

Supporting information for the manuscript

A zig-zag uranyl(V)-Mn(II) single chain magnet with high relaxation barrier.

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Contribution from

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1. General considerations.

All manipulations were carried out under an inert argon atmosphere using Schlenk techniques and an MBraun glovebox equipped with a purifier unit. The water and oxygen level were always kept at less than 1 ppm. The solvents were purchased from Aldrich in their anhydrous form conditioned under argon and were vacuum distilled from K/benzophenone (hexane, pyridine). $[\text{Mn}(\text{NO}_3)_2(\text{Py})_3]$ was obtained by extraction of the hydrated salts in hot pyridine followed by high vacuum drying at 40°C for 7 days. Cp^*_2Co was purchased from Aldrich and sublimated prior to use. The $\text{H}_2\text{Mesaldien}$ ligand was prepared as previously described.¹ The $[\text{UO}_2(\text{Mesaldien})]$ complex² was prepared from $\text{UO}_2(\text{NO}_3)_3$ and the $\text{H}_2\text{Mesaldien}$ ligand according to the procedures used for other uranyl(VI) complexes.^{3a, 3b, 3c} Elemental analyses were performed under argon by Analytische Laboratorien GMBH at Lindlar, Germany. ¹H NMR spectra were recorded on Bruker 200 MHz spectrometer. NMR chemical shifts are reported in ppm with solvent as internal reference.

Caution: Depleted uranium (primary isotope ^{238}U) is a weak α -emitter (4.197 MeV) with a half-life of 4.47×10^9 years. Manipulations and reactions should be carried out in monitored fume hoods or in an inert atmosphere glovebox in a radiation laboratory equipped with α - and β -counting equipment.

2. Synthesis

2.1 Synthesis of {[UO₂(Mesaldien)][Cp^{*}₂Co]}Py 1.Py

To a stirred orange suspension of [UO₂(Mesaldien)] (35.5mg, 0.06mmol, 1eq.) in 1mL of pyridine, a dark brown suspension of Cp^{*}₂Co (19.7mg, 0.06mmol, 1eq.) in 2mL of pyridine is added. The resulting dark green solution of [UO₂(Mesaldien)][Cp^{*}₂Co] is then stirred for two hours and the solution is filtrated. This solution is then layered with 10mL of hexane to afford after 3 days, dark green X ray quality crystals of 1.0.6Py (52.4 mg, 90 %). ¹H NMR (200 MHz, Py-D5, 298 K): δ = 6.86 (br s, 30H, Cp^{*}), 5.27 (tr, 2H), 4.37 (tr, 2H), 3.96 (d 2H), 3.68 (s, 2H), 1.14 (tr, 2H), -2.08 (d, 2H), -5.09 (d, 2H), -7.75 (s, 3H), -9.19 (d, 2H), -9.72 (tr, 3H).

Elemental analysis calcd (%) for 1.0.6Py, {[UO₂(Mesaldien)][Cp^{*}₂Co]}.0.6Py (C₄₂H₅₄CoN_{3,6}O₄U, M_r=970.21) C 51.99, H 5.61, N 5.20; found C 51.85, H 5.45, N 5.54.

2.2 Synthesis of {[UO₂(Mesaldien)][Mn(NO₃)(Py)₂]}_n.2.2Py

A white suspension of Mn(NO₃)₂Py₃ (67.2mg, 0.16mmol, 1eq.) in 5mL of pyridine is added to a dark green solution of [UO₂(Mesaldien)][Cp^{*}₂Co] (147.4mg, 0.16mmol, 1eq.) in 5 mL of pyridine to yield a red solution. Dark pink crystals form overnight and are collected by filtration and washed with 10*1mL pyridine until all traces of Cp^{*}₂CoNO₃ are removed yielding complex 2.1.6Py (106.2mg, 66% yield). X-ray quality single crystals of 2.2py were obtained from a diluted pyridine solution (5.4mM).

Elemental analysis calcd (%) for 2.1.6Py, {[UO₂(Mesaldien)][Mn(NO₃)(Py)₂]}(Py)_{1,6} (C₃₇H₃₉MnN_{7,6}O₇U, M_r=994.97) C 44.67, H 3.95, N 10.70; found C 44.57, H 4.10, N 11.07.

