

Supporting Information

Lanthanide(III) and lead(II) complexes of a chiral nonaaza macrocyclic amine based on 1,2-diaminocyclopentane †

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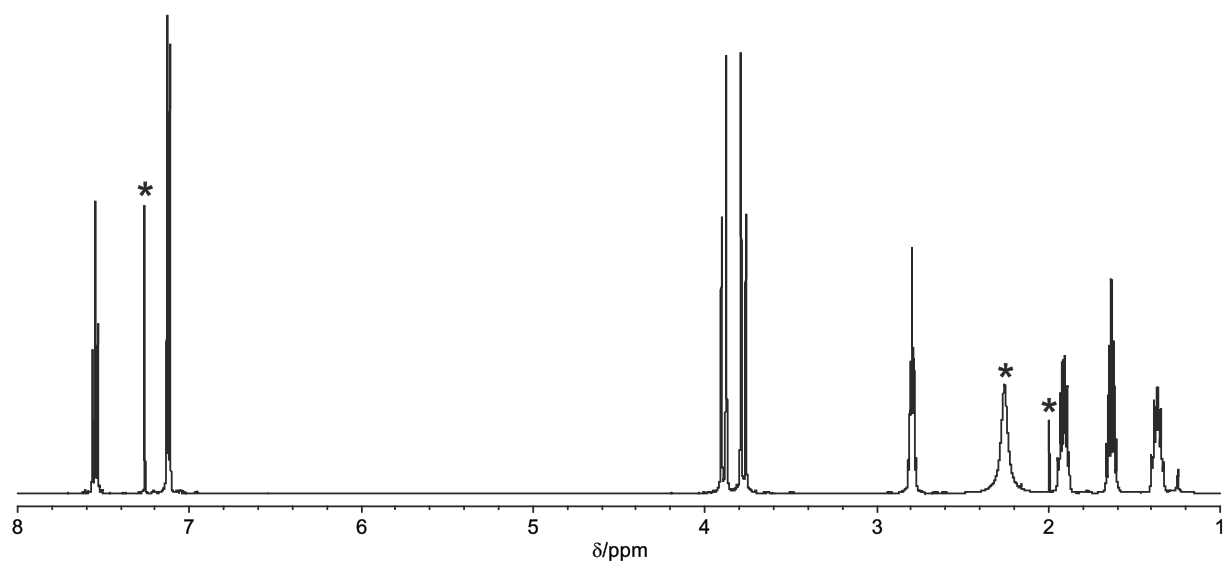


Figure S1. ^1H NMR spectrum of **R-2** (CDCl_3 , 300 K).

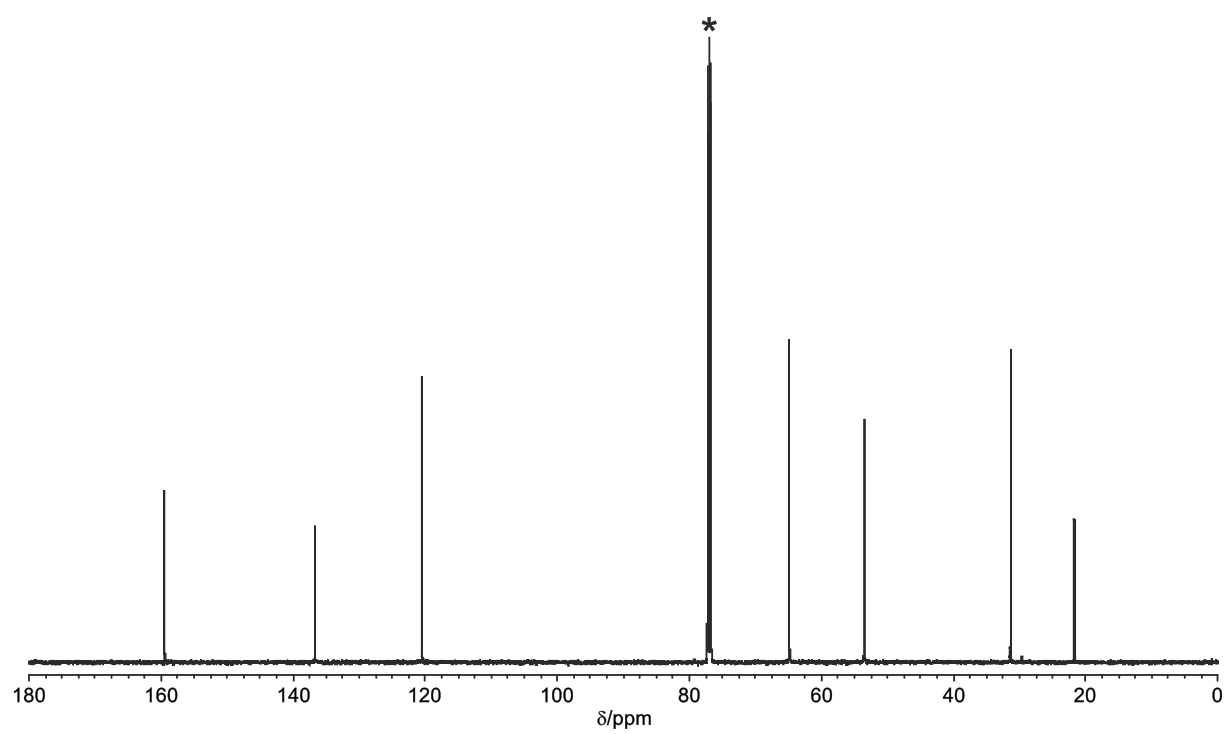


Figure S2 ^{13}C NMR spectrum of **R-2** (CDCl_3 , 300 K).

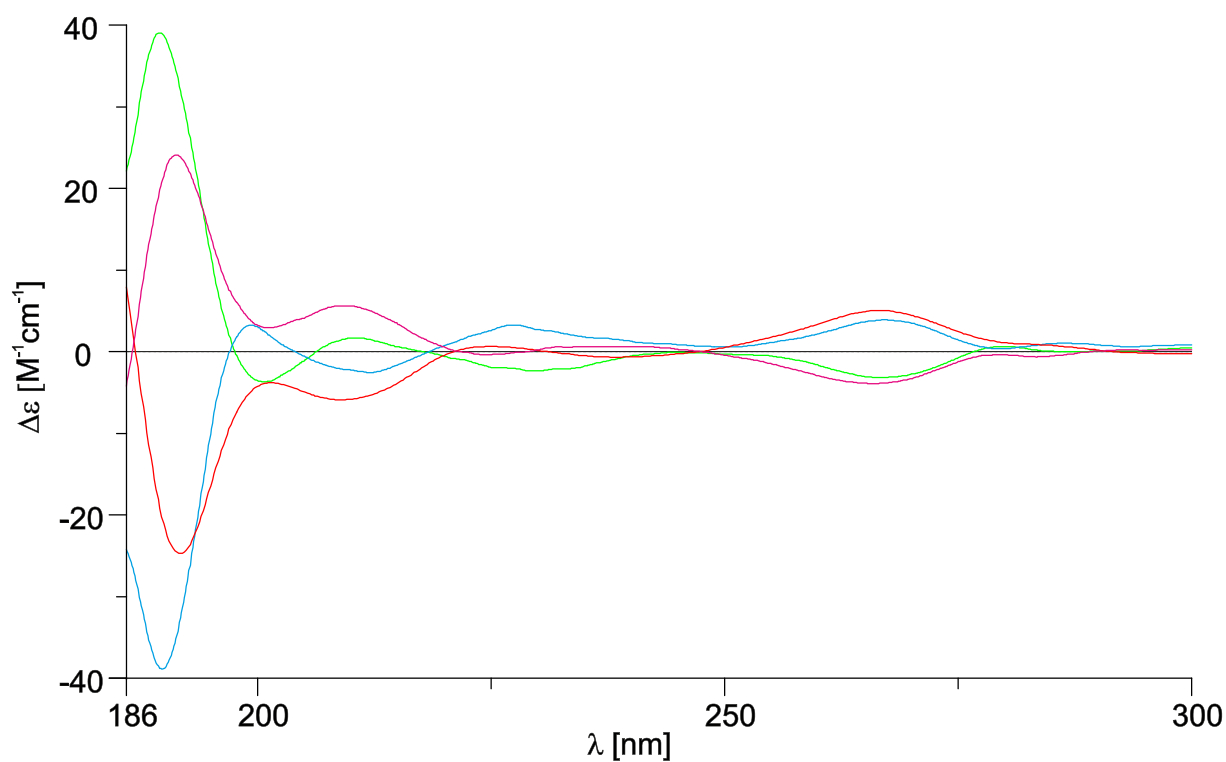


Figure S3. CD spectra of (*M*)-[Pr*R*-2](NO₃)₃·2H₂O (red), (*P*)-[Pr*S*-2](NO₃)₃·2.5H₂O (purple), [Pr*R*-1](NO₃)₃·H₂O (blue) and [Pr*S*-1](NO₃)₃·H₂O (green) complexes in H₂O solutions (1×10^{-3} M).

