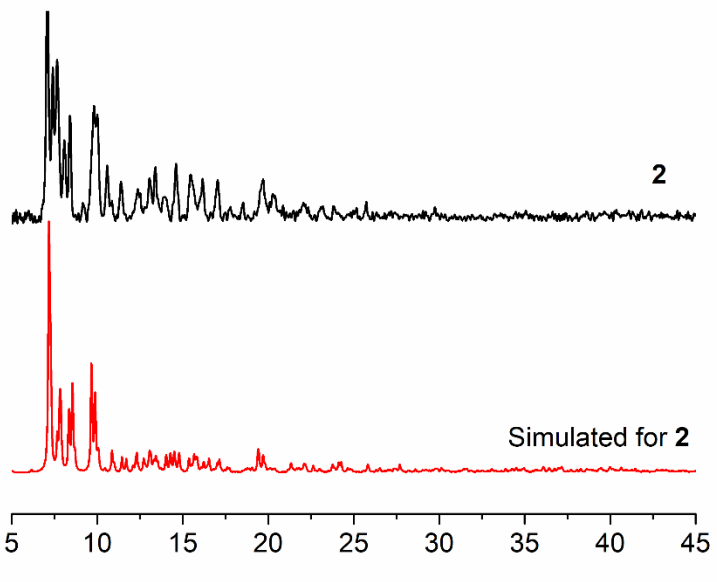
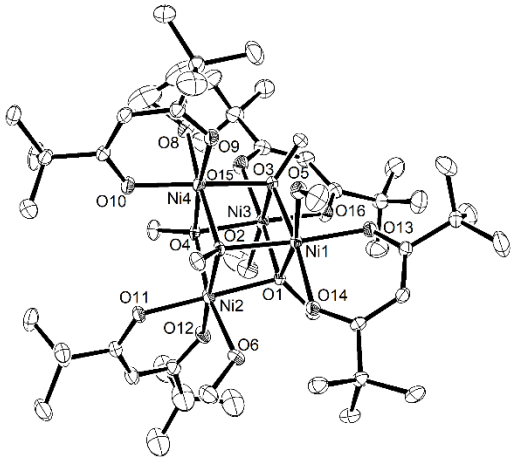


a)

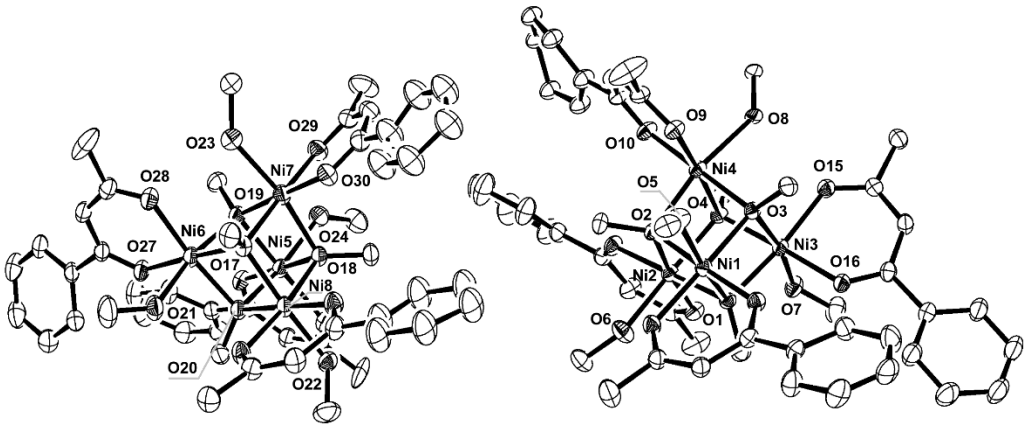


b)

Figure S1. Experimental and simulated powder X-ray diffraction (PXRD) patterns. The simulated PXRD patterns were obtained from crystal structures for **1** (a) and **2** (b) solved using single crystal XRD data.



a)



b)

Figure S2. ORTEP representation of asymmetric units of compounds **1** (a) and **2** (b). Hydrogen and fluorine atoms, as well as the ethyl ether molecule and part of the disorder in the phenyl or methyl groups in **2** were omitted for sake of clarity. Ellipsoids are at 30 % of probability level.

Table S1-Selected bond lengths and angles for **1** and **2**.

