

Salen-Based Metal Organic Frameworks of Nickel and the Lanthanides

Peter W. Roesky^{[a]*} Asamanjoy Bhunia,^[a] Yanhua Lan,^[a] Annie K. Powell,^[a] and
Sven Kureti^[b]

*^aInstitut für Anorganische Chemie, Karlsruher Institut für Technologie (KIT), Engesserstr. Geb.
30.45, 76128 Karlsruhe (Germany)*

*^bInstitut für Technische Chemie und Polymerchemie, Karlsruher Institut für Technologie
(KIT), Engesserstr. 18 76128, Karlsruhe (Germany)*

Supporting Information

9 pages

Experimental Section.

General considerations: NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane. Deuterated solvents were obtained from Chemotrade or Euriso-Top GmbH (99 atom % D). Elemental analyses were carried out with an Elementar vario EL III. TGA measurements were made on a Netzsch STA 429 instrument.

Ethylenediamine, 4-formyl-3-hydroxybenzoic acid and the solvents were used as purchased from commercial sources without further purification.

$\{[\text{Er}_2(\text{LNi})_3(\text{DMF})(\text{H}_2\text{O})_3]\cdot 4(\text{DMF})\cdot 10(\text{H}_2\text{O})\}_n$ (**2**): $[\text{Na}_4(\text{LNi})_2\cdot(\text{H}_2\text{O})_9]_n$ (**1**) (45 mg, 0.04 mmol) was dissolved in a few drops of water and 5 mL of DMF. $\text{Er}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ (0.071, 0.16 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. After 3 months, reddish orange crystals were collected by filtration, washed with cold methanol and diethyl ether and dried in vacuum. Yield: 22 mg, 49 % (based on Ni-salen). Anal. Calcd for $\text{C}_{69}\text{H}_{97}\text{Er}_2\text{N}_{11}\text{Ni}_3\text{O}_{36}$: C, 38.24; H, 4.51; N, 7.11. Found: C, 38.68; H, 3.99; N, 6.92. IR (KBr) : $\nu = 3380$ (m), 2964 (w), 2936 (w), 1664 (m), 1623 (s), 1589 (m), 1418 (w), 1390 (s), 1295 (w), 1217 (w), 1200 (w), 1137 (w), 1115 (w), 979 (m), 836 (w), 812 (w), 774 (s), 685 (w), 540 (w), 467 (w) cm^{-1} .

$\{[\text{Lu}_2(\text{LNi})_3(\text{DMF})(\text{H}_2\text{O})_3]\cdot 4(\text{DMF})\cdot 10(\text{H}_2\text{O})\}_n$ (**3**): $[\text{Na}_4(\text{LNi})_2\cdot(\text{H}_2\text{O})_9]_n$ (**1**) (45 mg, 0,04 mmol) was dissolved in few drops of water and 5 mL of DMF. $\text{Lu}(\text{NO}_3)_3\cdot 4\text{H}_2\text{O}$ (0.072, 0.16 mmol) was added and the reaction mixture was stirred at room temperature for 30 min. After 2 months, reddish orange crystals were collected by filtration, washed with cold methanol and diethyl ether and dried in vacuum. Yield: 25 mg, 55 % (based on Ni-salen). Anal. Calcd for $\text{C}_{69}\text{H}_{97}\text{Lu}_2\text{N}_{11}\text{Ni}_3\text{O}_{36}$: C, 37.97; H, 4.48; N, 7.06. Found: C, 38.89; H, 4.08; N, 6.88. IR (KBr) : $\nu = 3402$ (m), 2963 (w), 2919 (w), 1653 (m), 1620 (s), 1580 (m), 1519 (m), 1482 (m), 1424 (s), 1387 (w), 1344 (w), 1296 (s), 1218 (w), 1202 (w), 1115 (w), 1091 (w),

1058 (w), 977 (s), 899 (w), 848 (w), 812 (w), 779 (s), 684 (w), 620 (w), 540 (w), 470 (w) cm^{-1} . No NMR data could be collected because compound 3 is almost insoluble in any solvent we tried.