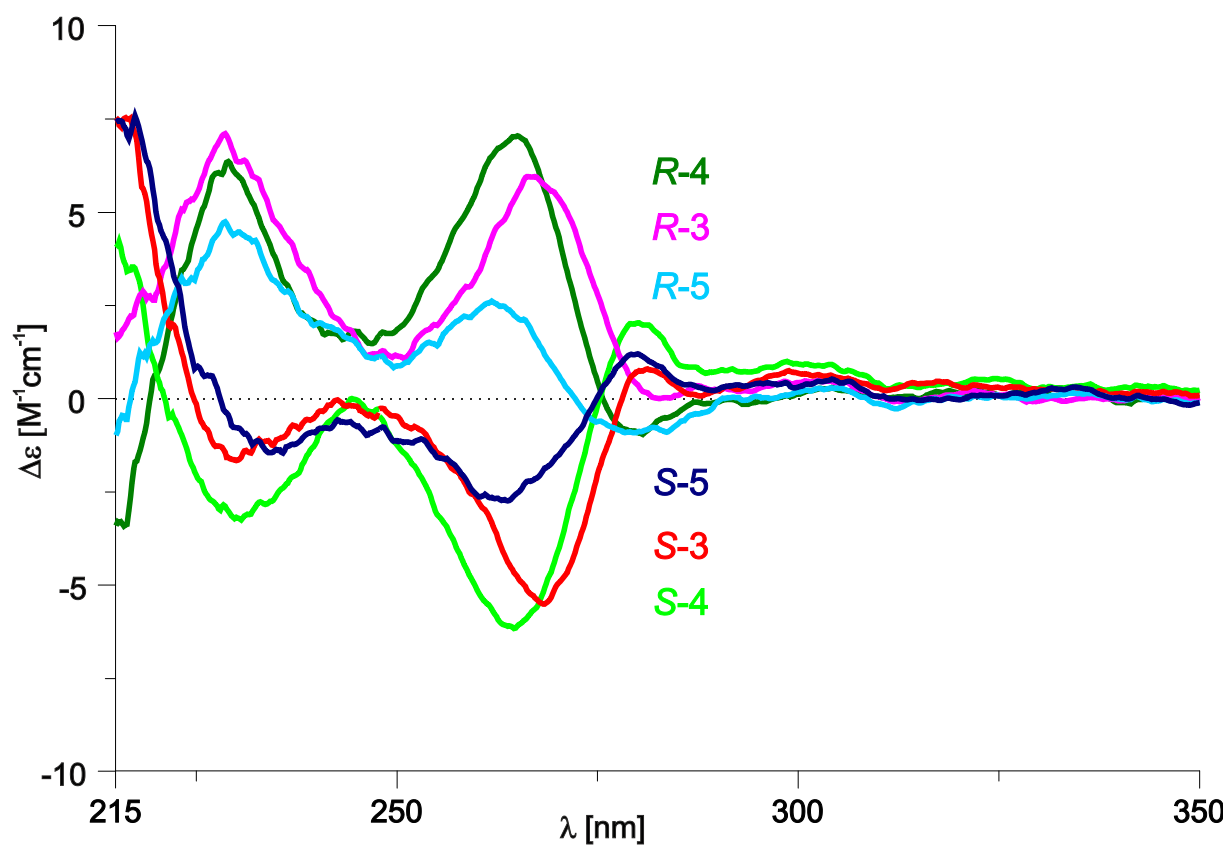


Figure S4. CD spectra of *R*-3, *R*-4, *R*-5, *S*-3, *S*-4 and *S*-5 complexes in CH₃CN solutions (1×10^{-3} M).

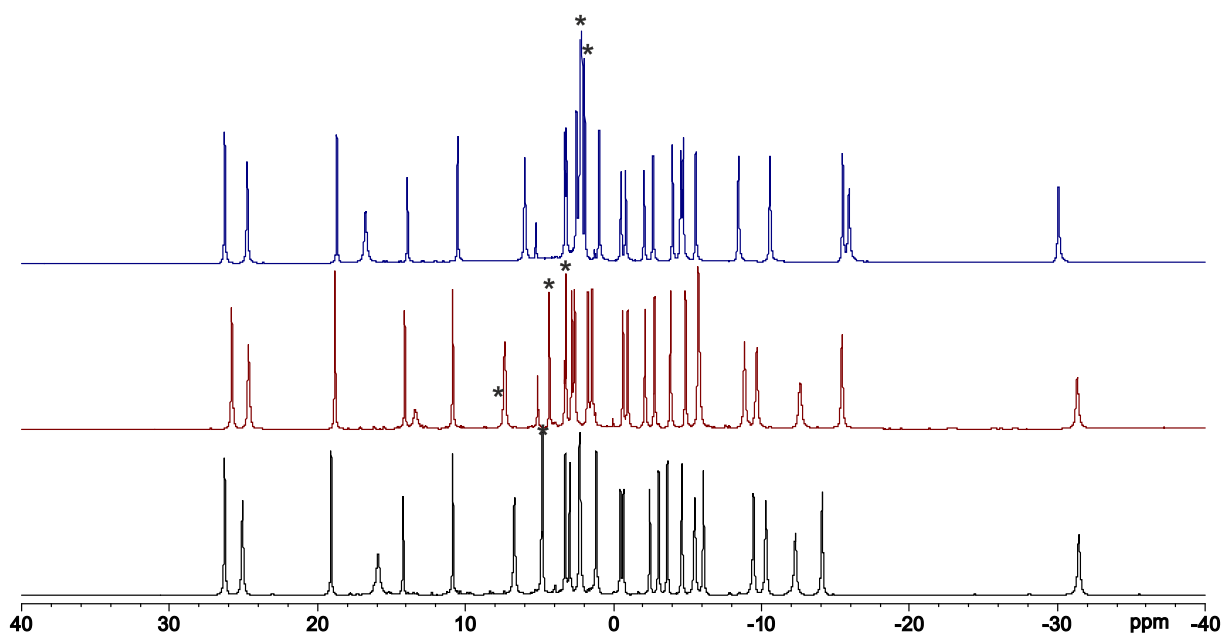


Figure S5. ^1H NMR spectra of **S-3**, (*P*)-[Pr**S-2**](NO₃)₃·2.5H₂O, in D₂O (black trace), CDCl₃/CD₃OD (v/v 2/1) (brown trace) and CD₃CN (blue trace) at 300K. * denote residual solvent signals.

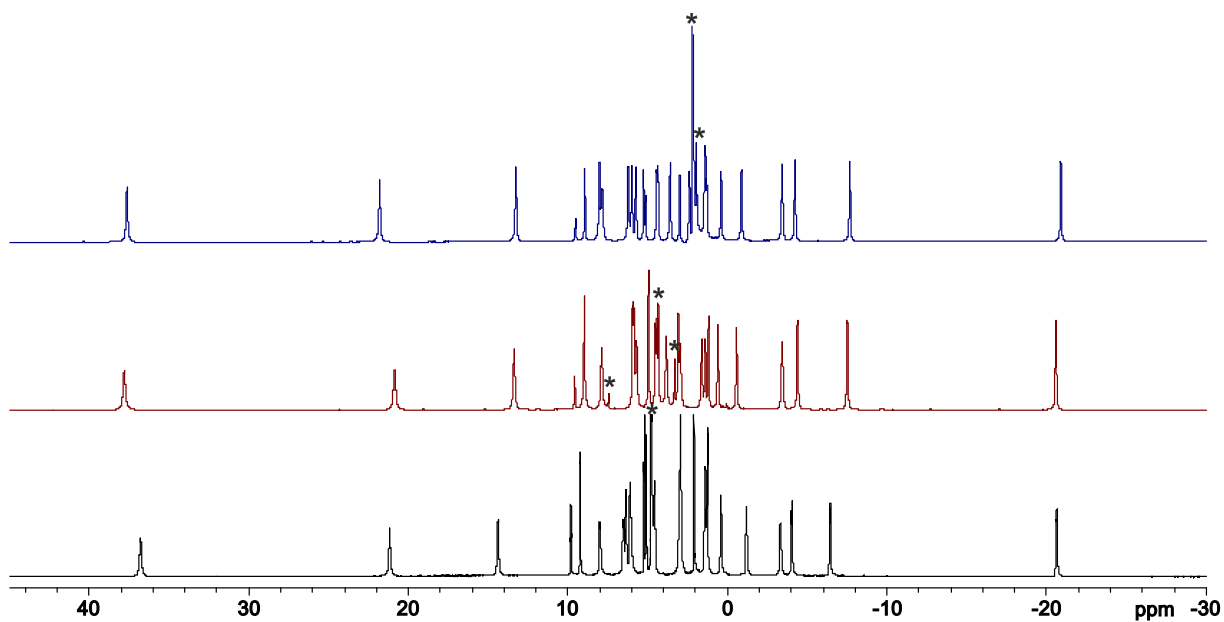


Figure S6. ^1H NMR spectra of **S-4**, (*P*)-[Eu**S-2**](NO₃)₃·2.5H₂O, in D₂O (black trace), CDCl₃/CD₃OD (v/v 2/1) (brown trace) and CD₃CN (blue trace) at 300K. * denote residual solvent signals.