Compound 1				Compound 2			
Labels	**Bond length (Å)**	**Labels**	**Angle (º)**	**Labels**	**Bond length (Å)**	**Labels**	**Angle (º)**
Ni1-O1	2.074(3)	Ni1-O1-Ni2	96.80(12)	Ni1-O1	2.051(5)	Ni1-O1-Ni2	95.88(9)
Ni1-O2	2.078(3)	Ni1-O2-Ni2	96.03(12)	Ni1-O2	2.050(3)	Ni1-O2-Ni2	96.40(9)
Ni1-O3	2.093(3)	Ni1-O1-Ni3	99.82(12)	Ni1-O3	2.049(2)	Ni1-O1-Ni3	98.61(10)
Ni1-O5	2.129(3)	Ni1-O3-Ni3	99.00(12)	Ni1-O5	2.099(3)	Ni1-O3-Ni3	98.71(10)
Ni1-O13	2.008(3)	Ni1-O2-Ni4	97.46(12)	Ni1-O13	2.020(2)	Ni1-O2-Ni4	96.32(10)
Ni1-O14	2.054(3)	Ni1-O3-Ni4	96.70(12)	Ni1-O14	2.041(3)	Ni1-O3-Ni4	96.35(9)
Ni2-O1	2.068(3)	Ni2-O2-Ni4	99.80(13)	Ni2-O1	2.059(2)	Ni2-O2-Ni4	98.21(10)
Ni2-O2	2.089(3)	Ni2-O4-Ni4	99.38(13)	Ni2-O2	2.044(2)	Ni2-O4-Ni4	97.96(10)
Ni2-O4	2.051(3)	Ni2-O1-Ni3	95.79(12)	Ni2-O4	2.056(2)	Ni2-O1-Ni3	96.41(9)
Ni2-O6	2.096(4)	Ni2-O4-Ni3	96.77(12)	Ni2-O6	2.098(3)	Ni2-O4-Ni3	96.57(9)
Ni2-O11	2.004(3)	Ni3-O3-Ni4	96.70(12)	Ni2-O11	2.024(3)	Ni3-O3-Ni4	96.30(9)
Ni2-O12	2.035(3)	Ni3-O4-Ni4	96.21(12)	Ni2-O12	2.031(3)	Ni3-O4-Ni4	96.46(9)
Ni3-O1	2.075(3)			Ni3-O1	2.054(2)	Ni5-O19-Ni6	99.04(12)
Ni3-O3	2.081(3)			Ni3-O3	2.053(2)	Ni5-O20-Ni6	98.48(12)
Ni3-O4	2.060(3)			Ni3-O4	2.052(2)	Ni5-O19-Ni7	96.18(11)
Ni3-O7	2.121(4)			Ni3-O7	2.123(3)	Ni5-O18-Ni7	96.11(11)
Ni3-O15	2.041(3)			Ni3-O15	2.037(3)	Ni5-O18-Ni8	96.98(11)
Ni3-O16	1.999(3)			Ni3-O16	2.022(2)	Ni5-O20-Ni8	95.87(11)
Ni4-O2	2.044(3)			Ni4-O2	2.056(2)	Ni6-O17-Ni7	96.23(12)
Ni4-O3	2.059(3)			Ni4-O3	2.056(2)	Ni6-O19-Ni7	95.98(12)
Ni4-O4	2.095(3)			Ni4-O4	2.052(2)	Ni6-O17-Ni8	96.45(13)
Ni4-O8	2.056(4)			Ni4-O8	2.105(3)	Ni6-O20-Ni8	96.83(13)
Ni4-O9	2.076(3)			Ni4-O9	2.042(3)	Ni7-O17-Ni8	99.05(12)
Ni4-O4	2.095(3)			Ni4-O10	2.010(2)	Ni7-O18-Ni8	99.02(11)
Ni1···Ni2	3.098(9)			Ni5-O18	2.043(3)		
Ni1···Ni3	3.174(8)			Ni5-O19	2.044(3)		
Ni1···Ni4	3.098(8)			Ni5-O20	2.062(3)		
Ni2···Ni3	3.074(8)			Ni5-O24	2.120(3)		
Ni2···Ni4	3.162(9)			Ni5-O25	2.007(3)		
Ni3···Ni4	3.093(8)			Ni5-O26	2.027(3)		
				Ni6-O17	2.059(3)		
				Ni6-O19	2.050(3)		
				Ni6-O20	2.049(3)		
				Ni6-O21	2.106(3)		
				Ni6-O27	2.027(3)		
				Ni6-O28	2.045(3)		
				Ni7-O17	2.037(3)		
				Ni7-O18	2.057(3)		
				Ni7-O19	2.054(3)		
				Ni7-O23	2.125(3)		
				Ni7-O29	2.022(3)		
				Ni7-O30	2.015(3)		
				Ni8-O17	2.056(3)		
				Ni8-O18	2.037(3)		
				Ni8-O20	2.054(3)		
				Ni8-O22	2.111(3)		
				Ni8-O31	2.014(3)		
				Ni8-O32	2.036(3)		
				Ni1···Ni2	3.051(7)		
				Ni1···Ni3	3.112(7)		
				Ni1···Ni4	3.059(6)		
				Ni2···Ni3	3.066(5)		
				Ni2···Ni4	3.099(8)		
				Ni3···Ni4	3.061(8)		
				Ni5···Ni6	3.114(9)		
				Ni5···Ni7	3.050(1)		
				Ni5···Ni8	3.055(8)		
				Ni6···Ni7	3.049(7)		
				Ni6···Ni8	3.069(8)		
				Ni7···Ni8	3.113(8)		

