The Reactivity of the Imine Bond within Polynuclear Nickel(II) Complexes

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Synthesis of Cubane **4**

The OV (0.076 g, 0.50 mmol) in methanol (2.0 mL) was added to the solution of $Ni(NO_3)_2 \cdot 6H_2O$ (0.073 g, 0.25 mmol) in 2.0 mL of methanol. Subsequently 2-AP (0.023 g, 0.25 mmol) in methanol (2.0 mL) was introduced to the solution. After 15 minutes of stirring, Et_3N (0.07 ml, 0.50 mmol) was added to the clear yellow-green solution. After ten minutes yellow-green precipitate began to form. The precipitate was collected after 15 minutes of further stirring. Yield 0.019 g (0.018 mmol, 29%). Elemental analysis: calcd. for $C_{40}H_{56}Ni_4O_{20}$: C: 44.01; H: 5.17, found: 42.51; H: 5.03. The disagreement between the calculated and measured value of EA may be caused by the replacement of methanol by water in some of the cubane molecules. Crystals for X-ray diffraction analysis were obtained at RT by slow evaporation of the remaining solvent. It must be noted that the cubane **4** would also crystallize from the residual solutions of the syntheses described in the manuscript in 2.1.2.1–2.1.2.3. Cubane **4′** was found in the residue after the synthesis of **1.** The methanol in **4′** is partly substituted by ethanol (on the basis of X-ray data).

Table S1. Crystallographic data for cubane **4** and **4′** (T = 120 K).

Complex	**4**	**4′**
Empirical formula	$C_{40}H_{56}Ni_4O_{20}$	$C_{42}H_{58}Ni_4O_{20}$
Formula weight	1091.68	1117.72
Wavelength [Å]	0.71073	1.54186
Crystal system	Tetragonal	Tetragonal
Space group	$I4_1/a$	$I4_1/a$
a (Å)	21.9977(7)	22.2276(11)
b (Å)	21.9977(7)	22.2276(11)
c (Å)	9.4996(3)	9.5788(6)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ (°)	90.00	90.00
V (Å^3)	4596.8(3)	4732.6(6)
Z	4	4
D_c (g cm^{-3})	1.577	1.569
μ (mm^{-1})	1.69	2.45
F (000)	2272	2328
Reflection collected	28673	16748
Unique reflections	2255	2134

Parameters	151	161
R_{int}	0.046	0.071
GOOF	1.041	1.07
$R_1[I > 2\sigma(I)]$	0.0343	0.0685
wR_2 (all data)	0.0891	0.1187
CCDC number	2072194	2072195

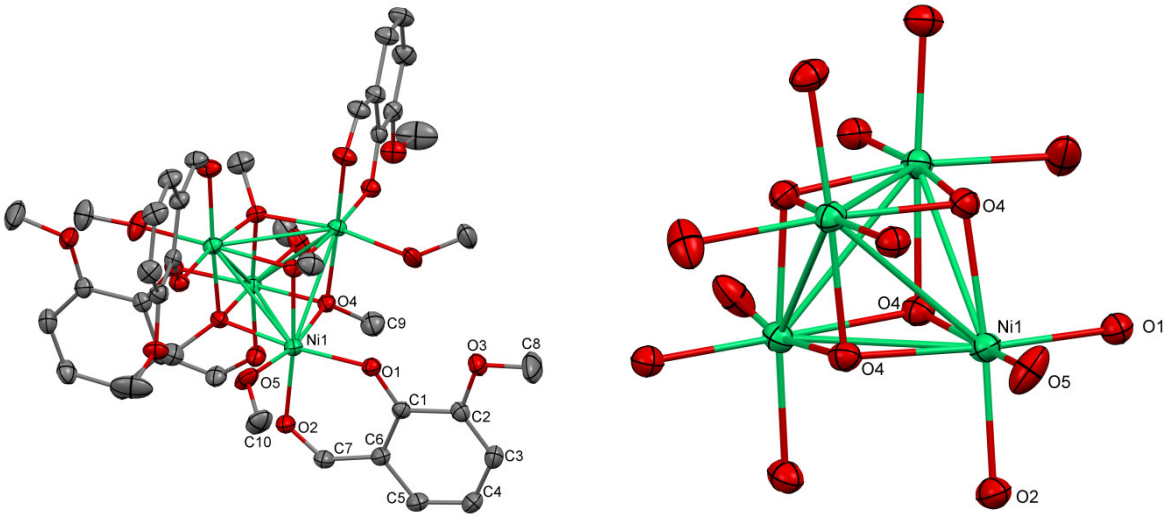


Figure S1. Molecular structures of **4**. Numbering given for the independent part. Important bond lengths/distances [Å]: Ni1–O1 2.0059(19); Ni1–O2 2.028(2); Ni1–O4 2.0355(19); Ni1–O4^{i} 2.0406(19); Ni1–O4^{ii} 2.0593(19); Ni1–O5 2.096(2); Ni1–Ni1^{i} 3.0659(6); Ni1–Ni1^{ii} 3.0872(6); ^{i} y + 1/4, − x + 3/4, − z + 3/4; ^{ii} − x + 1, − y + 1/2, z.