$\{[\text{Dy}(\text{LNi})(\text{DMSO})(\text{NO}_3)]_2(\text{H}_2\text{O})\cdot(\text{DMSO})\}_n$ (**4**): H_4L (109 mg, 0.3 mmol) was dissolved in DMSO / THF (25/5 mL). The resulting solution was added to a solution of NaOH (25 mg, 0.6 mmol) in 1 mL of water. The reaction mixture was stirred for 5 min and then $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (52 mg, 0.2 mmol) and $\text{Dy}(\text{NO}_3)\cdot 5\text{H}_2\text{O}$ (178 mg, 0.4 mmol) were added. The reaction mixture was then heated under reflux for 2 h, and then cooled to room temperature. Then, the mixture was filtered and kept for crystallization at room temperature. After one month, red needle shaped crystals were collected, washed with diethyl ether and dried in vacuum. Yield: 54 mg, 21 % (based on H_4L). Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{DyN}_3\text{NiO}_{13}\text{S}_2$: C, 31.92; H, 3.41; N, 5.08. Found: C, 32.48; H, 3.83; N, 4.69. IR (KBr) : $\nu = 3423$ (m), 2997 (w), 2919 (w), 1619 (s), 1561 (m), 1518 (s), 1483 (w), 1422 (s), 1410 (w), 1343 (w), 1294 (m), 1217 (w), 1200 (w), 1138 (w), 1092 (w), 1017 (m), 977 (m), 892 (w), 844 (w), 814 (w), 775 (s), 742 (w), 685 (w), 654 (w), 540 (w), 467 (w) cm^{-1} .

TGA measurements:

All the compounds are very robust. At room temperature they retain their crystalline behavior for couple of months. TGA measurements were performed for all compounds (see supporting information). The TGA of complex **2** shows that eight of the lattice water molecules are lost at the temperature 45-102 °C (obsd 6.08 %, calcd 6.6 %). Then the compound is stable up to 160 °C. The other guest solvent molecules (four DMF and two water molecules) are lost in the temperature range 160-360 °C (obsd 14.31 %, calcd 15.13 %). After the loss of guest solvent molecules, the network began to decompose with the continuous weight loss up to 450 °C. Compound **3** shows a slightly different TGA curve. Eight lattice water molecules are lost at the temperature 55-140 °C (obsd 6.52 %, calcd 6.6 %). The other two water molecules and the four DMF lattice solvent molecules are lost in the temperature range 140-326 °C (obsd 13.44 %, calcd 14.98%). After the loss of guest solvent molecules, the network began to decompose with the continuous weight loss up to 450 °C. The TGA curve of complex **4** is different. The weight loss of 4.3 % was observed at the temperature 30-90 °C which corresponds to the loss of the coordinated water molecules (calcd 5.27 %). Then the compound is stable up to 160. The two DMSO molecules were lost in the temperature 160-310 °C (obsd 19.38 %, calcd 18.87 %). Then the compound starts to decompose with continuous weight loss up to 450 °C.