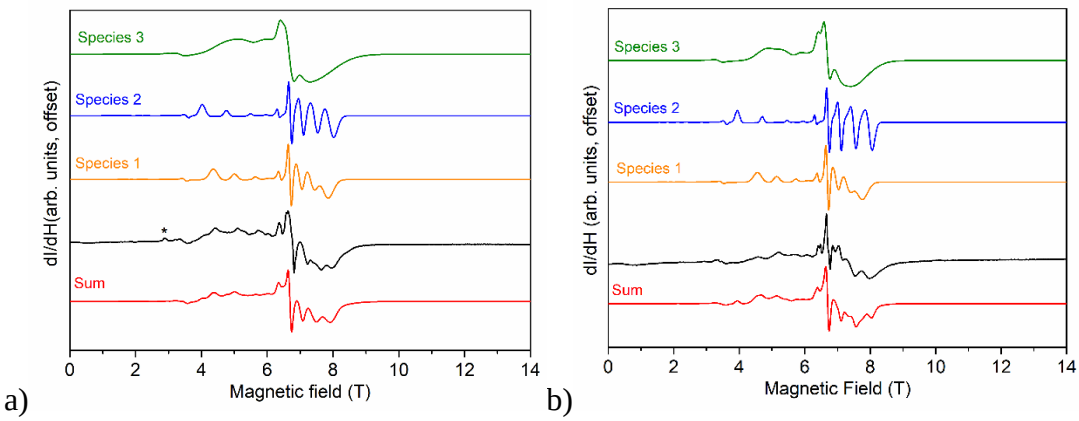


Figure S3. Spectral simulations at 204.8 GHz for **1** (a) and 203.2 GHz for **2** (b) at 7K according to the parameters shown in Table 3 in the main text. Experimental data are shown in black. The simulated spectra were appropriately weighted and summed as shown above. The features marked by (*) are due to surface adsorbed molecular oxygen.

