Europium(II) Compounds: Simple Synthesis of a Molecular Complex in Water and Coordination Polymers with 2,2'-Bipyrimidine Mediated Ferromagnetic Interactions

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Supporting Information

Synthetic procedures. Synthesis were performed under an inert atmosphere of argon. All the solvents were degassed by bubbling argon in 20 mL of solvent for two hours.

Preparation of $[Eu(Cl)(bpm)_2(H_2O)_4][Cl]$. (**1**) 280 mg (1.8 mmol) of $EuCl_2$ are added to a solution of 197 mg (0.9 mmol) of 2-2'-bipyrimidine dissolved in 0.5 mL of deoxygenated water. Dark brown crystals of **2** immediately formed. After filtration, washing with acetonitrile, and drying under vacuum, 285 mg (0.45 mmol, 50%) of **2** are collected. Anal. calcd for $C_{16}H_{22}Cl_2N_8O_5Eu$: C, 30.54; H, 3.52; N, 17.81%. Found: C, 30.49; H, 3.42; N, 17.97%.

Preparation of $[Eu(Cl)_2(bpm)(MeOH)]_n$ (2). In a dry glovebox, a 100 mL flask was charged with 600 mg (3.8 mmol) of 2, 2'-bipyrimidine and 845 mg (3.8 mmol) of $EuCl_2$. The flask was connected to a high-vacuum line and 20 mL of MeOH were transferred under vacuum. The reaction medium immediately turned dark brown. After stirring for 2h at room temperature, a brown solid was recovered by filtration and dried under vacuum. After re-crystallization from hot methanol, 1.22g (3.1 mmol, 81%) of **2** were isolated as dark brown crystals. Elemental analysis: Anal. Calcd. For $C_{8.5}H_8Cl_2N_4O_{0.5}Eu$: %C, 25.71, %H, 2.03, %N, 14.11. Found: %C, 25.98, %H, 2.43, %N, 13.69.

Preparation of $\{[Eu(bpm)_2(H_2O)_3][I]_2 \cdot 0.5bpm\}_\infty$ (3). The experimental procedure described for **1** has been used with 385 mg (0.9 mmol) of EuI_2 and 300 mg (1.9 mmol) of bpm in 0.5 mL of deoxygenated water. 341 mg (0.4 mmol, 45%) of dark brown crystals were obtained from this solution. Anal. calcd for $EuC_{20}H_{21}I_2N_{10}O_3$: C, 28.09; H, 2.47; N, 16.38%. Found: C, 27.81; H, 2.56; N, 15.98%.

Preparation of $\{[Eu(I)(bpm)(MeOH)_{0.5}][I]\}_\infty$ (4). The experimental procedure described for **2** has been used with 200 mg (0.5 mmol) of EuI_2 and 80 mg (0.5 mmol) of bpm in 5 mL of methanol. The solution immediately turned dark brown and 212 mg (0.32 mmol, 64 %) of

crystals were collected from this solution. Anal. calcd for $EuC_{11}H_{18}I_2N_4O_3$: C, 20.02; H, 2.75; N, 8.49%. Found: C, 19.82; H, 2.75; N, 8.57%.

Crystallography. The data were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[1] using graphite-monochromated Mo-Kα radiation (λ 0.71073 Å). The crystals were introduced in glass capillaries with a protecting "Paratone-N" oil (Hampton Research) coating. The unit cell parameters were determined from ten frames, then refined on all data. The data were processed with HKL2000.[2] Absorption effects were corrected empirically with the program SCALEPACK.[2] The structures were solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[3] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen atoms were found on Fourier-difference maps and all the others were introduced at calculated positions. All were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, CH) or 1.5 (CH_3) times that of the parent atom. For compound **2**, ADDSYM (PLATON)[4] indicates a 96% fit for the centrosymmetric space group *Pnma*. However, firstly, a significant number of observed reflections do not follow the reflection conditions for this group and, secondly, refinement of the model proved extremely unstable and did not give a *R*1 factor lower than 6%. For these reasons, it was deemed preferable to retain the chiral space group $P2_12_12_1$ and to consider the structure as pseudo-centrosymmetric only. The uncoordinated bpm molecule in **3** is disordered around a binary axis; it has been given a 0.5 occupancy parameter and was refined with restraints on geometry and displacement parameters. The drawings were done with Balls & Sticks.[5] ***Crystal data for 1***: $C_{16}H_{22}Cl_2EuN_8O_5$, M = 629.28, monoclinic, space group $P2_1/c$, a = 8.8617(8), b = 32.465(4), c = 8.0104(9) Å, β = 102.643(7)°, V = 2248.7(4) Å^3, Z = 4, $\mu(Mo_{K\alpha})$ = 3.073 mm^{-1}, 69169 measured reflections, 4257 independent, 3161 with $I > 2\sigma(I)$, 289 parameters, $R1$ = 0.039, $wR2$ = 0.067, S = 0.997. ***Crystal data for 2***: $C_{8.5}H_8Cl_2EuN_4O_{0.5}$,