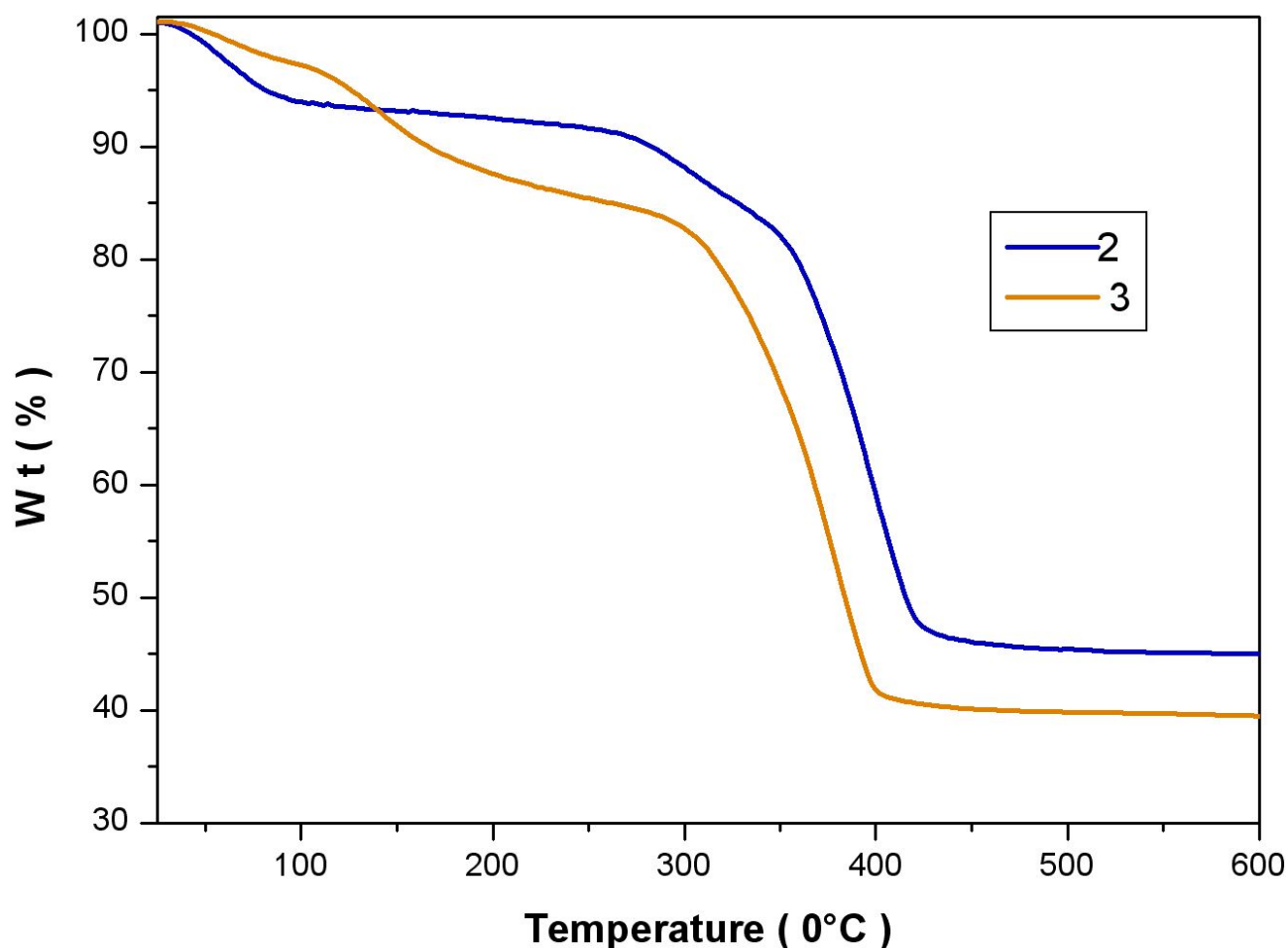


Figure S1. TGA for **2** and **3** in temperature range of 25 to 600 °C at the heating rate of 5 °C/ min under the N₂ atmosphere.