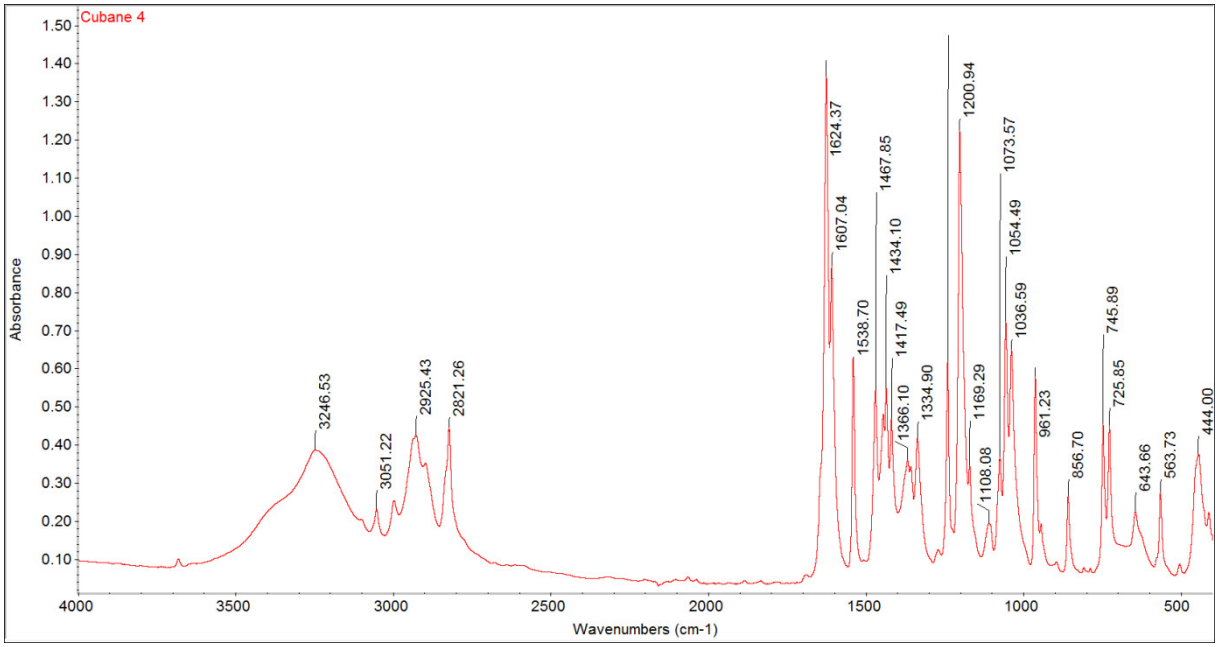
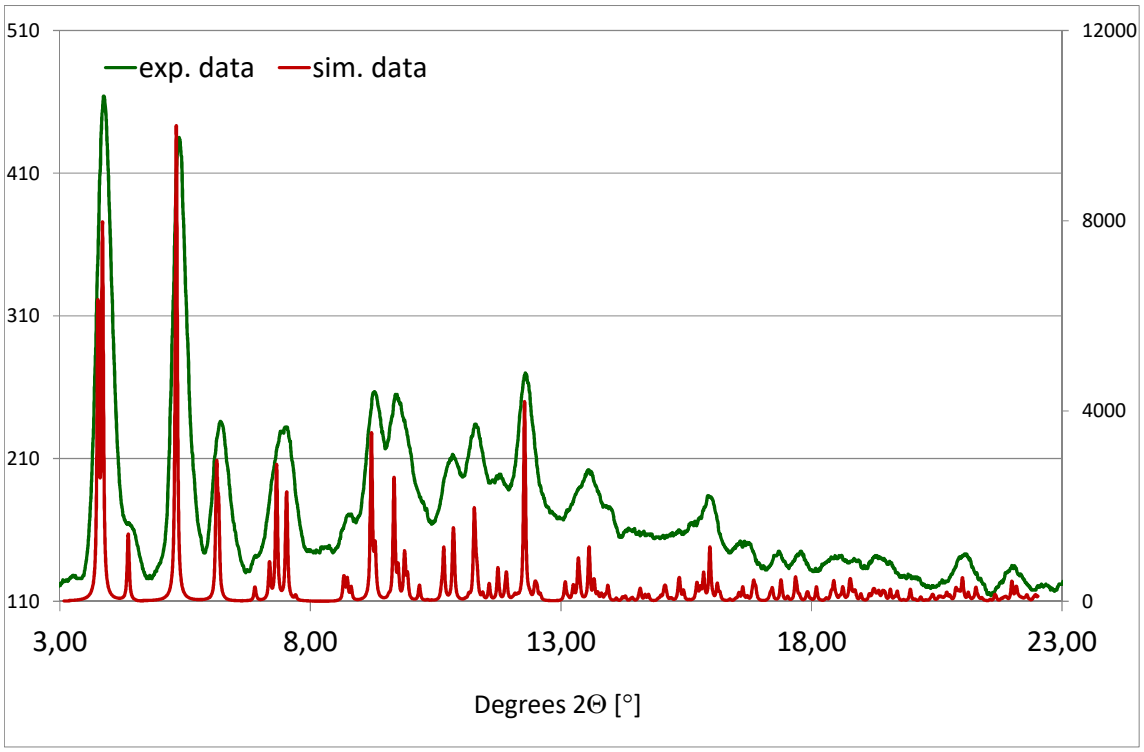