3. X-ray Crystallography.

Diffraction data were taken using an Oxford-Diffraction XCallibur S kappa geometry diffractometer (Mo-K α radiation, graphite monochromator, $\lambda = 0.71073$ Å). To prevent evaporation of co-crystallised solvent molecules the crystals were coated with light hydrocarbon oil and the data were collected at 150 K. The cell parameters were obtained with intensities detected on three batches of 5 frames. The crystal-detector distance was 4.5 cm. The number of settings and frames has been established taking in consideration the Laue symmetry of the cell by CrysAlisPro Oxford-diffraction software.⁴ 143 for **1** and 257 for **2** narrow data were collected for 1° increments in ω with respectively a 2 s and 100s exposure time. Unique intensities detected on all frames using the Oxford-diffraction Red program were used to refine the values of the cell parameters. The substantial redundancy in data allows empirical absorption correction for **1** and analytical absorption correction for **2** ABSPACK Oxford-diffraction program.⁴ Space groups were determined from systematic absences, and they were confirmed by the successful solution of the structure. The structures were solved by flipping charge method using the Superflip software and refined with SHELXTL 6.14 package.⁵ All non-hydrogen atoms were found by difference Fourier syntheses and refined on F^2 . Hydrogen atoms were fixed in ideal position. Experimental details for X-ray data collections of **1** and **2** are given in Table S1. CCDC Numbers for compounds **1** and **2** are 1058487-1058488.

In spite of the efforts made several A alert remain in the checkcif of the complex **1**.

However, these alert don't caste any doubt on the overall connectivity of this structure.

Comments on A alerts in the checkcif of compound **1**:

PLAT113_ALERT_2_A ADDSYM Suggests Possible Pseudo/New Space group. P42212
Check

The solved structure space group has been chosen as P4₂. Several other space groups were also tested including P 4₂ 2₁ 2 and P 4₂/m n m. From these tests we concluded that:

A symmetry centered space group results always in a fully disordered structure, with ALL the atoms occupying two positions except uranium and cobalt. Moreover the resulting anisotropic displacement parameters would create supplementary alerts in the checkcif.

A non-symmetry centered space group as P 4₂ 2₁ 2 leads always to a 0.5 flack parameter. Despite all our efforts to identify a twin law, nothing was found that leads to an improved structure solution. All the tested alternative solutions did not result in the improvement of the

residue and therefore for all these reasons, the authors decided to publish the structure in the lowest symmetry space group $P 4_2$.

PLAT413_ALERT_2_A Short Inter XH3 .. XHn H11B .. H36B .. 1.85 Ang.

Due to the disorder of the central tertiary amine, this methyl group C11 supports two sets of hydrogens with 0.47 / 0.53 occupation factors. The other atoms correspond to one of the methyl group of the cobaltocenium ion. It is not unusual that methyl group rotates and adopts two different positions at 60° . In this kind of data collection, it has been impossible to observe hydrogen atoms by Fourier transform and they have been fixed in the lowest energy position.

Table S1. Crystallographic data of **1** and **2**

	1.2Py	2.2Py
Formula	C ₄₄ H ₅₆ CoN ₄ O ₄ U	C ₃₉ H ₄₁ MnN ₈ O ₇ U
Crystal size (mm)	0.85 x 0.48 x 0.47	0.378 x 0.052 x 0.013
cryst syst	Tetragonal	Monoclinic
space group	P 4 ₂	I 2/a
volume (Å ³)	4106.56(18)	8010(4)
a (Å)	15.8348(3)	25.9044(9)
b (Å)	15.8348(3)	13.2058(3)
c (Å)	16.3777(5)	23.7598(8)
α (deg)	90	90
β (deg)	90	99.772(3)
γ (deg)	90	90
Z	4	8
formula weight (g/mol)	1001.88	1026.77
density (g cm ⁻³)	1.620	1.703
absorption coefficient (mm ⁻¹)	4.389	4.412
F(000)	1996	4032
temp (K)	150(2)	150.0(2)
total no. reflections	14109	24050
unique reflections [R(int)]	10601 [R(int) = 0.0331]	12079 [R(int) = 0.0656]
Final R indices [I > 2σ(I)]	R1 = 0.0525, wR2 = 0.1141	R1 = 0.0501, wR2 = 0.0697
Largest diff. peak and hole (e.Å ⁻³)	3.443 and -1.227e.Å ⁻³	2.624 and -1.820e.Å ⁻³
GOF	1.031	0.967

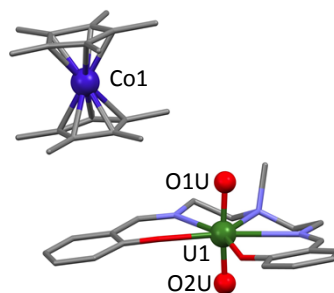


Figure S1. Mercury view of the structure of **1** (ligands were represented in pipes style, H and co-crystallised solvent molecules and disorder of the tertiary amine environment were omitted for clarity, C are represented in grey, O in red, Co in blue, N in light blue and U in green.)