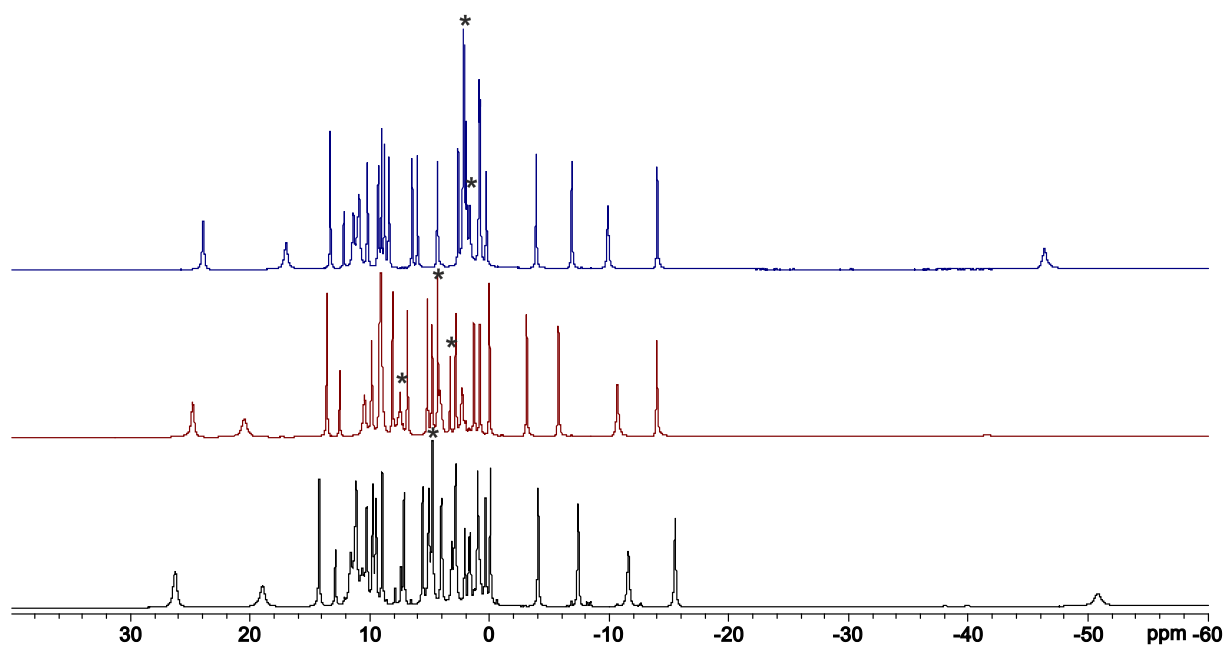


Figure S7. ^1H NMR spectra of *S-5*, (*P*)-[Yb*S-2*](NO₃)₃·3H₂O, in D₂O (black trace), CDCl₃/CD₃OD (v/v 2/1) (brown trace) and CD₃CN (blue trace) at 300K. * denote residual solvent signals.

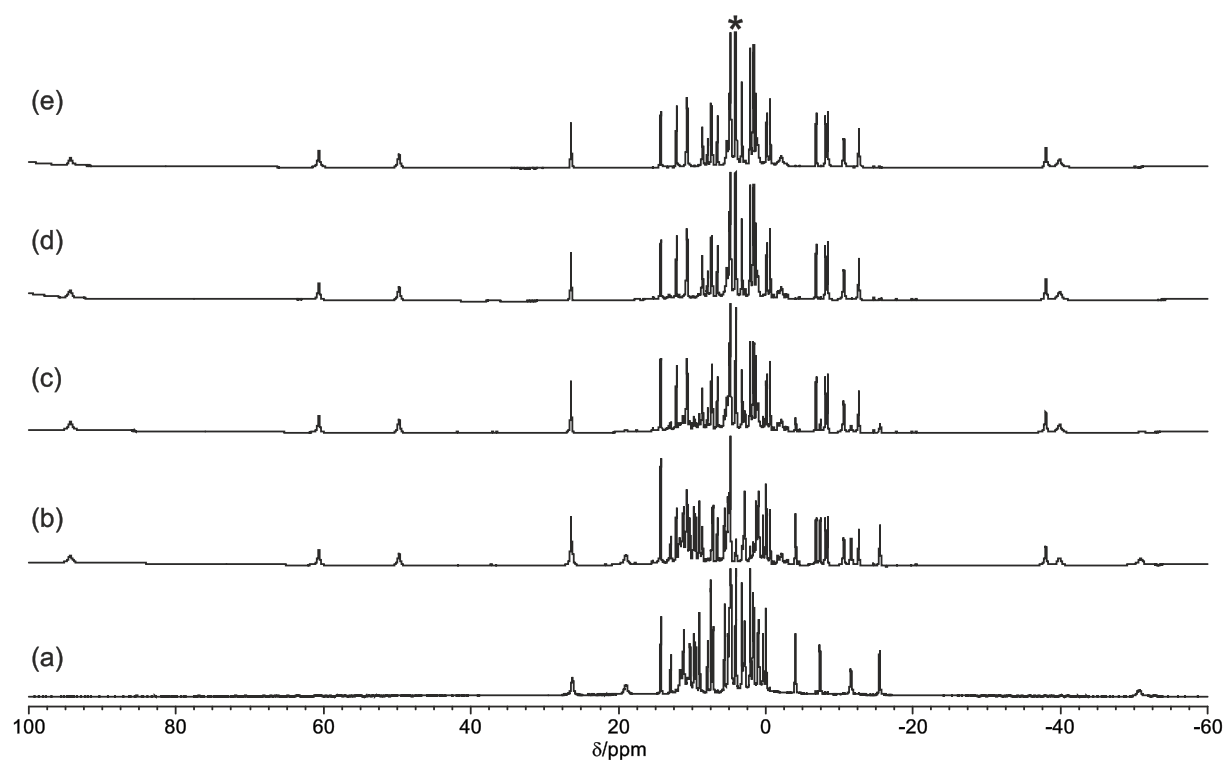


Figure S8 ^1H NMR spectra (in D₂O) of an isolated sample of *S-5* (a), the sample of filtrate after separation of *S-5*, measured immediately (b), after 50 min (c), after 170 min (d) and after 26 h (e) after dissolution.

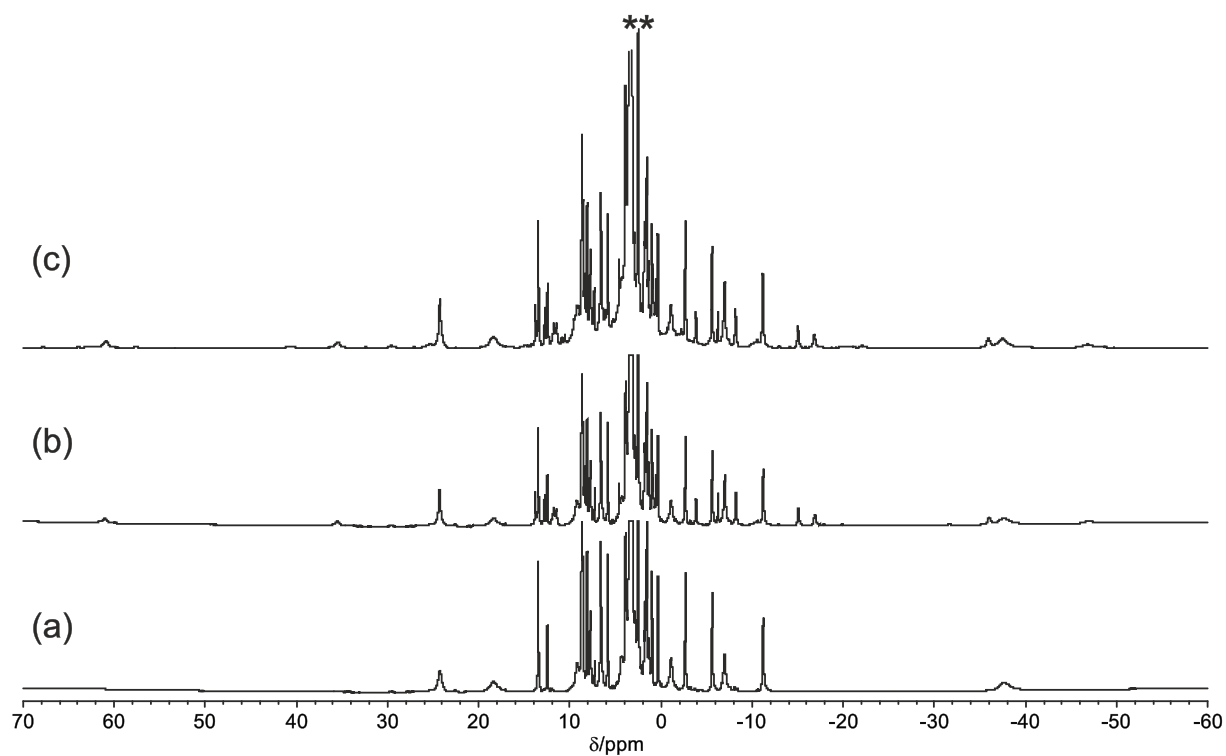


Figure S9. ^1H NMR spectra of created in situ complexes from mixture of **R-2** and 10 eq of $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in DMSO-d_6 : (a) after 2.5 h at RT, (b) after heating the sample for 1 h at 100°C , (c) after heating the sample for 39 h at 100°C .