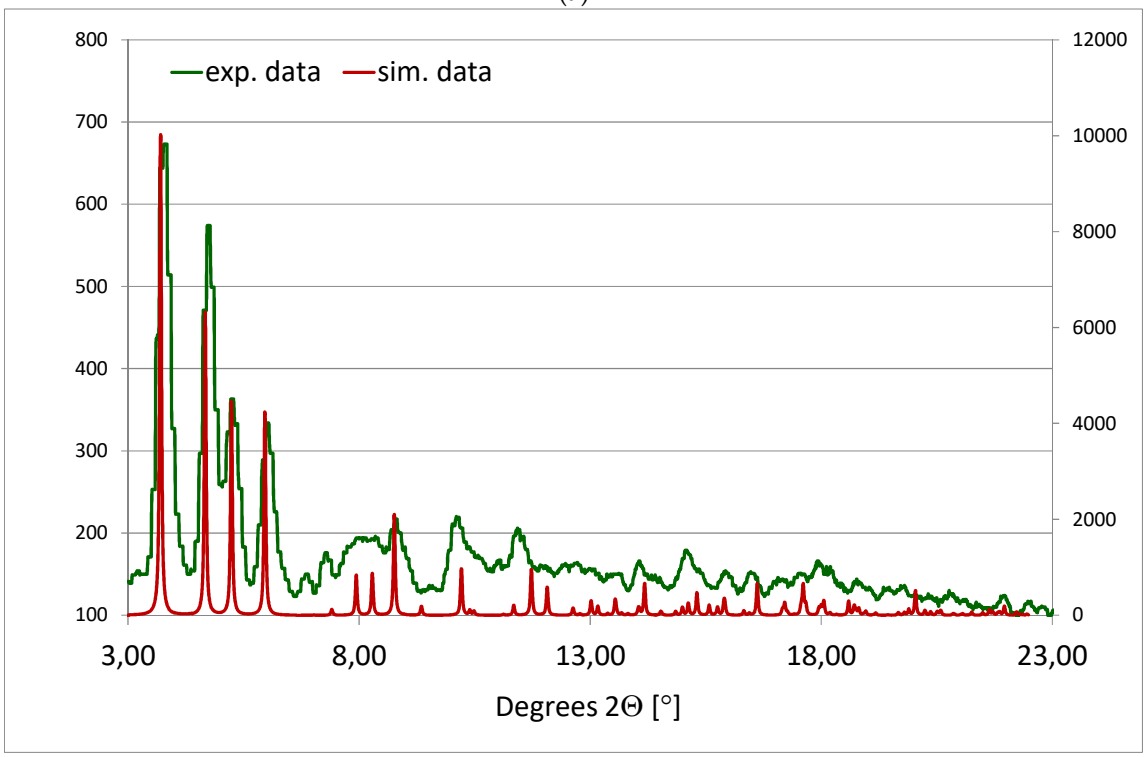


