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Supplementary information for:

Strong ferromagnetic exchange coupling in a $\{Ni^{II}_4\}$ cluster mediated through an air-stable tetrazine-based radical anion

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Experimental section

Materials

All manipulations were carried out under aerobic/ambient conditions. Chemicals were purchased from TCI, Alfa Aesar, and Stream Chemicals, and used without further purification.

Synthesis

3,6-bis(2-pyrimidyl)-1,2,4,5-tetrazine (BpymTz):
The ligand was prepared according to a modified procedure and exhibit spectral data identical to a previous report.[1]
To a dark yellow solution of 2-cyanopyrimidine (3 g, 28 mmol, 1 eq) and hydrochloric acid (4.5 mL, 55 mmol, 2 eq) in THF (40 mL) was added drop wise hydrazine hydrate (79%) (10.2 mL, 160 mmol, 6 eq). The resulting mixture was stirred under reflux over 4 h, then 40 mL of water was added to hydrolyse the reaction. THF was removed under reduced pressure and the product was extracted several times with CH_2Cl_2. The organic phase was combined and the solvent was removed under reduced pressure to afford H_2BPymTz as a bright orange solid. The compound was used in the next step without further purification. H_2BPymTz was dissolved in DMF and NO_2 gas was bubbled through the solution over 30 min. the gas was generated by the reaction of concentrated HNO_3 with copper turnings. Upon bubbling, a bright purple precipitated was formed and the solid was filtrated off and washed with cold water to afford 4.5 g of BPymTz in 68 % yield. ^{1}H NMR (400 MHz; $CDCl_3$) δ 9.18 (d, *J* = 4.9 Hz, 4H), 7.63 (t, *J* = 4.9 Hz, 2H).

$[Ni^{II}_4(BPymTz)(Cl)_6(DMF)_8]Cl_2$ (1):
To a purple solution of BPymTz ligand (59 mg, 0.25 mmol) in DMF (20 mL) was added $NiCl_2{\cdot}6H_2O$ (237.69 mg, 1 mmol). After being stirred for 1 min the suspension turned dark green. The mixture was placed in a sealed vial. Orange rectangular crystals of **1** (yield = 30%) were collected by filtration after several days. Selected IR (cm^{-1}) 3233.69 (s), 1643.55 (s), 1590.16 (m), 1497.71 (m), 1436.65 (m), 1378.44 (s), 1251.30 (m), 1204.48 (m), 1108.05 (s), 1056.52 (m), 1030.94 (w), 760.98 (m), 682.95 (m), 661.21 (m). Elemental Analysis: Expected: C 31.06% H 4.83% N 17.04% Found: C 31.21% H 4.63% N 16.96%

Physical measurements

X-ray crystallography
Suitable crystals were mounted on a glass fiber. A Bruker APEX-II CCD device was used to collect unit cell and intensity data using graphite Mo Kα radiation (λ = 0.71073). The data reduction included a correction for Lorentz and polarization effects, with an applied multiscan absorption correction (SADABS). The crystal structure was solved and refined using the SHELXTL program suite.[2] Direct methods yielded all non-hydrogen atoms, which were refined with anisotropic thermal parameters. All hydrogen atom positions were calculated geometrically and were riding on their respective atoms.

FTIR spectroscopy

Solid-state infrared spectra were obtained on a Varian 640 FT-IR spectrometer in the 400-4000 cm^{-1} range.

Magnetic measurements

Variable temperature magnetic susceptibility and magnetization measurements were performed on a crushed polycrystalline sample of 1 using a Quantum Design MPMS-XL7 SQUID magnetometer equipped with a 7 T dc magnet, in the temperature range 1.8 - 300 K for dc applied fields up to 7 T. An *M vs. H* measurement was

performed at 100 K to confirm the absence of ferromagnetic impurities. Diamagnetic corrections were applied to the sample holder and to the observed paramagnetic susceptibility of 1 using Pascal constants.

Table S1. Crystallography data of the complex **1**

Empirical formula	$C_{34}H_{63}Cl_7N_{16}Ni_4O_{8.5}$
Formula weight	1314.91
Crystal system	Monoclinic
Space group	C2/c
a/Å	11.7191(4)
b/Å	23.4564(7)
c/Å	21.6135(7)
α/ °	90
β/ °	91.4944(14)
γ/ °	90
V/ Å^3	5939.27
Z	4
T/K	200(2)
Radiation	Mo-K_α
Wavelength	0.71073
D_C/mg m^{-3}	1.470
μ/mm^{-1}	1.619
Reflections collected	7335
Goodness-of-fit on F^2	1.021
R1,wR2 (>2σ(I))[a]	0.0406, 0.1266

Table S2. Selected bond lengths (Å) for **1**.