M = 397.05, orthorhombic, space group $P2_12_12_1$, *a* = 9.7048(4), *b* = 13.1460(3), *c* = 17.5916(6) Å, *V* = 2244.32(13) $Å^3$, *Z* = 8, $\mu(Mo_{K\alpha})$ = 6.043 mm^{-1}, 32795 measured reflections, 4205 independent, 3906 with $I > 2\sigma(I)$, 291 parameters, *R*1 = 0.023, *wR*2 = 0.057, *S* = 1.046. ***Crystal data for 3***: $C_{20}H_{21}EuI_2N_{10}O_3$, *M* = 855.23, monoclinic, space group *C*2/*c*, *a* = 31.7279(17), *b* = 10.1284(6), *c* = 20.2074(14) Å, β = 123.588(4)°, *V* = 5409.5(6) $Å^3$, *Z* = 8, $\mu(Mo_{K\alpha})$ = 4.643 mm^{-1}, 80299 measured reflections, 5142 independent, 4099 with $I > 2\sigma(I)$, 355 parameters, *R*1 = 0.043, *wR*2 = 0.119, *S* = 1.011. ***Crystal data for 4***: $C_{11}H_{18}EuI_2N_4O_3$, *M* = 660.05, triclinic, space group $P\bar{1}$, *a* = 8.7106(6), *b* = 9.2393(7), *c* = 11.6831(12) Å, α = 93.001(4), β = 93.467(6), γ = 94.709(5)°, *V* = 933.81(14) $Å^3$, *Z* = 2, $\mu(Mo_{K\alpha})$ = 6.677 mm^{-1}, 29025 measured reflections, 3526 independent, 2728 with $I > 2\sigma(I)$, 193 parameters, *R*1 = 0.048, *wR*2 = 0.118, *S* = 1.000.

1 *Kappa-CCD Software*, Nonius BV: Delft, The Netherlands, 1998.

2 Z. Otwinowski, W. Minor, *Methods Enzymol.*, 1997, **276**, 307.

3 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 2008, **64,** 112.

4 A. L. Spek, *PLATON*, University of Utrecht, The Netherlands, 2000.

5 T. C. Ozawa, S. J. Kang, *J. Appl. Cryst.*, 2004, **37**, 679.

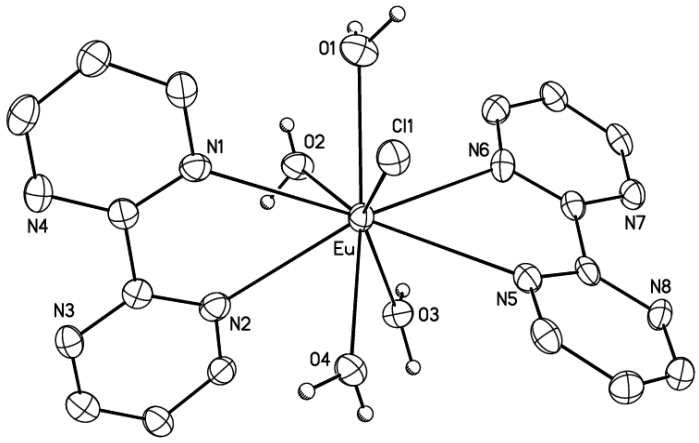

Figure S1. View of complex **1**. The counterion, solvent molecule and carbon-bound hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level.