Figure S2. FT-IR spectrum of **4**.



(**a**)



(**b**)

Figure S3. XRD powder spectra of (**a**) **3** and (**b**) **4**. Simulated spectra were calculated with Mercury and re-calculated to Mo Kα using the Bragg equation (the Default calculation in Mercury returns the values for Cu Kα).

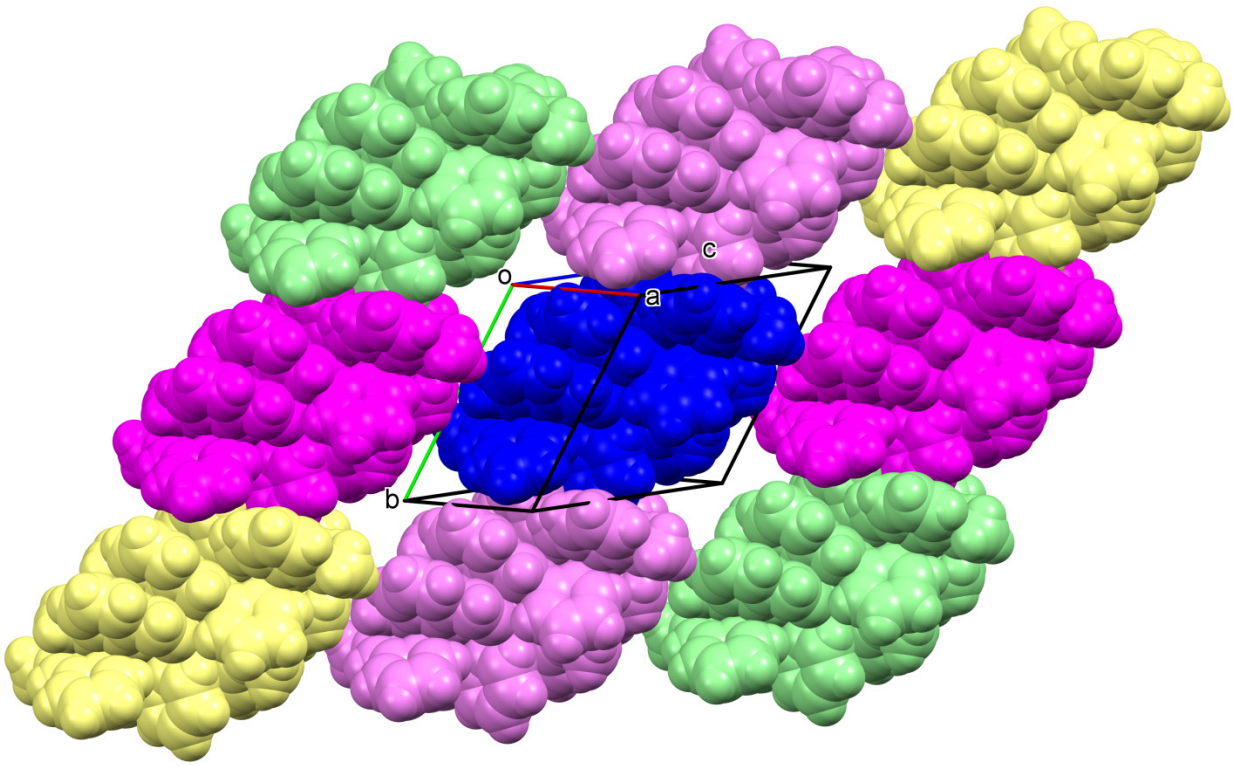


Figure S4. Crystal packing of **1**

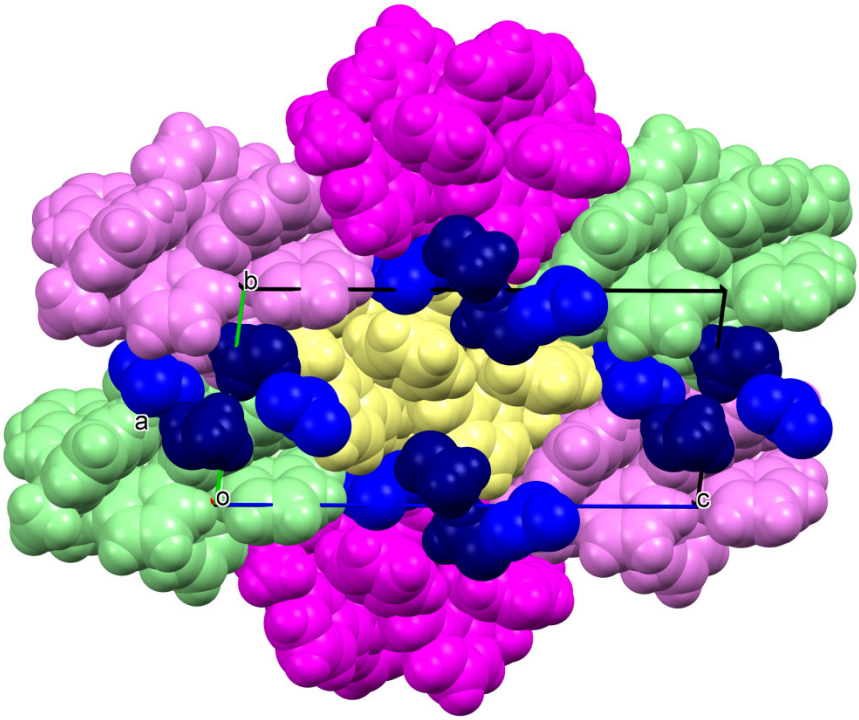


Figure S5. Crystal packing of **2.** Darker blue—methanol, lighter blue—nitrate.