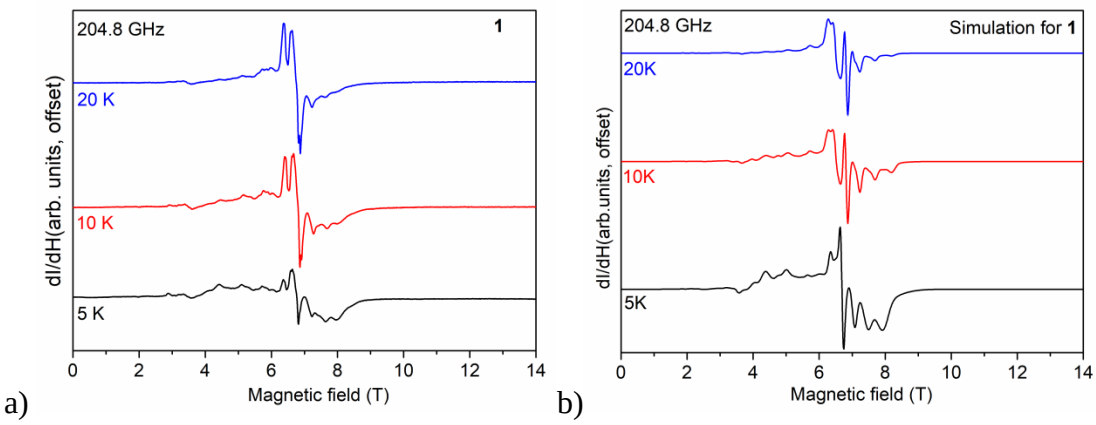
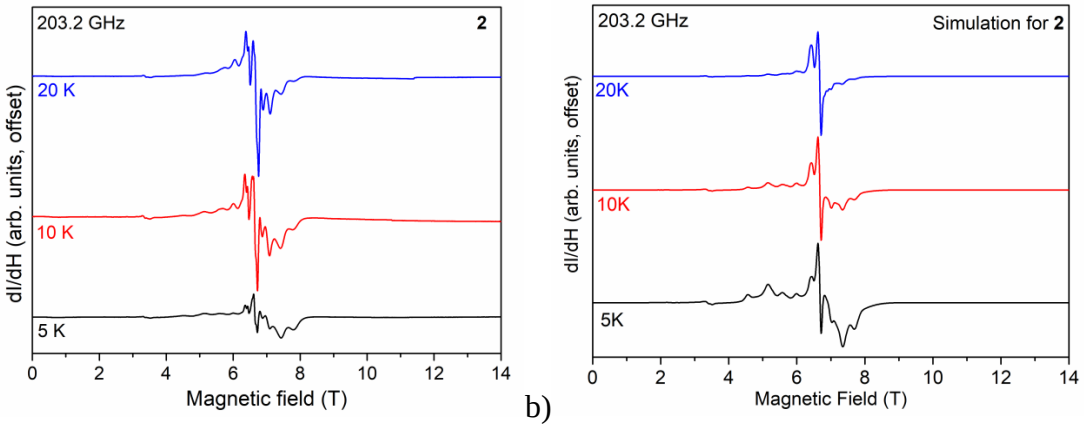
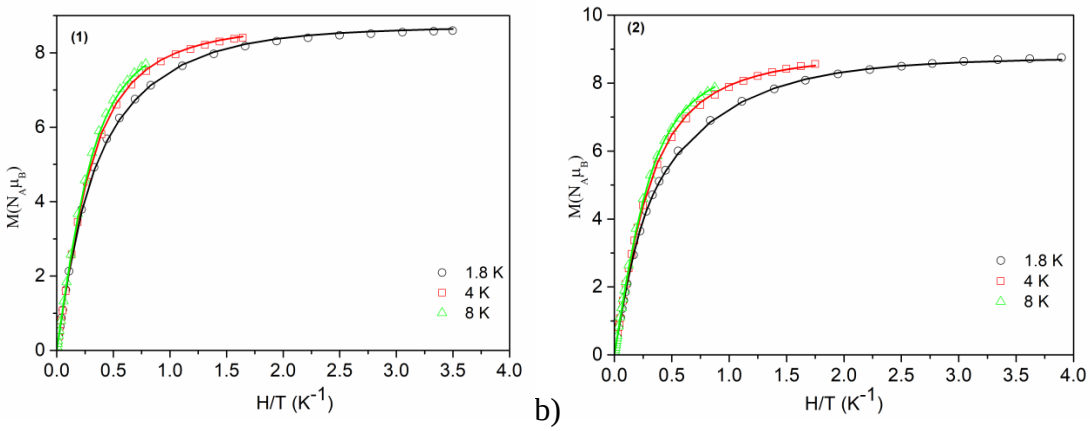


Figure S4. a) Temperature-dependent powder EPR spectra collected from 5 to 20 K at 204.8 GHz for **1**. b) Spectral simulations at 204.8 GHz according to the parameters shown in Table 3 in the main text.



a) b)

Figure S5. a) Temperature-dependent powder EPR spectra collected from 5 to 20 K at 203.2 GHz for **2**. b) Spectral simulations at 203.2 GHz according to the parameters shown in Table 3 in the main text.



a) b)

Figure S6. Magnetization versus H/T plots for compounds **1**(a) and **2**(b). The solid lines represent the best-fit curves using Eq. 3 with the parameters reported in the main text.