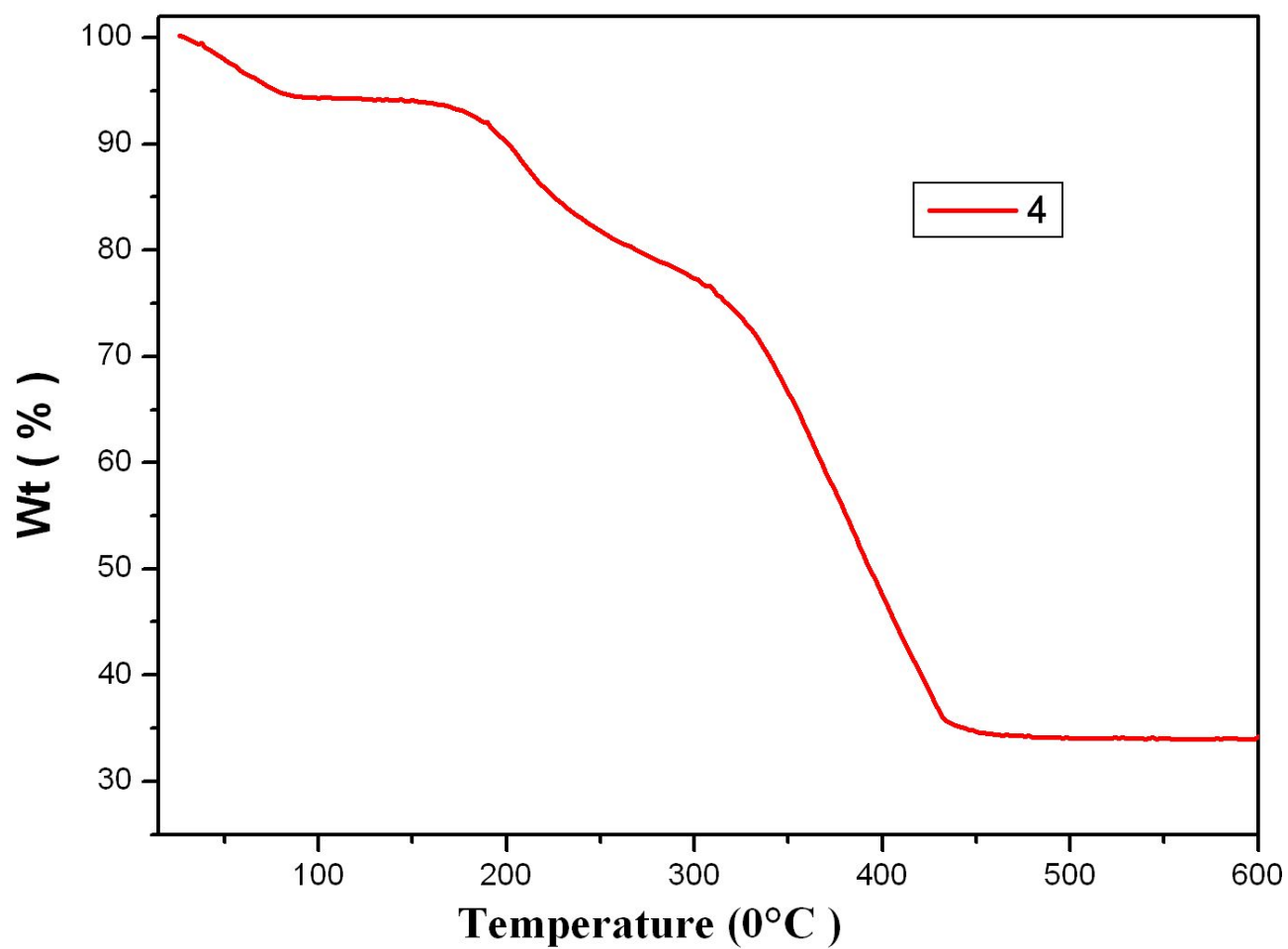
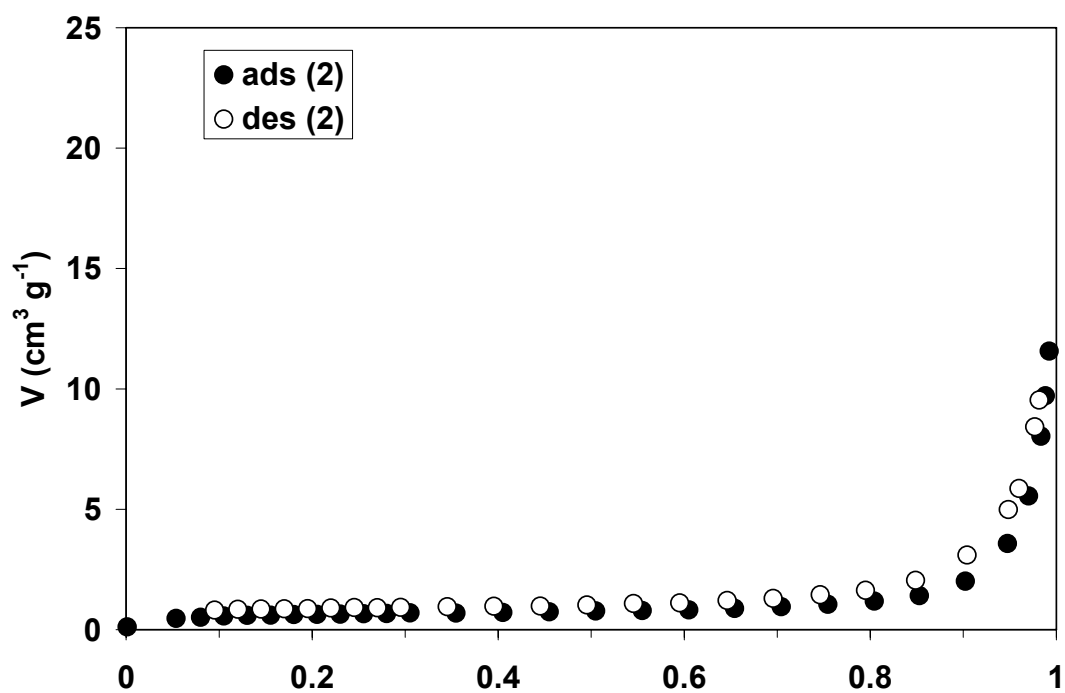