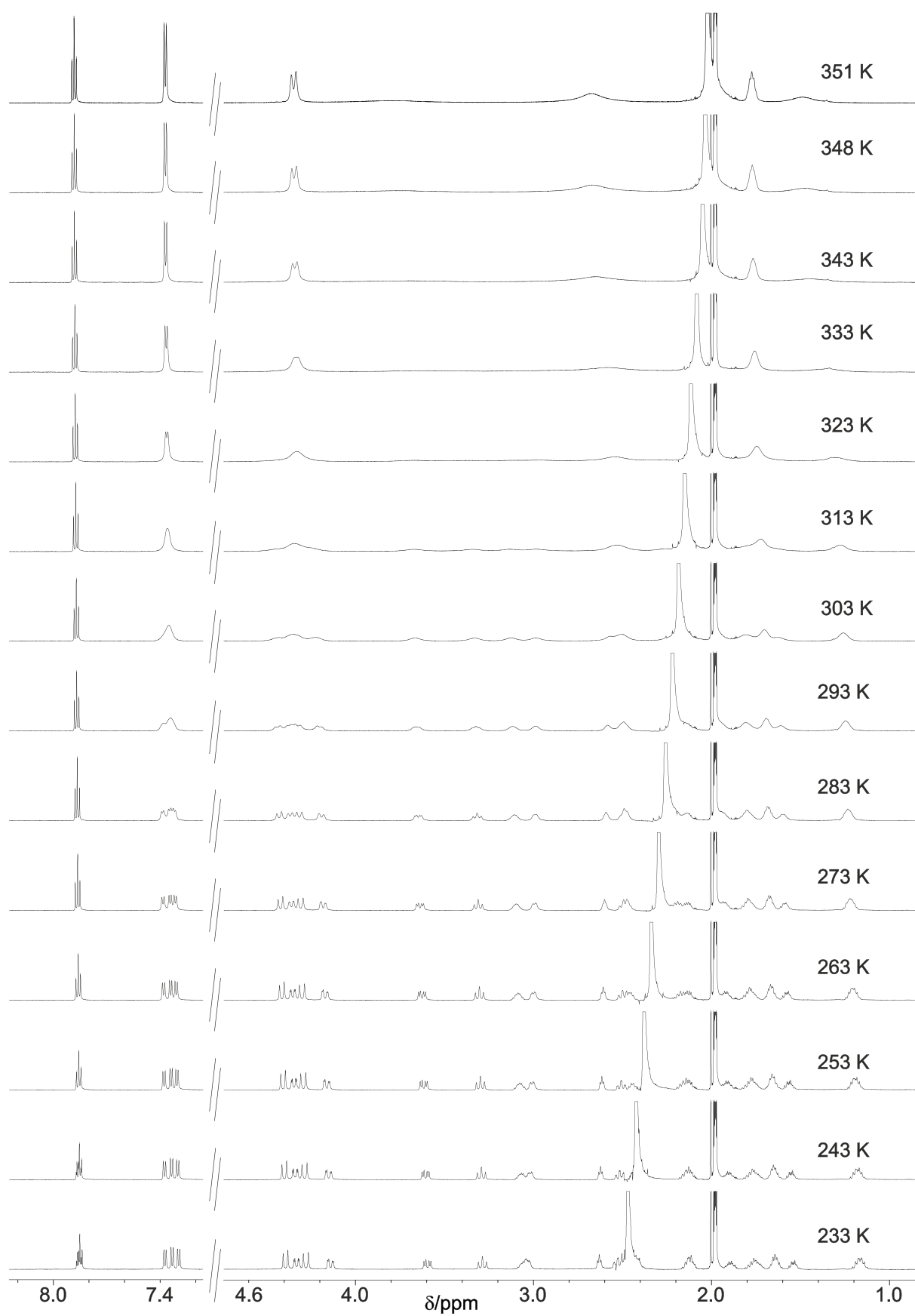


Figure S10. Temperature dependence of ¹H NMR signals of *S-5* in CD₃CN solution.

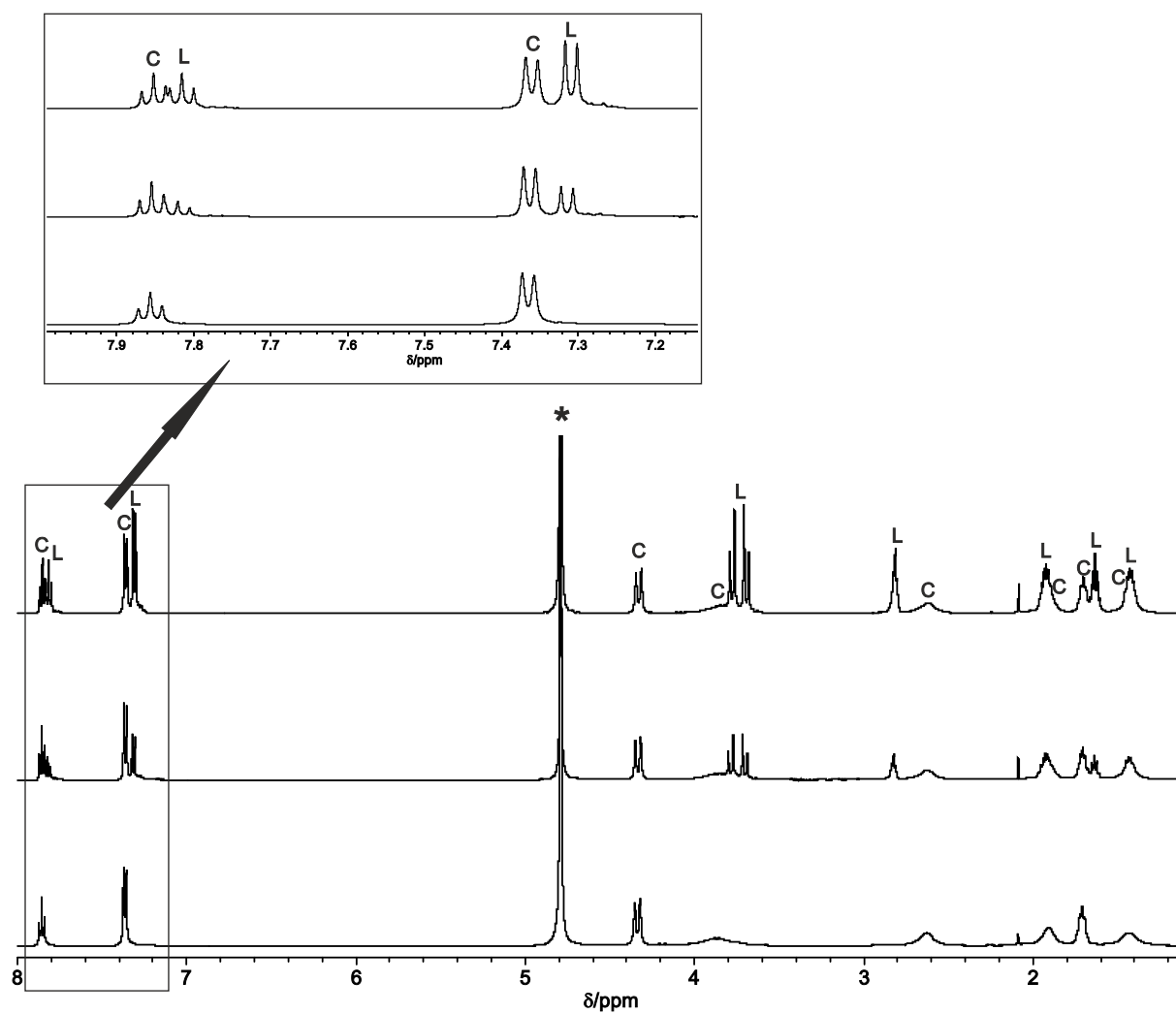


Figure S11 ^1H NMR spectra of *S-5* in D_2O (bottom), after addition of 0.53 eq of *S-2* (middle) and after addition of 1.1 eq of *S-2* (top). *, C and L denote residual solvent, complex and ligand signals, respectively.