^{1}H NMR DATA of isolated Ni complexes

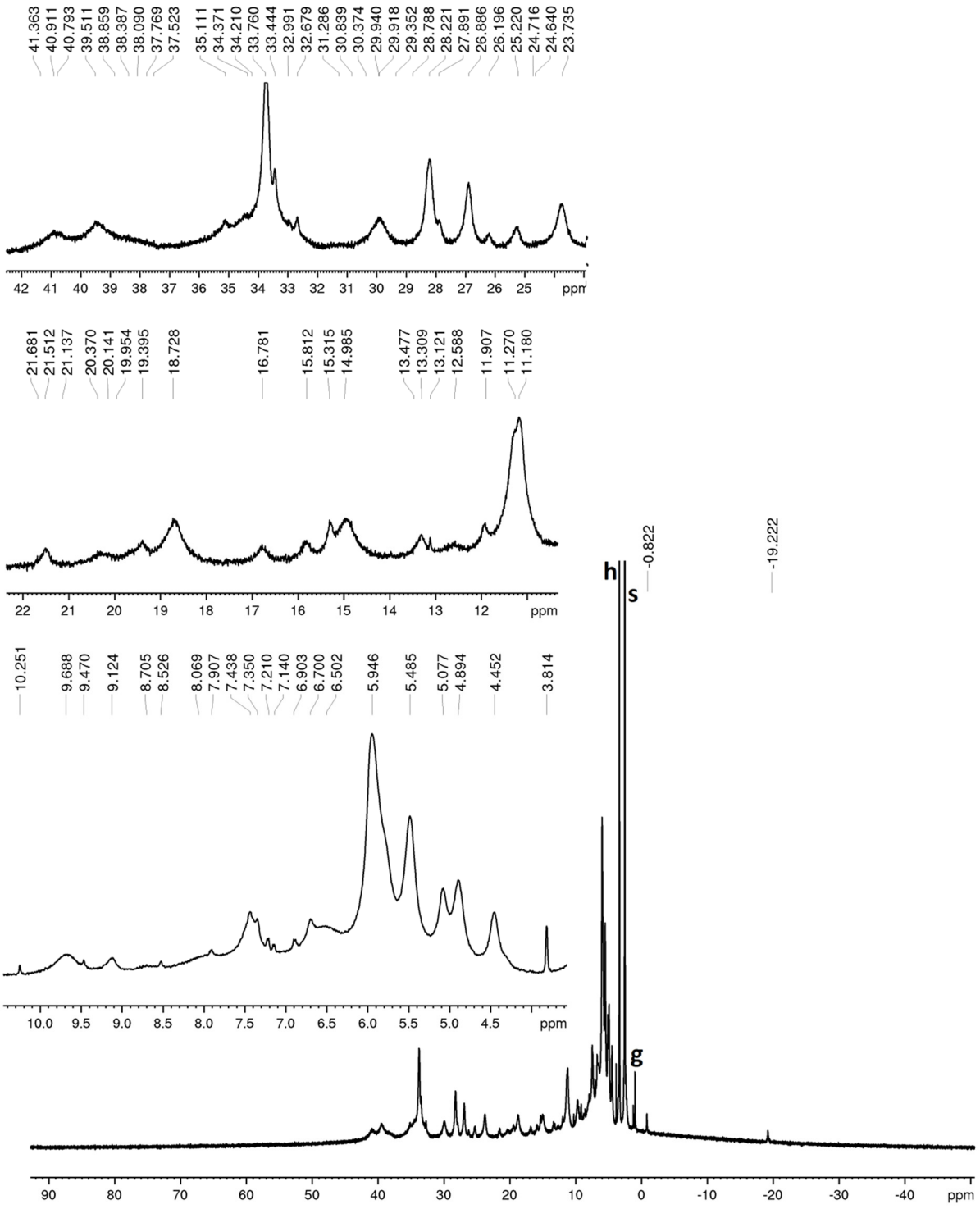


Figure S6. ^{1}H NMR of **1** at room temperature in DMSO-*d*$_6$. Abbreviations in the figure: **g**—grease, **h**—H_2O in deuterated solvent DMSO-*d*$_6$, **s**—residual signal of deuterated solvent DMSO-*d*$_6$.