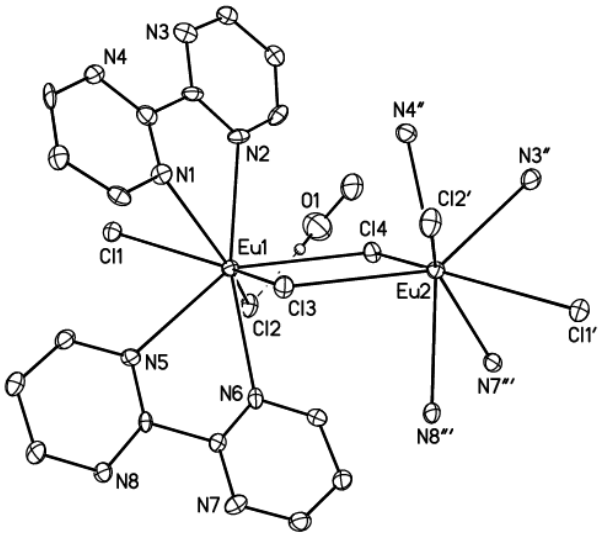

Figure S2. View of complex **2**. Hydrogen atoms are omitted, except for the one involved in a hydrogen bond (dashed line). Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: ' = 3/2 – *x*, –*y*, *z* – 1/2; '' = *x* – 1/2, 1/2 – *y*, –*z*; ''' = *x* – 1/2, –1/2 – *y*, –*z*.

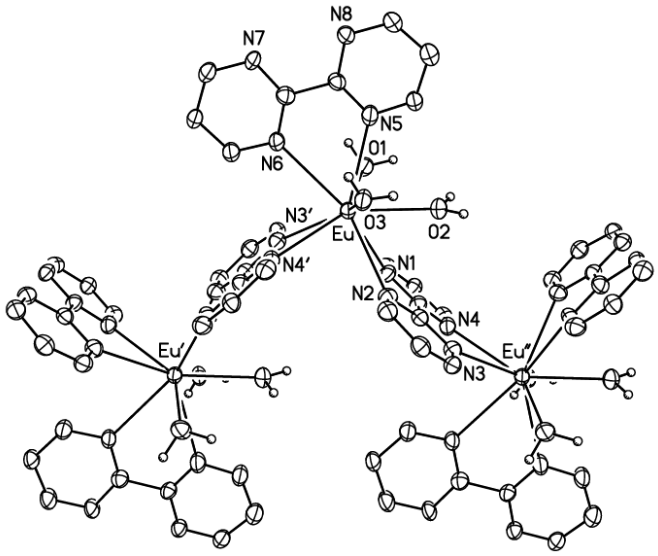

Figure S3. View of complex **3**. Counter-ions, uncoordinated bpm molecules and carbon-bound hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: ' = 3/2 – *x*, *y* – 1/2, 1/2 – *z*; " = 3/2 – *x*, *y* + 1/2, 1/2 – *z*.

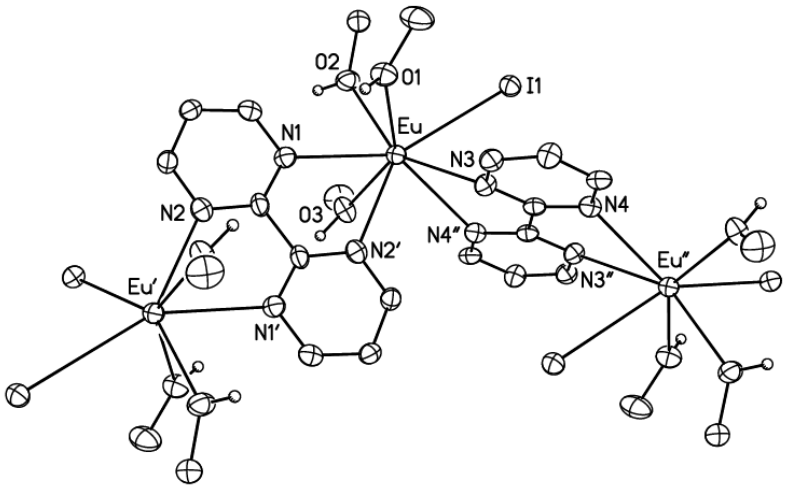

Figure S4. View of complex **4**. Counter-ions and carbon-bound hydrogen atoms are omitted. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: ' = –*x*, –*y*, 1 – *z*; " = –*x*, –*y*, 2 – *z*.

Magnetism measurements.

Magnetic susceptibility measurements were carried out with a Quantum Design MPMS5 magnetometer with an applied field of 1 kOe. The independence of the susceptibility value with regard on the applied field was checked at room temperature. The susceptibility data were corrected from the diamagnetic contribution of the sample holder and from the diamagnetic contributions of the sample calculated by using Pascal's constant tables.