

## Electronic Supporting Information

### ***In situ* generation of Ph<sub>3</sub>PO in cyanido-bridged {Fe<sup>III</sup>Ln<sup>III</sup>}<sub>2</sub> heterometallic squares (Ln = Eu, Sm)**

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## Experimental details

### Materials

The chemicals used, i.e.  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Ph}_3\text{PO}$ , as well as the acetonitrile solvent were of reagent grade and were purchased from commercial sources. The  $\text{Ph}_4\text{P}[\text{Fe}\{\text{HB}(\text{pz})_3\}(\text{CN})_3] \cdot \text{H}_2\text{O}$  precursor<sup>1</sup> ( $\text{Ph}_4\text{P}^+$  = tetraphenylphosphonium) and the pyim ligand<sup>2</sup> were prepared as described in the literature. Elemental analyses (C, H, N) were performed using a PerkinElmer 2400 analyzer. The values of the Fe : Ln molar ratio (1 : 1 for **1** and **2**) were determined by electron probe X-ray microanalysis at the Servicio Interdepartamental of the University of Valencia.

**Synthesis of 1 and 2:** an acetonitrile solution (20 cm<sup>3</sup>) of  $\text{Ph}_4\text{P}[\text{Fe}\{\text{HB}(\text{pz})_3\}(\text{CN})_3] \cdot \text{H}_2\text{O}$  (0.067 mmol) was poured into an acetonitrile solution (20 cm<sup>3</sup>) containing pyim (0.067 mmol) and the corresponding lanthanide salt as  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.067 mmol) [Ln = Eu (**1**), Sm(**2**)]. A similar reaction was carried out but in the presence of  $\text{Ph}_3\text{PO}$  (0.067 mmol). In both cases, X-ray quality crystals of **1** and **2** were obtained after ca. two weeks. Yield: ca. 70 %. IR (KBr/cm<sup>-1</sup>): 3281 (m), 3147 (m), 2544 (m), 2151(m), 2130 (m), 1471 (s), 1338 (s), 1314 (s), 1152 (s), 777 (m), 725 (m), 696 (m) (**1**); 3275 (m), 3145 (m), 2544 (m), 2149 (m), 2130 (m), 1471 (s), 1338 (s), 1336 (s), 1151 (s), 795 (m), 724 (m), 696 (m) (**2**). Anal. Calcd. for  $\text{C}_{80}\text{H}_{70}\text{B}_2\text{Eu}_2\text{Fe}_2\text{N}_{30}\text{O}_{14}\text{P}_2$  (**1**): C 44.14; H 3.21; N 19.31. Found: C 43.90; H 3.15; N 19.16%;  $\text{C}_{80}\text{H}_{68}\text{B}_2\text{Fe}_2\text{N}_{30}\text{O}_{14}\text{P}_2\text{Sm}_2$  (**2**): C 44.24; H 3.13; N 19.35. Found: C 44.10; H 3.20; N 19.31%.

**Caution:** cyanides are highly toxic and should be handled with great caution. We worked at the mmol scale and the preparations were performed in a well-ventilated fume hood. Concentrated aqueous solutions of sodium hypochlorite and sodium hydroxide were used to transform the cyanide from the waste into cyanate.

**Magnetical measurements.** Variable-temperature magnetic susceptibility measurements on polycrystalline samples of **1** and **2** were carried out with a Quantum Design MPMSXL-5 SQUID magnetometer in the temperature range of 1.9–300 K and under applied magnetic fields of 0.1 T ( $100 \leq T \leq 290$  K) and 500 G ( $1.9 \leq T < 100$  K). The magnetization versus magnetic field measurements were performed at 2.0 K in the field range of 0–5 T. The magnetic data were corrected for the diamagnetic contributions of the constituent atoms and also for the sample holder (a plastic bag).