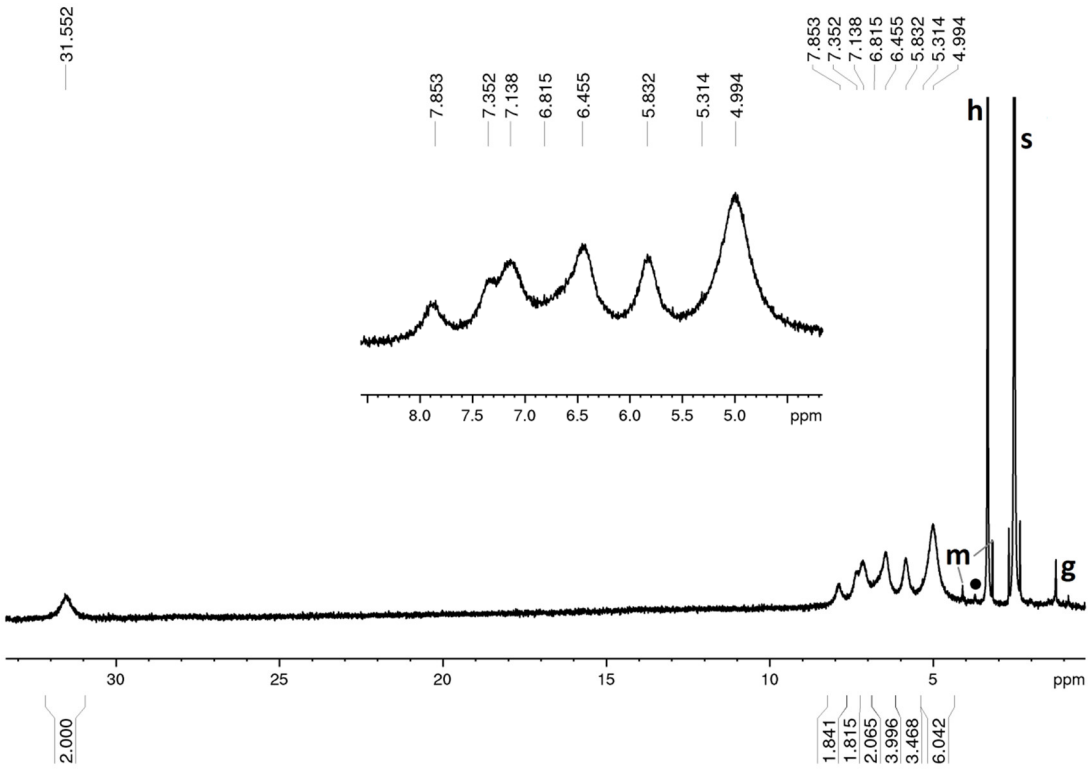


Figure S7. ^{1}H NMR of **3** at room temperature in DMSO-d_6. Abbreviations in the figure: **g**—grease, **h**—H_2O in deuterated solvent DMSO-d_6, **m**—methanol, **s**—residual signal of deuterated solvent DMSO-d_6, ●—unidentified compound.