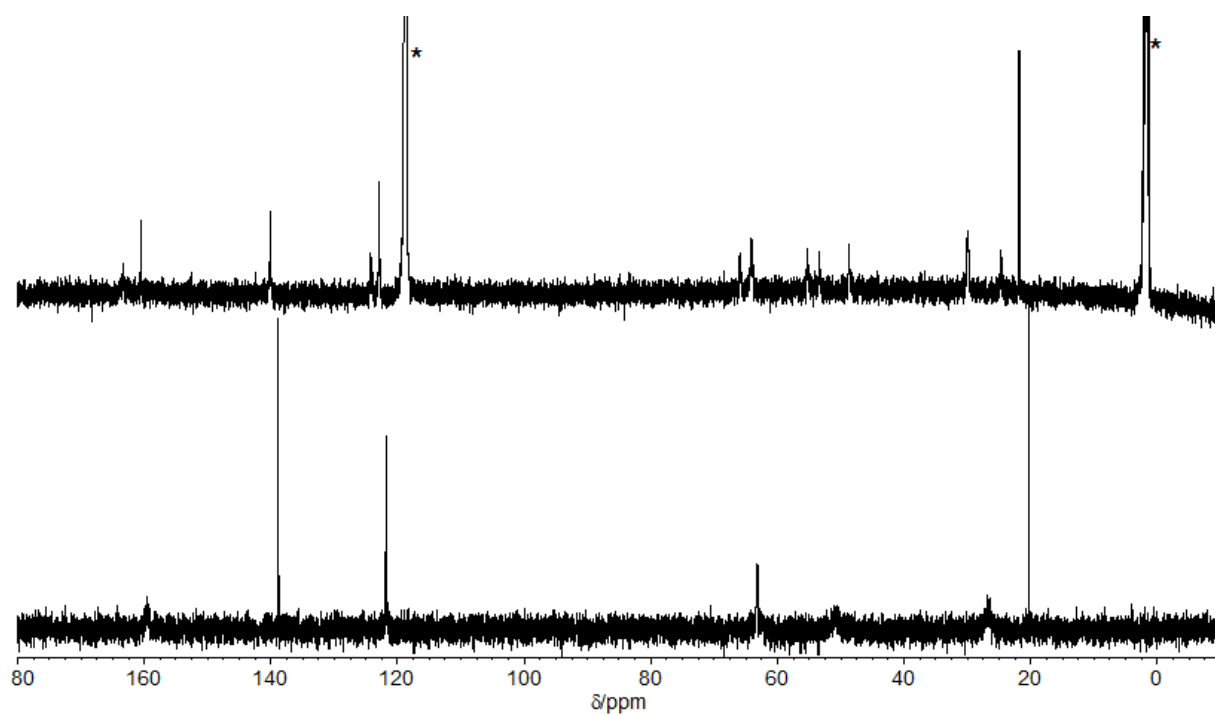


Figure S12. ^{13}C NMR spectra of **R-6** complex in D_2O (lower spectrum) and CD_3CN (upper spectrum) solution.

Crystallographic data

Crystals of free ligand **S-2** were grown from acetonitrile solution. Crystals of its complexes $[\text{PrS-2}](\text{NO}_3)_3 \cdot 1.5\text{CH}_3\text{CN} \cdot 1.2\text{H}_2\text{O}$, $[\text{EuS-2}](\text{NO}_3)_3 \cdot 2.2\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$, $[\text{YbS-2}](\text{NO}_3)_3 \cdot 1.6\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ were grown from methanol/acetonitrile solutions, $[\text{PbS-2}](\text{NO}_3)_2 \cdot 1.6\text{CH}_3\text{CN}$ from acetonitrile and $[\text{PbS-2}](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ from water solutions.

The crystallographic measurements were performed at 100(2)–122(2) K on a κ -geometry XCALIBUR *R* or XCALIBUR *PX* (ω scan) four-circle diffractometer with graphite-monochromatized Mo *K α* or Cu *K α* radiation (see details in Table S1). Data were corrected for Lorentz and polarization effects. Data collection, cell refinement, data reduction, and analysis were carried out with CRYSLIS CCD and CRYSLIS RED, respectively.^[1] Analytical absorption correction was applied to the data with the use of CRYSLIS RED. The structures of $[\text{PrS-2}](\text{NO}_3)_3 \cdot 1.5\text{CH}_3\text{CN} \cdot 1.2\text{H}_2\text{O}$ and $[\text{PbS-2}](\text{NO}_3)_2 \cdot 1.6\text{CH}_3\text{CN}$ were solved by direct methods using the SHELXS-97^[2] program and refined on F^2 by a full-matrix least-squares technique using SHELXL-2013^[2] with anisotropic thermal parameters for the ordered and fully occupied non-H atoms. Because crystals of Eu and Yb complexes are isomorphous with Pr compound, the refinements of their structures were started by using the coordinates of ordered heavy atoms taken from complex $[\text{PrS-2}](\text{NO}_3)_3 \cdot 1.5\text{CH}_3\text{CN} \cdot 1.2\text{H}_2\text{O}$. Similarly, both crystals of Pb complexes are isomorphous, and therefore the refinement of $[\text{PbS-2}](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was started using the non-solvent atomic coordinates from $[\text{PbS-2}](\text{NO}_3)_2 \cdot 1.6\text{CH}_3\text{CN}$.

C-bonded H atoms in all crystals, and N-bonded H atoms in the crystals of the complexes were included from geometry, and were refined using a riding model, with C–H = 0.95–1.00 Å, N–H = 1.00 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C},\text{N})$ for CH, CH₂ and NH, or $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for CH₃. Amine H atoms in **S-2** and water H atoms in $[\text{PbS-2}](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ were found in difference Fourier maps, and were refined isotropically with N–H and O–H, H \cdots H distances restrained to 0.900(2) and 0.840(2), 1.380(2) Å, respectively, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$ or $1.5U_{\text{eq}}(\text{O})$, and then they were constrained to ride on their parent atoms (AFIX 3 instruction in SHELXL-2013^[2]).

Isomorphous crystals of $[\text{PrS-2}](\text{NO}_3)_3 \cdot 1.5\text{CH}_3\text{CN} \cdot 1.2\text{H}_2\text{O}$, $[\text{EuS-2}](\text{NO}_3)_3 \cdot 2.2\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ and $[\text{YbS-2}](\text{NO}_3)_3 \cdot 1.6\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$ are orthorhombic (space group *C222*₁) with two crystallographically independent complex cations: **A** – in general position, and **B** – in a special position, on a 2-fold axis (passing through the Ln^{III} cation, pyridine N1, C1 atoms, and cyclopentane C19 atom). Cations **B** are disordered, and were refined differently in Pr, Eu and Yb compounds. In $[\text{PrS-2}](\text{NO}_3)_3 \cdot 1.5\text{CH}_3\text{CN} \cdot 1.2\text{H}_2\text{O}$,

only one pyridine ring, and one cyclopentane ring of **B** were found to be disordered and were refined in two positions each, with site occupation factors = 0.5 (for two sites of py ring) and 0.60(8)/0.40(8) (for cyclopentane). In [Eu**S-2**](NO₃)₃·2.2CH₃CN·0.5H₂O and [Yb**S-2**](NO₃)₃·1.6CH₃CN·0.5H₂O, the whole complex cation **B** was refined in two positions with s.o.fs. = 0.5 each.

Four from five nitrates in Pr and Eu crystals lie in general positions. Two from them in [Pr**S-2**](NO₃)₃·1.5CH₃CN·1.2H₂O, and three in [Eu**S-2**](NO₃)₃·2.2CH₃CN·0.5H₂O are disordered into two sites and were refined with occupancy factors 0.637(15)/0.363(15) and 0.709(14)/0.291(14) for Pr crystal, and 0.62(2)/0.38(2), 0.50(3)/0.50(3) and 0.543(11)/0.457(11) for Eu crystal. In this regard, model finally accepted for [Yb**S-2**](NO₃)₃·1.6CH₃CN·0.5H₂O is similar to that for Eu crystal, with the difference lying in additional disorder of one of the NO₃⁻, which was refined in three sites, one of which lies in a special position. Thus, the occupancy factors for disordered nitrates in Yb crystal are:0.55(2)/0.45(2), 0.46(2)/0.34(2)/0.198(11) and 0.524(15)/0.476(15).. The fifth NO₃⁻ is located on a 2-fold axis. In Eu and Yb crystals additional disorder for this nitrate was applied (see details in CIFs).

All three acetonitrile molecules in [Pr**S-2**](NO₃)₃·1.5CH₃CN·1.2H₂O, all six CH₃CN positions in [Eu**S-2**](NO₃)₃·2.2CH₃CN·0.5H₂O, and three from four CH₃CN positions in [Yb**S-2**](NO₃)₃·1.6CH₃CN·0.5H₂O are partially occupied (some of them are also disordered) and were refined with occupancy factors 0.941(15), 0.338(5)/0.338(5)/0.162(5)/0.162(5) (for four positions), and 0.180(8)/0.180(8) (two positions) in Pr crystal, 0.870(19), 0.73(2), 0.405(11)/0.405(11) (two positions), 0.228(6)/0.228(6) (two positions), 0.25, and 0.125/0.125 (two positions) in Eu crystal, and 0.48(2), 0.62(2) and 0.25 in Yb crystal. One of the acetonitrile molecules in [Pb**S-2**](NO₃)₂·1.6CH₃CN was found to be disordered and was refined in two sites, with s.o.f.s = 0.571(10) and 0.429(10). The other solvent molecule is partially occupied [s.o.f. = 0.583(8)].