Ni(1)-N(1)	
Ni(1)-O(1)	
Ni(1)-O(2)	
Ni(1)-N(4)#1	
Ni(1)-Cl(2)	
Ni(1)-Cl(1)	
Ni(2)-N(2)	
Ni(2)-O(3)	
Ni(2)-O(4)	
Ni(2)-N(3)	
Ni(2)-Cl(3)	
Ni(2)-Cl(1)	

Table S3. Selected angles (°) for **1**.

N(1)-Ni(1)-O(1)	
N(1)-Ni(1)-O(2)	
O(1)-Ni(1)-O(2)	
N(1)-Ni(1)-N(4)#1	
O(1)-Ni(1)-N(4)#1	
O(2)-Ni(1)-N(4)#1	
N(1)-Ni(1)-Cl(2)	
O(1)-Ni(1)-Cl(2)	
O(2)-Ni(1)-Cl(2)	
N(4)#1-Ni(1)-Cl(2)	
N(1)-Ni(1)-Cl(1)	
O(1)-Ni(1)-Cl(1)	
O(2)-Ni(1)-Cl(1)	
N(4)#1-Ni(1)-Cl(1)	
Cl(2)-Ni(1)-Cl(1)	
N(2)-Ni(2)-O(3)	
N(2)-Ni(2)-O(4)	
O(3)-Ni(2)-O(4)	
N(2)-Ni(2)-N(3)	
O(3)-Ni(2)-N(3)	
O(4)-Ni(2)-N(3)	
N(2)-Ni(2)-Cl(3)	

Table S4. TD-DFT results for the energy states (cm^{-1}) in the neutral and reduced version of the ligand.

Neutral Ligand	**Anion**
1 11227.6	1 1981.1
2 17152.3	2 7332.3
3 21384.0	3 9017.3
4 23404.2	4 10290.0
5 23988.9	5 14123.9
6 24756.0	6 15788.3
7 26044.7	7 16416.5
8 26293.7	8 18680.6

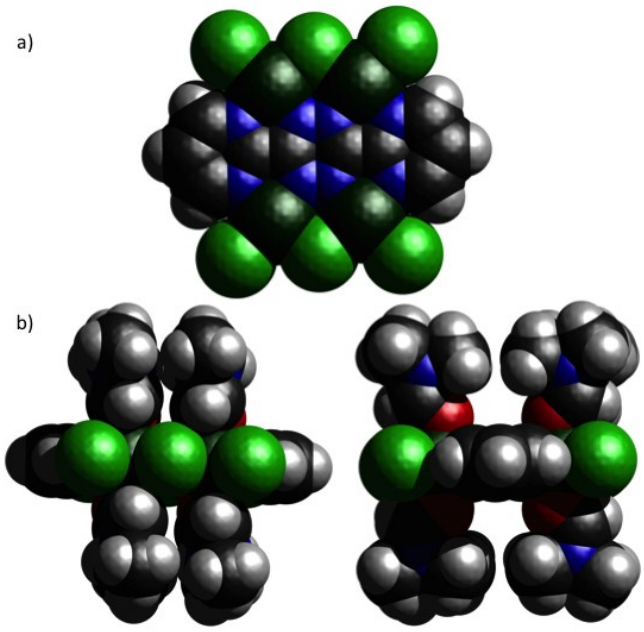

Figure S1. Space-filling model of the molecular structure of 1 highlights the featuring of the metal ions, chlorine atoms and DMF solvent molecule in the coordination environment. a) Top view of the structure. In the center of the picture is placed the ligand BPymTz. The DMF solvent molecules were omitted to emphasize the metal accommodation in the ligand pocket. b) Side (right) and front (left) views of the complex. Atom colors: Ni (dark green), H (light grey), C (dark grey), N (blue), O (red) and Cl (light green).