Description of the structure of 1: The structure of **1** reveals a monomeric uranyl(V) complex, where the U atom is seven-coordinated, with a slightly distorted pentagonal bipyramidal geometry, by two trans oxo groups, three nitrogens and two oxygens from the Schiff base ligand. The mean U=O bond distances lie in the range of the values typically observed for uranyl(V) complexes (U1-O1U 1.846(8)Å and U1-O2U 1.845(8)Å).

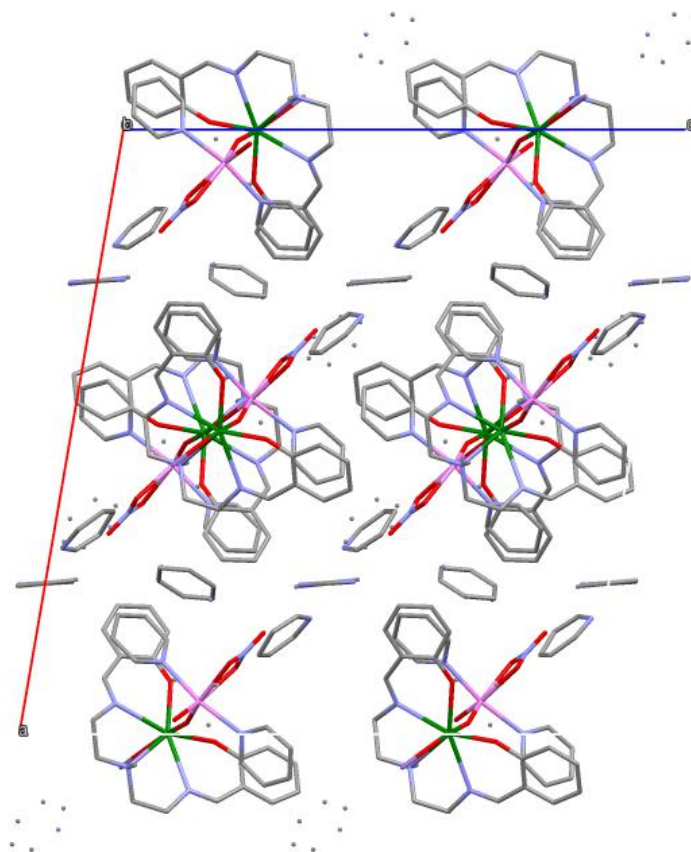


Figure S2. Cell packing along the b axis of complex 2.2Py.

4. NMR spectra

Figure S3. ^1H NMR (200MHz, Py-D5, 298 K) of complex $\{[\text{UO}_2(\text{Mesaldien})][\text{Cp}_2^*\text{Co}]\} \mathbf{1}$

5. Magnetic studies

Variable-temperature magnetic susceptibility and isothermal magnetisation versus field data were recorded in the temperature range 1.8–300 K with a Quantum Design MPMS-XL 7T and a Quantum Design MPMS-XL 5.0 Superconducting Quantum Interference Devices (SQUID). Measurements were carried out on finely ground polycrystalline samples of **2** restrained in eicosane (to prevent sample torqueing). Suprasil-Quartz tubes were used as sample holders and were sealed under vacuum before measurement. Reproducibility of the magnetic measurement was verified by the independent measurement of three samples from three different synthetic batches. The contribution to the signal of the empty sample holder was measured and subtracted from the total signal. Experimental data were further corrected

for the diamagnetic contribution of the compounds using tabulated Pascal's constants. Magnetic calibration was performed using a cylindrical palladium standard having approximately the same geometry of the measured samples. Isothermal magnetization loops were measured while sweeping the magnetic field at a constant rate, from +7 to -7 T and back, with the sample fixed at temperatures ranging from 3.6 to 7.5 K. The real and imaginary components, χ' and χ'' , of the complex ac magnetic susceptibility were measured as a function of temperature (3.6-7.5 K) and frequency (0.1 -1400 Hz) using a Quantum Design MPMS-XL 7T magnetometer. All ac measurements were performed under an oscillating field of 1.55 G.