Figure S2. TGA for **4** in temperature range of 25 to 600 °C at the heating rate of 5 °C/ min under the N₂ atmosphere.

BET measurements

N₂ adsorption/desorption isotherms were performed on a multi-point BELSORP-mini II from BEL. N₂ was used as adsorbate being considered to penetrate the pores of compounds **2** and **3**. The respective sample was pretreated at 150°C for 2 h in vacuum (10⁻⁴ mbar) to avoid decomposition of the framework. Then, it was cooled to -196°C and the N₂ isotherm was recorded. From the adsorption data recorded at p/p₀ ratios between 0.05 and 0.30 the BET surface area was derived.



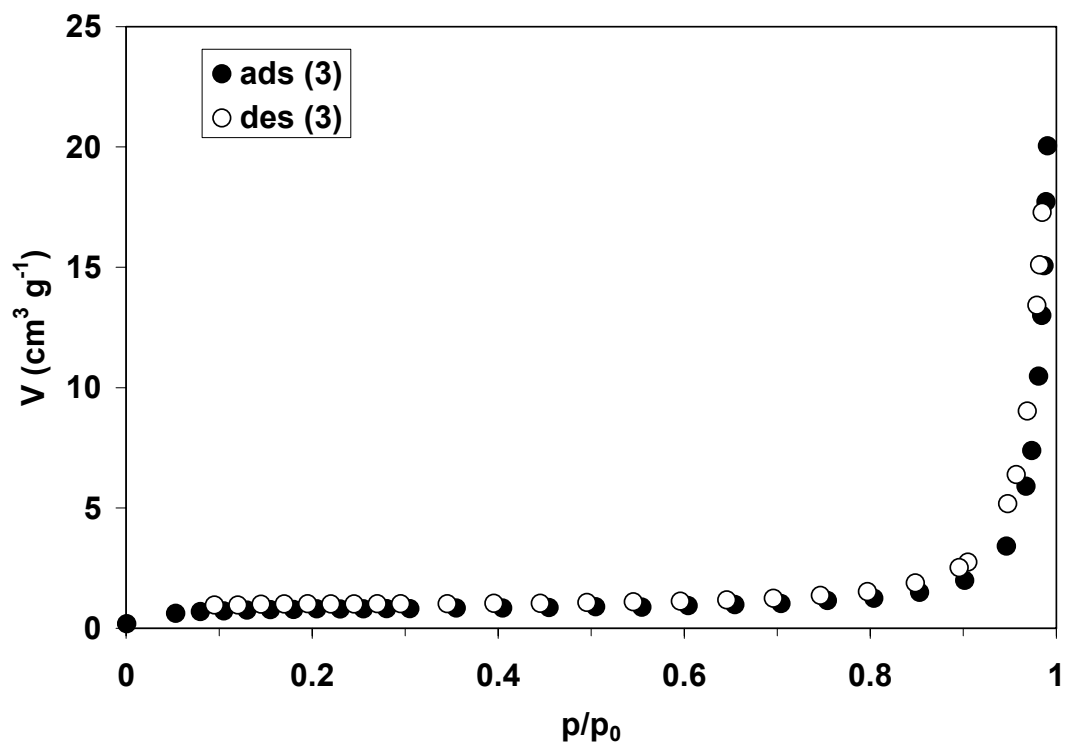


Figure S3. N_2 adsorption/desorption isotherm of compounds **2** (top) and **3** (bottom) recorded at -196°C .

Magnetic measurements

Magnetic Measurements: The magnetic measurements were carried out with the use of a Quantum Design SQUID magnetometer MPMS. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on the polycrystalline samples dispersed in eicosane. The magnetic data were corrected for the sample holder.