^{1}H NMR spectra for the effective magnetic moment determination in solution (Evans method)

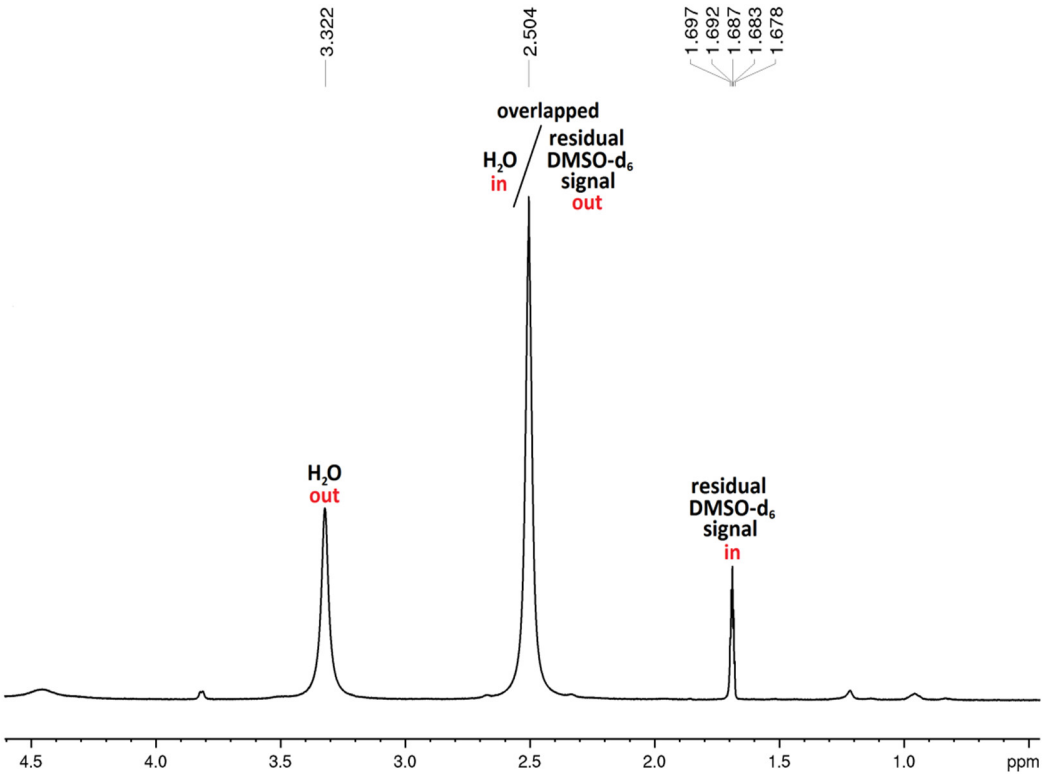


Figure S8. ^{1}H NMR of DMSO-*d*$_6$ in the presence of paramagnetic compound **1** solution in DMSO-*d*$_6$ at room temperature. Abbreviations in the figure: **out**—outer tube, **in**—inner tube/capillary.