Positions of water molecules in Pr, Eu and Yb complexes are partially occupied. Their O atoms were refined with (an)isotropic thermal parameters (see details in CIFs). Their H atoms were not found in the Fourier maps. The finally accepted formulas are [Pr**S-2**](NO₃)₃·1.5CH₃CN·1.2H₂O, [Eu**S-2**](NO₃)₃·2.2CH₃CN·0.5H₂O and [Yb**S-2**](NO₃)₃·1.6CH₃CN·0.5H₂O. However, the amount of solvent molecules should be treated as a rough approximation.

Some geometrical restraints (SAME, SADI instructions in SHELXL-2013^[2]), restraints on anisotropic displacement parameters (SIMU), and constraints on the fractional coordinates

and anisotropic displacement parameters (EXYZ and EADP instructions) were applied in the refinement procedures if appropriate. Figures presenting the molecular structures were made using the DIAMOND^[3] program. Details of structures refinements are given in Table S1 and the crystallographic information files (CIFs) deposited at the CCDC and provided as ESI.

References

- (1) *CrysAlis CCD* and *CrysAlis RED* in Xcalibur Software; Oxford Diffraction Ltd.: Abingdon, England, 2009.
- (2) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112–122.
- (3) Brandenburg, K. *DIAMOND*, Version 3.2; Crystal Impact GbR: Bonn, Germany, 2014.

Table S1. Crystallographic data for the crystals.

	S-2	[Pr S-2](NO ₃) ₃ · 1.5CH ₃ CN· 1.2H ₂ O	[Eu S-2](NO ₃) ₃ · 2.2CH ₃ CN· 0.5H ₂ O	[Yb S-2](NO ₃) ₃ · 1.6CH ₃ CN· 0.5H ₂ O	[Pb S-2](NO ₃) ₂ · 1.6CH ₃ CN	[Pb S-2](NO ₃) ₂ · 4H ₂ O
CCDC No.	1405208	1405209	1405210	1405211	1405212	1405213
Chemical formula	C ₃₆ H ₅₁ N ₉	C ₃₉ H _{57.9} N _{13.5} O _{10.2} Pr	C _{40.4} H _{58.6} EuN _{14.2} O _{9.5}	C _{39.2} H _{56.8} N _{13.6} O _{9.5} Yb	C _{39.2} H _{55.8} N _{12.6} O ₆ Pb	C ₃₆ H ₅₉ N ₁₁ O ₁₀ Pb
<i>M_r</i>	609.85	1019.99	1047.17	1043.62	1006.75	1013.13
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁	Orthorhombic, <i>C</i> 222 ₁	Orthorhombic, <i>C</i> 222 ₁	Orthorhombic, <i>C</i> 222 ₁	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁	Orthorhombic, <i>P</i> 2 ₁ 2 ₁ 2 ₁
Temperature (K)	100(2)	100(2)	100(2)	122(2)	100(2)	100(2)
<i>a</i> , <i>b</i> , <i>c</i> (Å)	12.180(4), 9.051(3), 15.766(4)	16.139(3), 18.968(6), 46.829(12)	16.089(4), 19.277(5), 46.964(12)	16.021(4), 19.178(6), 47.202(15)	12.221(3), 15.222(3), 22.433(5)	12.389(3), 15.220(3), 22.064(5)
α, β, γ (°)	90, 110.68(3), 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90	90, 90, 90
<i>V</i> (Å ³)	1626.1(9)	14336(6)	14566(6)	14503(7)	4173.2(16)	4160.4(16)
<i>Z</i>	2	12	12	12	4	4
Radiation type	Cu <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	0.59	1.09	1.36	2.00	4.11	4.12
Crystal size (mm)	0.10 × 0.06 × 0.02	0.29 × 0.20 × 0.16	0.57 × 0.30 × 0.29	0.55 × 0.50 × 0.30	0.22 × 0.19 × 0.10	0.19 × 0.10 × 0.09
Diffractometer	Xcalibur <i>PX</i>	Xcalibur <i>R</i>	Xcalibur <i>R</i>	Xcalibur <i>R</i>	Xcalibur <i>R</i>	Xcalibur <i>R</i>
Absorption correction	Analytical	Analytical	Analytical	Analytical	Analytical	Analytical
<i>T</i> _{min} , <i>T</i> _{max}	0.951, 0.986	0.787, 0.849	0.551, 0.720	0.431, 0.604	0.475, 0.696	0.559, 0.737
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	10816, 4731, 2423	77426, 20901, 17040	76917, 20980, 18677	29929, 17678, 16148	69480, 20950, 18610	52597, 8177, 8011
<i>R</i> _{int}	0.096	0.041	0.036	0.025	0.042	0.038
(sin θ/λ) _{max} (Å ⁻¹)	0.602	0.703	0.703	0.703	0.853	0.617
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.052, 0.083, 0.85	0.054, 0.157, 1.05	0.063, 0.153, 1.16	0.057, 0.144, 1.12	0.032, 0.056, 1.02	0.025, 0.055, 1.12
No. of reflections	4731	20901	20980	17678	20950	8177
No. of parameters	406	926	895	845	528	523
No. of restraints	7	221	462	400	9	12
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
Δρ _{max} , Δρ _{min} (e Å ⁻³)	0.19, -0.23	1.11, -2.02	1.34, -1.79	, -1.86	1.32, -1.39	2.29, -1.10
Absolute structure parameter	–	-0.012(4)	-0.001(3)	0.004(4)	-0.0074(19)	0.000(2)

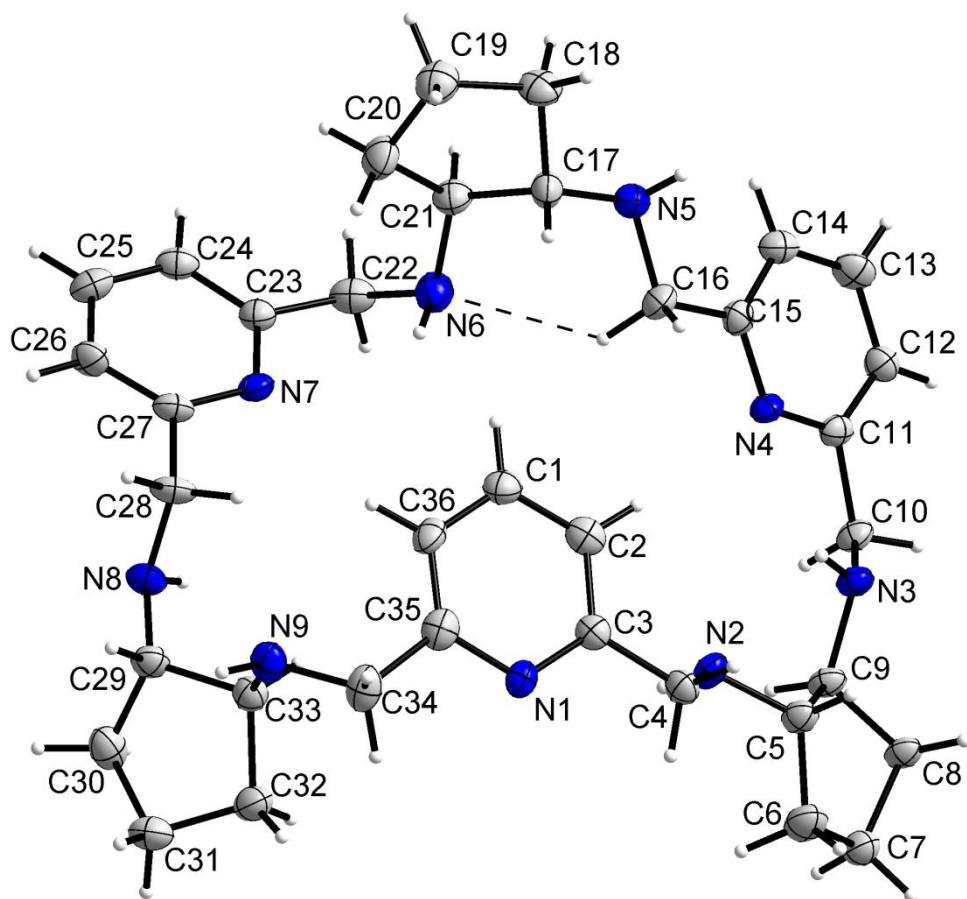


Figure S13. The asymmetric unit of *S-2*, showing the atom-numbering scheme and the intramolecular hydrogen contact (dashed line). Displacement ellipsoids are shown at the 50% probability level.