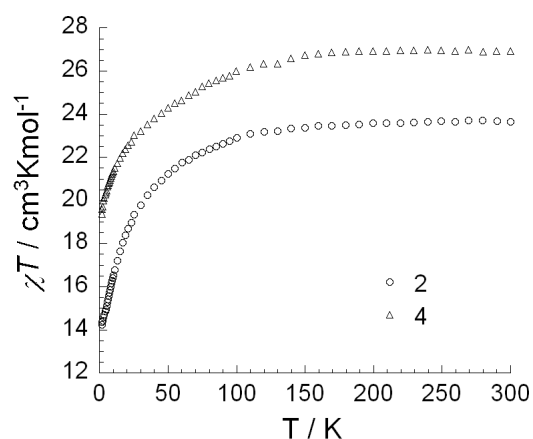


Figure S4. Temperature dependence of the χT products for compounds **2** and **4** at 0.1 T (with χ being the molar susceptibility defined as M/H).

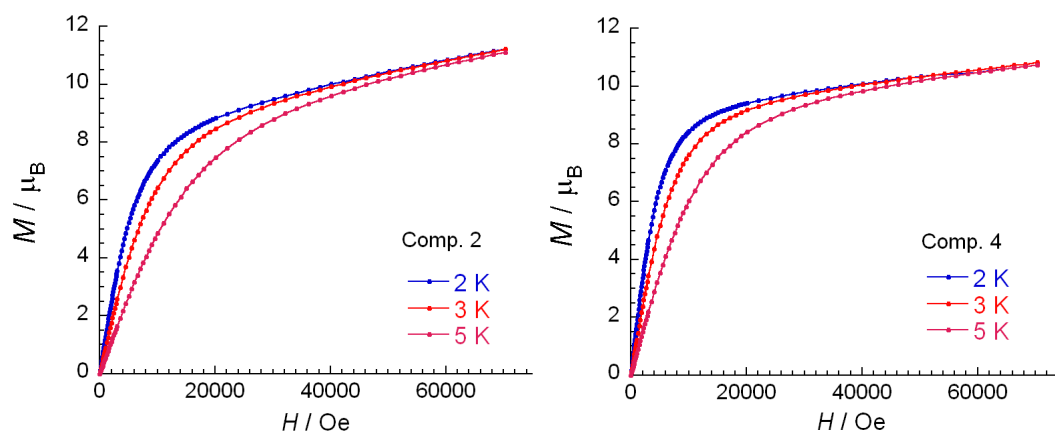


Figure S5. Low-temperature magnetization curves for compounds **2** and **4**.

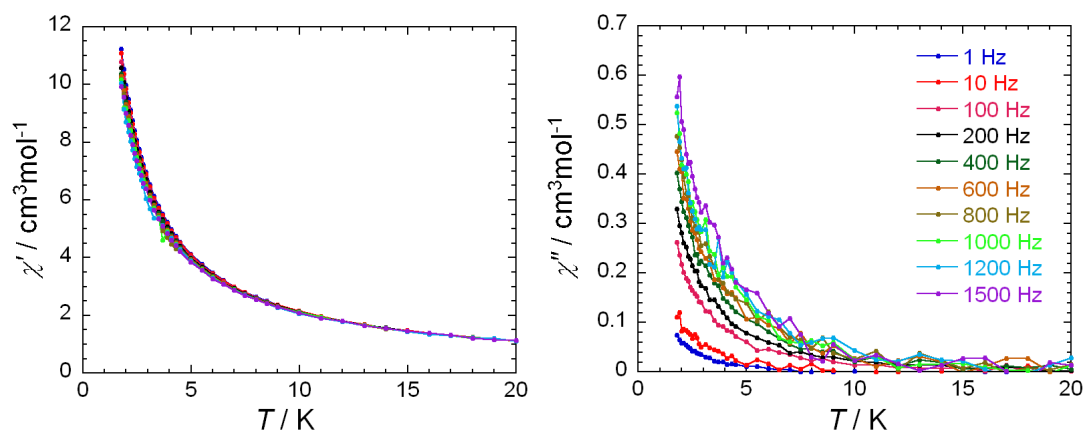


Figure S6. Temperature dependence of the in-phase and out-of-phase components of the ac magnetic susceptibility at indicated frequencies, for **4** under zero dc field.