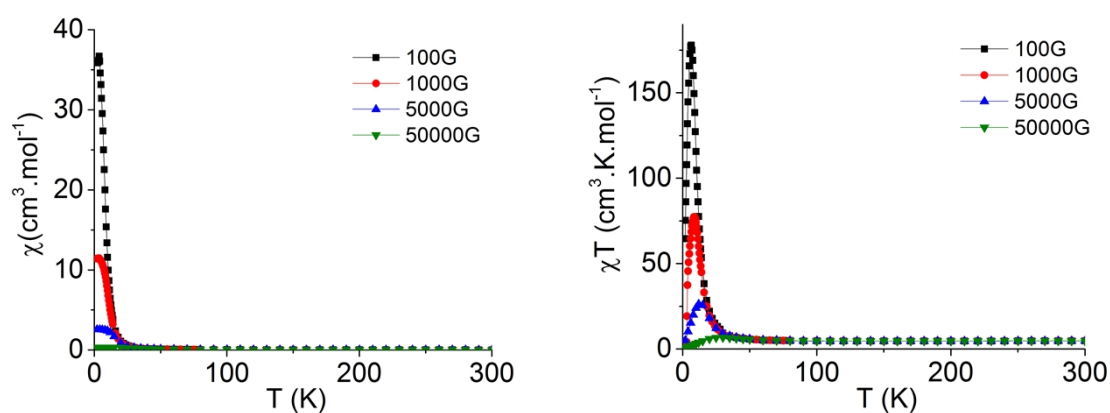


Figure S4. (left) Temperature dependence of the magnetic susceptibility χ as a function of temperature T for **2** in field-cooled regime measured at three different fields between 0.01 and 5 T. (right) Temperature dependence of χT for the same fields.

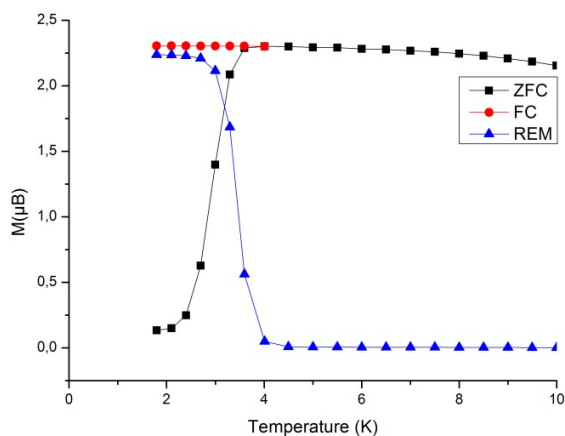


Figure S5. Temperature dependence of the magnetization of **2** measured in zero field-cooled (ZFC), field cooled (FC) regimes and remnant magnetization at magnetic fields of 0.5 T.