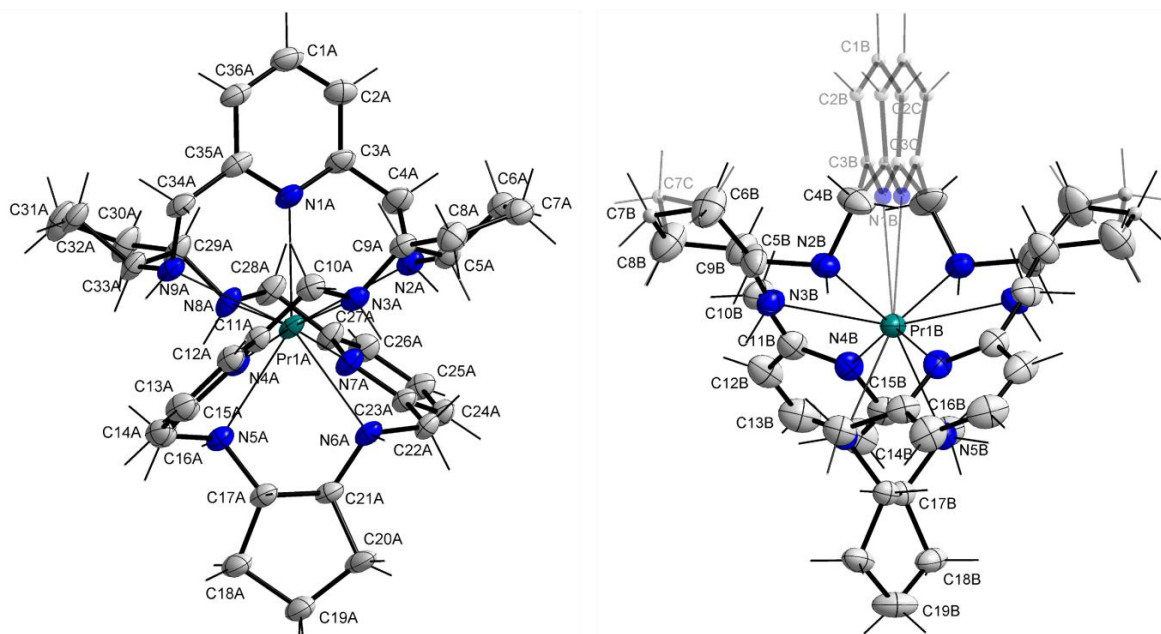
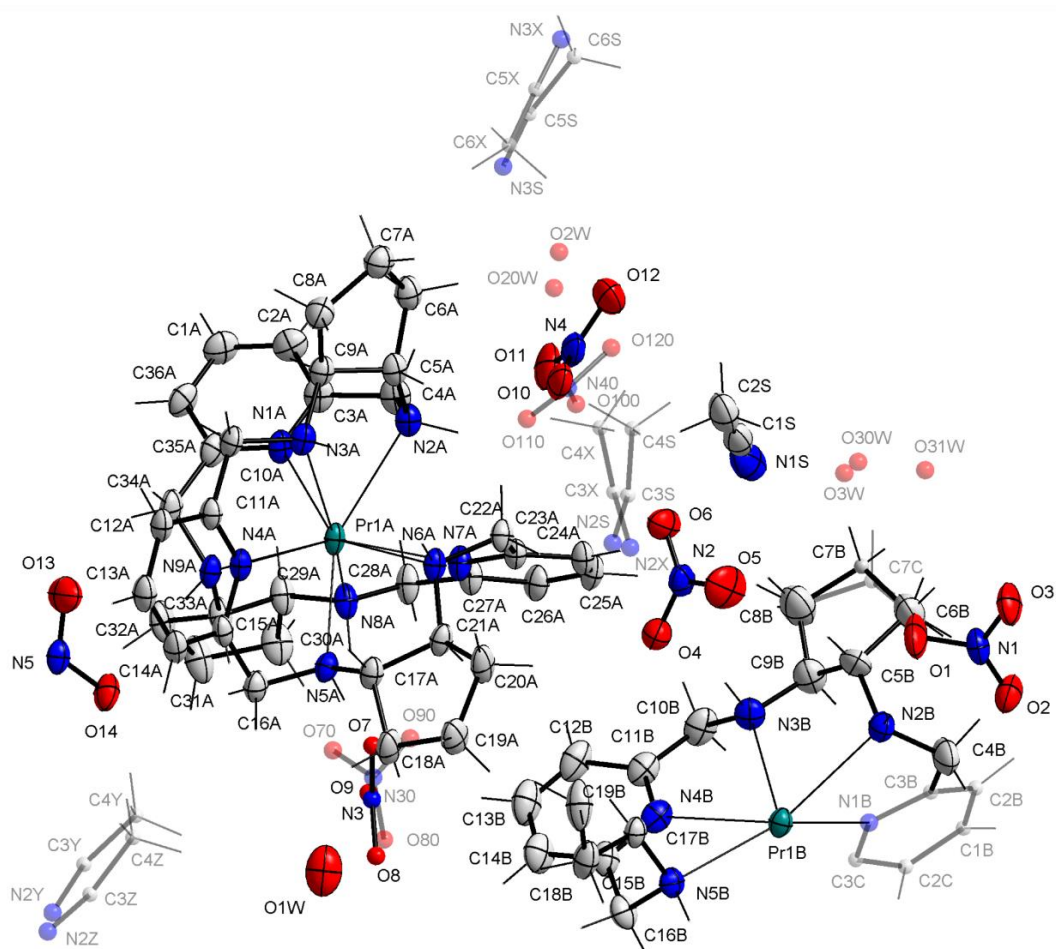


Figure S14. The asymmetric unit of $[\text{PrS-2}](\text{NO}_3)_3 \cdot 1.5\text{CH}_3\text{CN} \cdot 1.2\text{H}_2\text{O}$ (top), along with the separate cations **A** (bottom left) and **B** (bottom right), showing the atom-numbering scheme, and the disorder in **B** and solvent molecules. Transparent bonds and atoms represent positions with s.o.f. ≤ 0.5 . Displacement ellipsoids are shown at the 30% probability level.

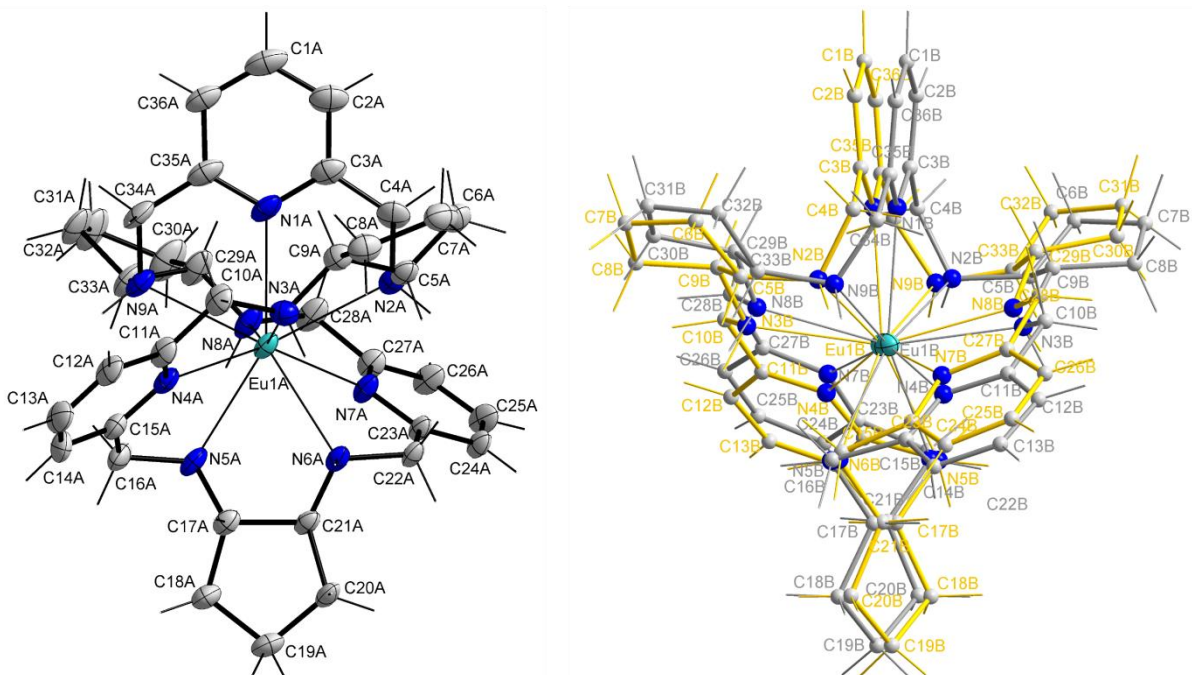


Figure S15. Cation **A** (left) and **B** (right) present in $[\text{EuS-2}](\text{NO}_3)_3 \cdot 2.2\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$, showing the atom-numbering scheme, and the disorder in **B**. Site occupation factors for grey (x, y, z) and yellow ($x, 1-y, 1-z$) positions of **B** = 0.5. Displacement ellipsoids are shown at the 30% probability level.