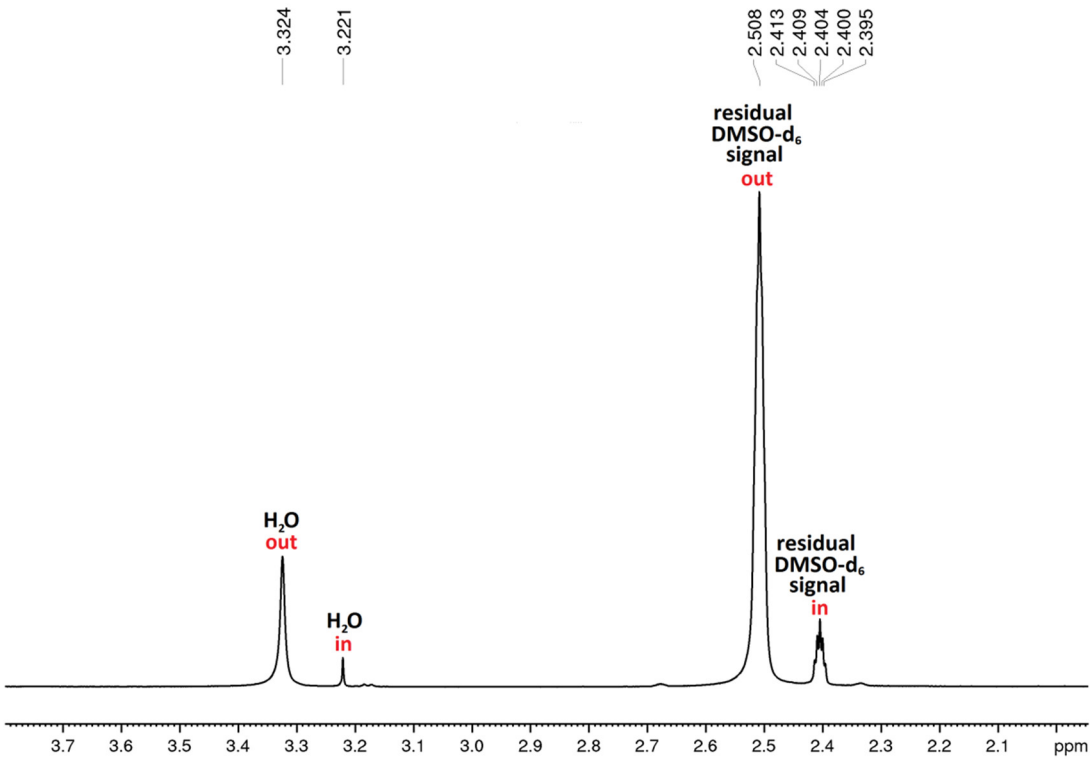


Figure S9. ^{1}H NMR of DMSO-d_6 in the presence of paramagnetic compound **3** solution in DMSO-d_6 at room temperature. Abbreviations in the figure: **out** – outer tube, **in** – inner tube/capillary.

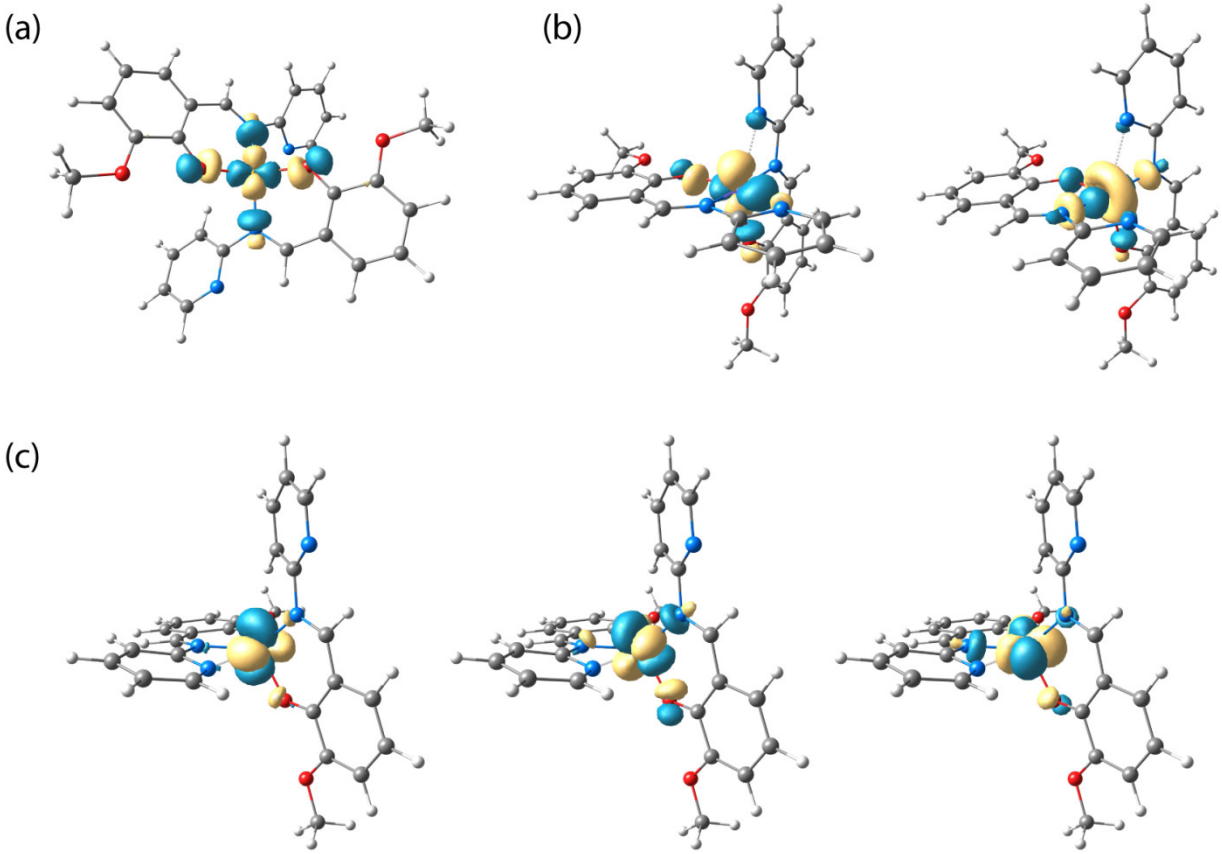


Figure S10. Singly occupied orbitals of the M(L1)$_2$ models of (**a**) Cu, (**b**) Ni, and (**c**) Co.