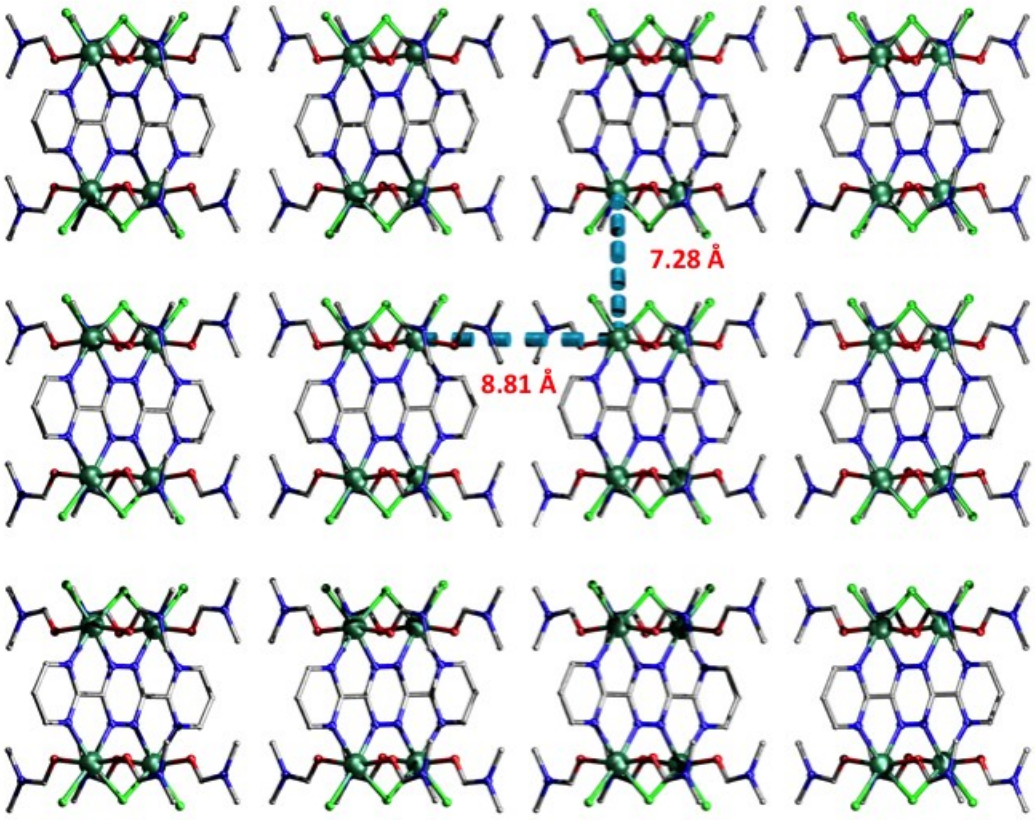

Figure S2. Crystal packing diagram of 1 along the *a* axis of the unit cell showing the metal-metal distance along the *b* and *c* axis.