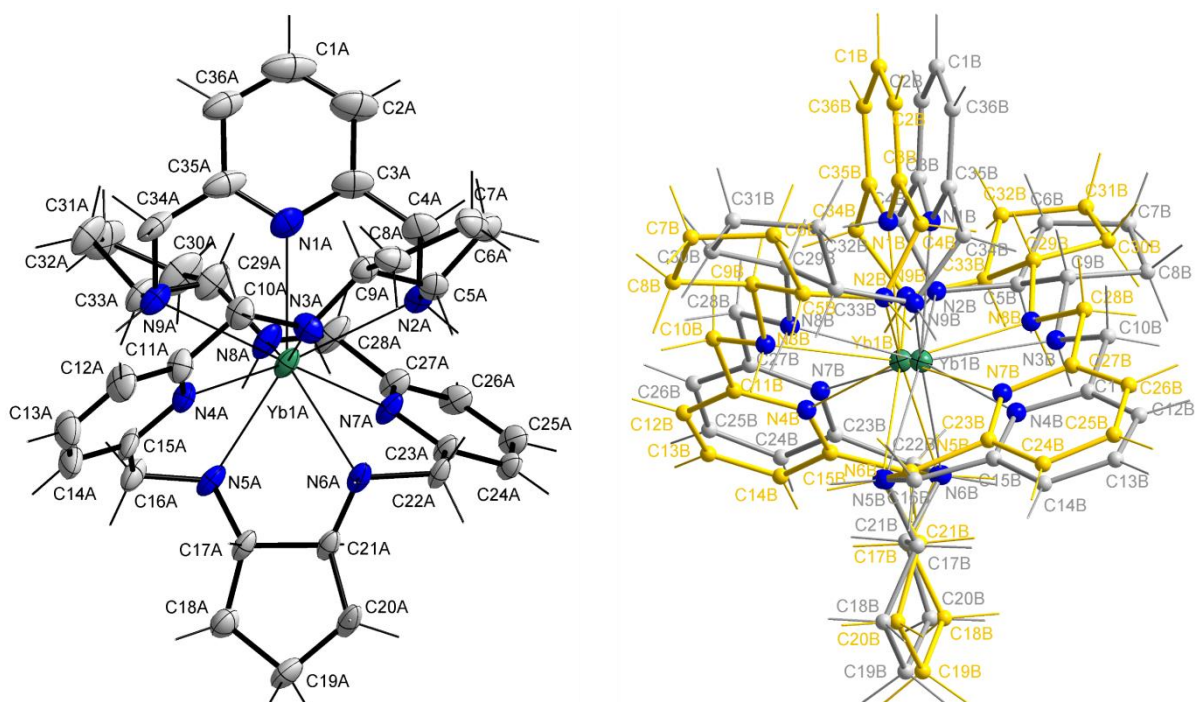


Figure S16. Cation **A** (left) and **B** (right) present in $[\text{YbS-2}](\text{NO}_3)_3 \cdot 1.6\text{CH}_3\text{CN} \cdot 0.5\text{H}_2\text{O}$, showing the atom-numbering scheme, and the disorder in **B**. Site occupation factors for grey (x, y, z) and yellow ($x, 1-y, 1-z$) positions of **B** = 0.5. Displacement ellipsoids are shown at the 30% probability level.

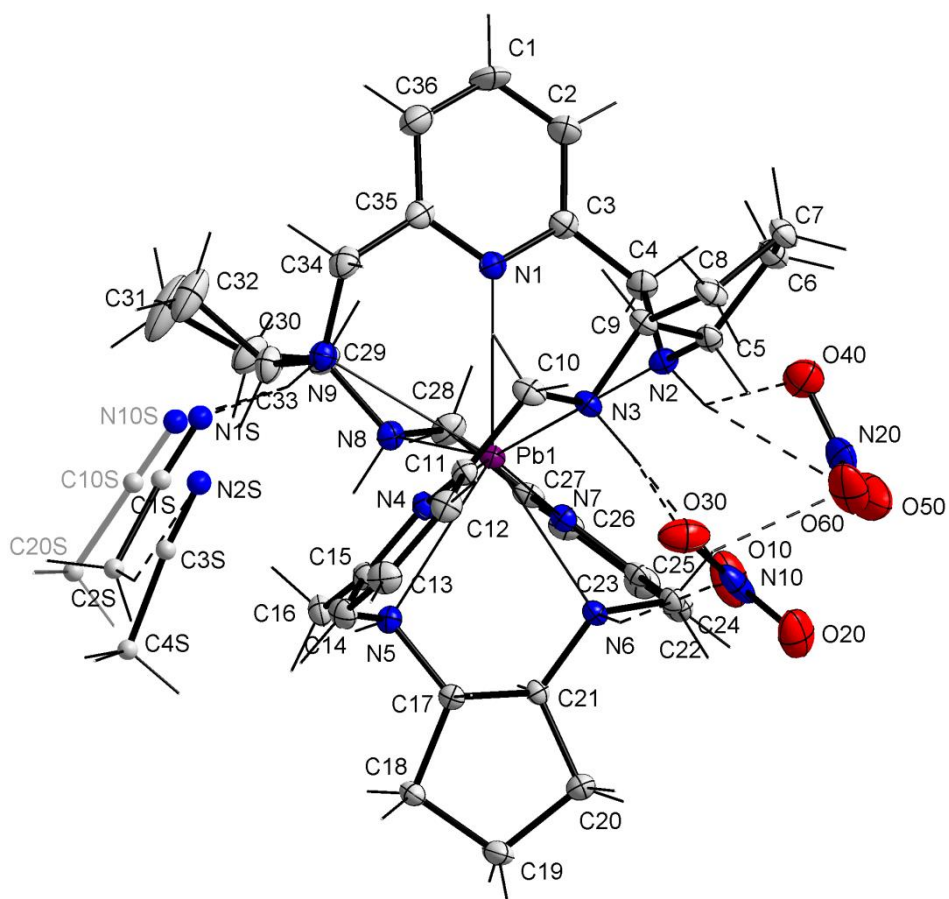


Figure S17. The asymmetric unit of $[\text{PbS-2}](\text{NO}_3)_2 \cdot 1.6\text{CH}_3\text{CN}$, showing the atom-numbering scheme, the symmetry-independent hydrogen contacts (dashed lines), and the disorder of acetonitrile molecule. Transparent bonds and atoms represent positions with s.o.f. < 0.5 . Displacement ellipsoids are shown at the 50% probability level.

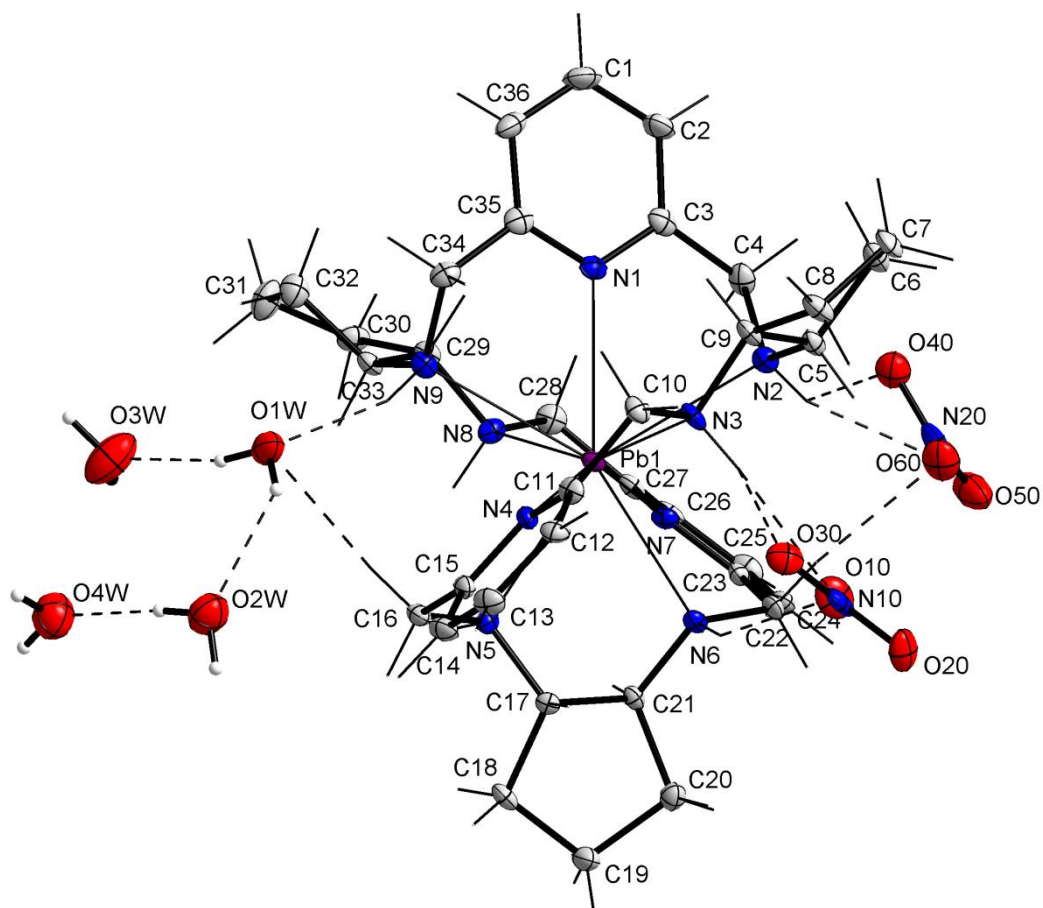


Figure S18. The asymmetric unit of $[\text{PbS-2}](\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, showing the atom-numbering scheme and the symmetry-independent hydrogen contacts (dashed lines). Displacement ellipsoids are shown at the 50% probability level.