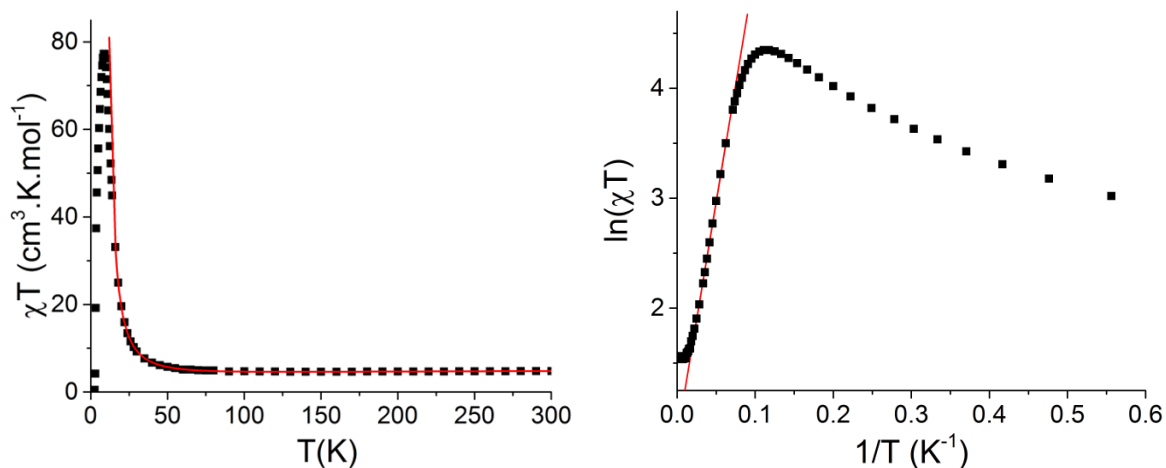


Figure S6. Plots of χT versus T (left) and $\ln(\chi T)$ versus $1/T$ (right) for a polycrystalline sample of **2**, measured at 0.1 T applied field. The red line represents the fit with using the respective equations $\chi T = C_1 \exp(\Delta_1/k_B T) + C_2 \exp(\Delta_2/k_B T)$ (giving $\Delta_1/k_B = 44.0$ K, $\Delta_2/k_B = -81.8 \pm 5.9$ K, $C_1 = 2.13$ cm³ K mol⁻¹ and $C_2 = 3.05$ cm³ K mol⁻¹) between 16 and 300 K and $\chi T = C_{\text{eff}} \exp(\Delta/k_B T)$ (giving Δ/k_B of 42.8 K and $C_{\text{eff}} = 2.28$) of the linear regime between 16 and 45K ($1/T$ from 0.063 to 0.022 K⁻¹).

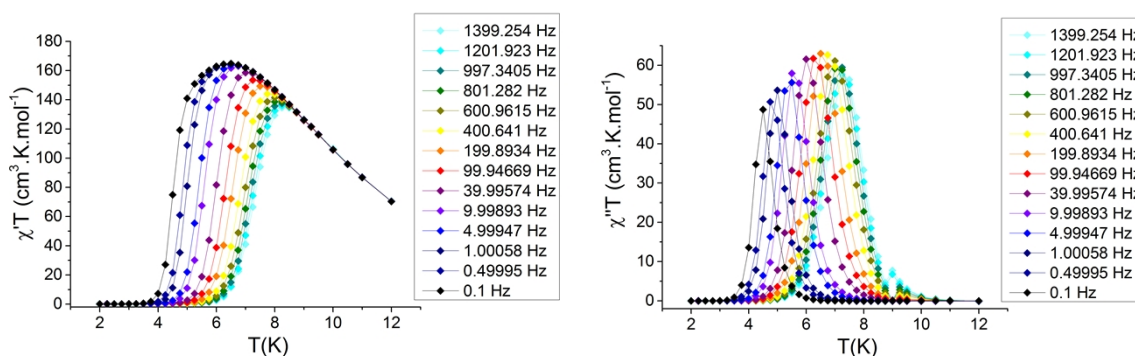


Figure S7. Plots of (left) $\chi'' T$ versus T and (right) $\chi'' T$ versus T for a polycrystalline sample of **2**, measured at zero-dc field and 1.5G ac field.

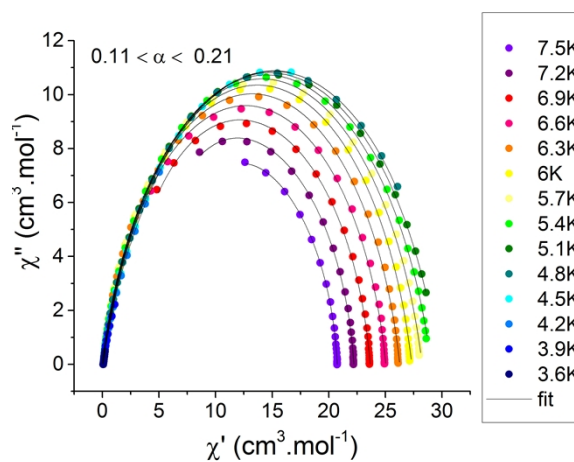


Figure S8. Cole-Cole plots and Debye fits (straight lines) for **2** measured at zero-dc field and an ac field of 1.55 G oscillating at frequencies between 0.1 and 1400 Hz.

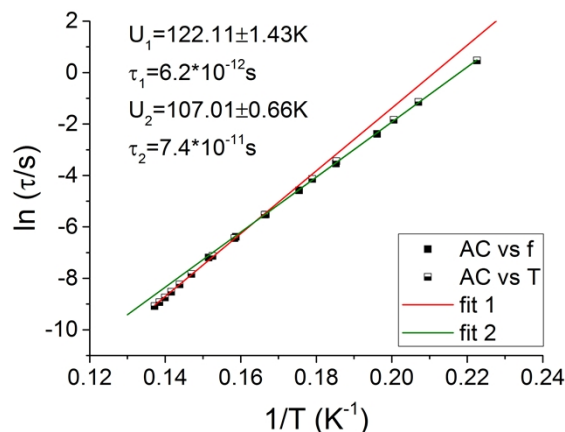


Figure S9. Arrhenius plot displaying T-dependence of the relaxation times for **2**. Half filled squares indicate that the corresponding relaxation time was extracted from fitting the frequency-dependent ac susceptibility curves with a modified Debye model, whereas the black squares indicate that the temperature corresponding to the peak maximum in ac curves was measured at constant frequency.

References

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