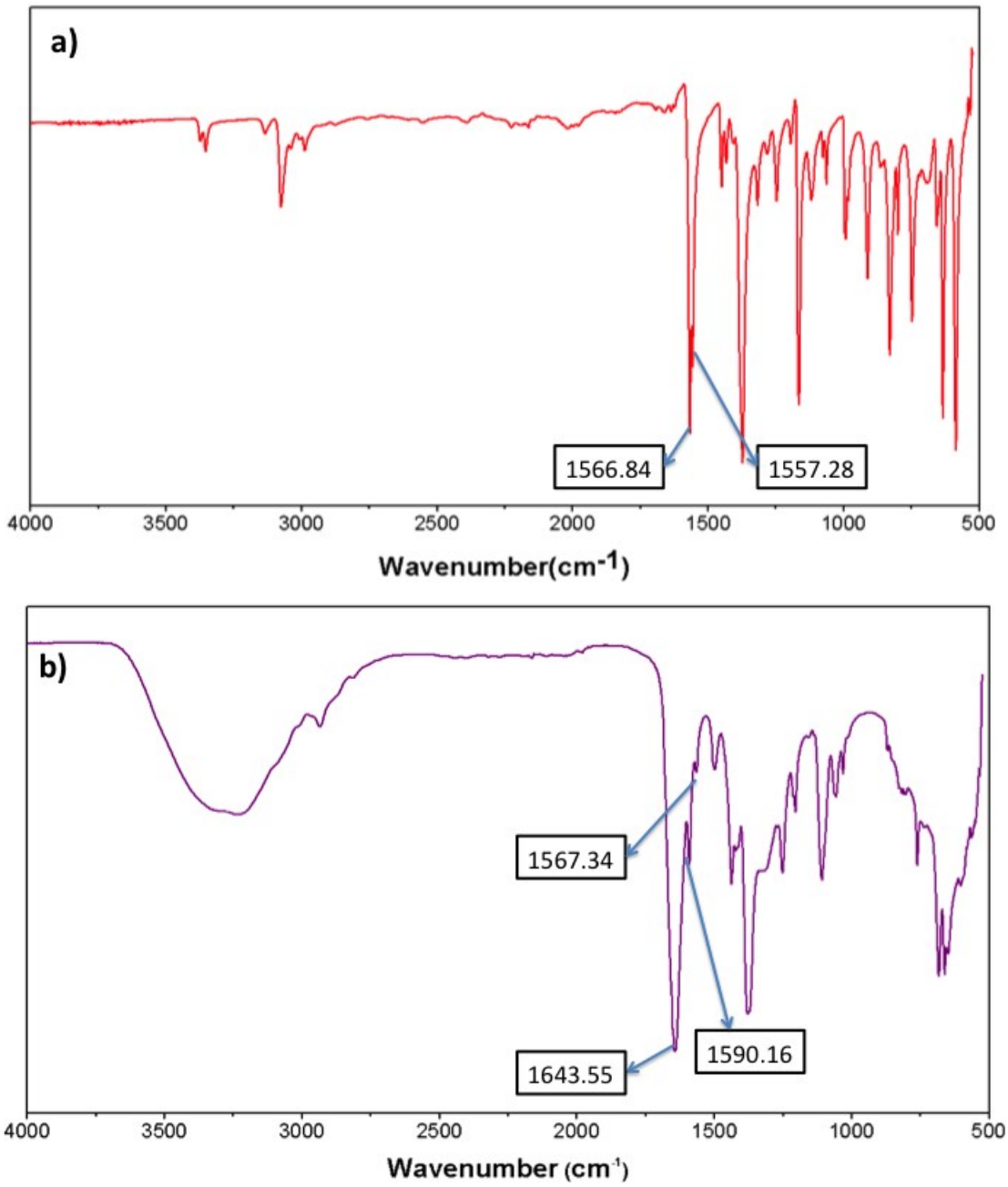

Figure S3. FT-IR spectra of ligand a) and complex b) at room temperature. The doublet at 1566.84 and 1557.28 cm^{-1} in a) indicates bpym ring-stretching while in b) the doublet at 1590.16 and 1567.34 cm^{-1} indicates bpym-bridged ligand. In the plot b) DMF absorption peak is characterized by the strong intensity at 1643.55 cm^{-1}.

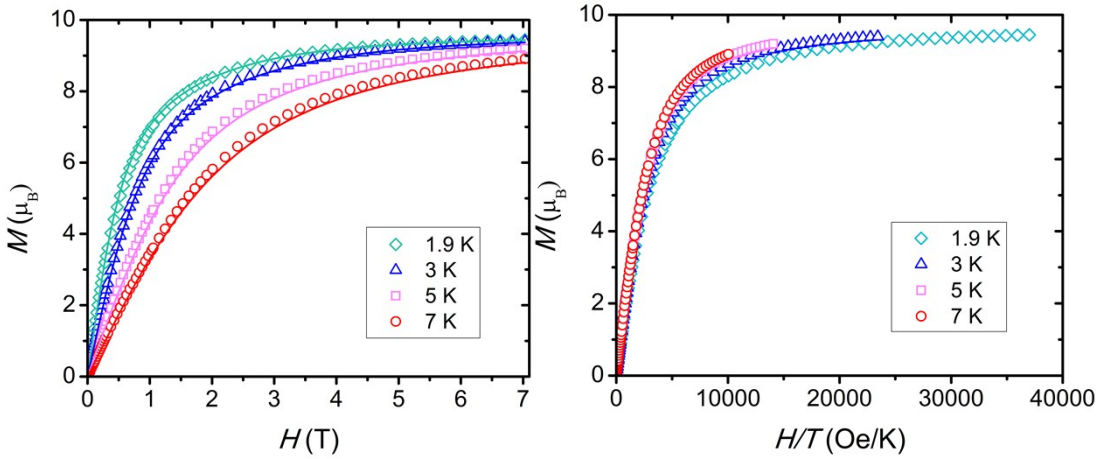

Figure S4. *M vs. H* (left) and *M vs. H*/*T* (right) plots for **1** between 1.9 and 7 K. Solid lines in the *M vs. H* plot correspond to the best fit obtained using the model described in the text.

References

1 W. Kaim, J. Z. Fees, *Naturforsch. B* 50b, **1995**, 123

2 (a) G. M, Sheldrick. SHELTXL; Siemans Analytical X-ray Instruments Inc.: Madison, WI, 1995. (b) G. M, Sheldrick. SHELX97 – *Programs for Solving and Refining X-ray Structures*; University of Gottingen, Gottingen, Germany, 1997.