**Crystallographic data collection and structure determination.** Data collection was performed at 100 K using Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$  with Bruker D8 Venture area-detector diffractometers. The structures were solved by intrinsic phasing (SHELXT-2013)<sup>3</sup> and refined by full-matrix least-squares procedures based on  $F^2$  with all measured reflections (SHELXL-2013).<sup>3,4</sup> The multiscan absorption correction implemented in SADABS<sup>5</sup> was applied to the data. All non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were introduced at their idealized positions and were refined using a riding model. The Diamond program<sup>6</sup> was used for generating the structural drawings for this publication.<sup>5</sup> A summary of the crystallographic data and structure refinement for the three compounds is given in Table S1. CCDC 1907944 (for **1**) 1907945 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

**Table S1.** Crystal data and details of the structure determination of compounds **1** and **2**

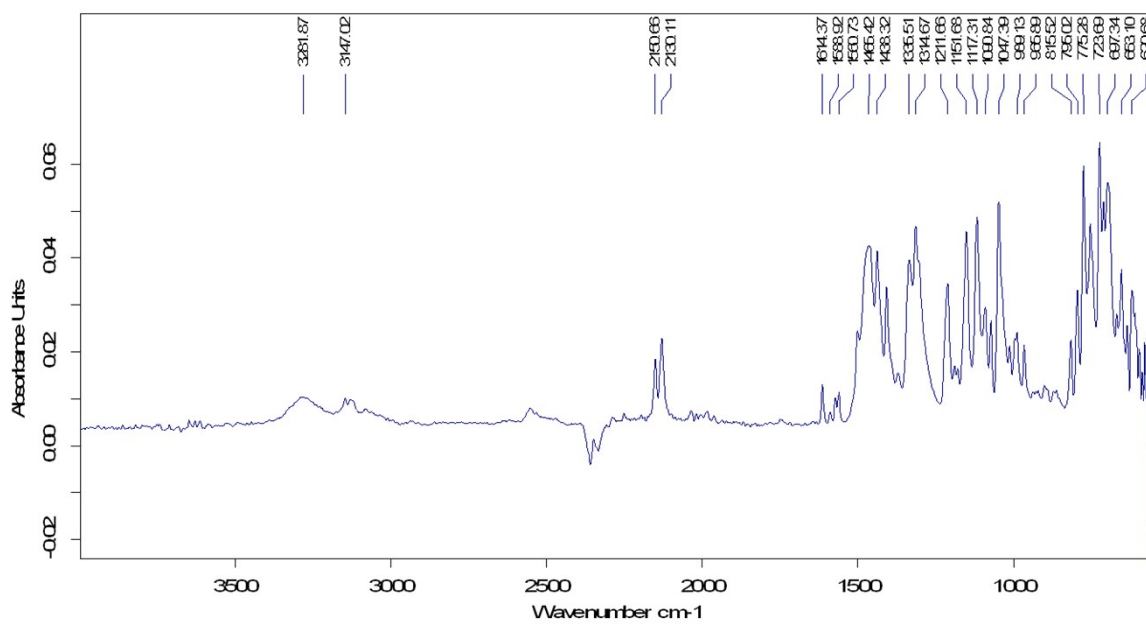
	<b>1</b>	<b>2</b>
Formula	C <sub>80</sub> H <sub>70</sub> B <sub>2</sub> Eu <sub>2</sub> Fe <sub>2</sub> N <sub>30</sub> O <sub>14</sub> P <sub>2</sub>	C <sub>80</sub> H <sub>68</sub> B <sub>2</sub> Sm <sub>2</sub> Fe <sub>2</sub> N <sub>30</sub> O <sub>14</sub> P <sub>2</sub>
Formula weight	2174.84	2169.60
$T(K)$	100(2)	100(2)
Crystal system	triclinic	triclinic
Space group	$P-1$	$P-1$
$a(\text{\AA})$	9.3973(7)	9.3796(6)
$b(\text{\AA})$	14.5965(11)	14.6171(9)
$c(\text{\AA})$	17.0615(14)	17.0712(12)
$\alpha(^{\circ})$	85.914(3)	85.834(2)
$\beta(^{\circ})$	83.284(3)	83.227(3)
$\gamma(^{\circ})$	71.364(3)	71.398(2)
$V(\text{\AA}^3)$	2200.9(3)	2201.2(3)
$Z$	1	1
$D_{\text{calcd}}(\text{g cm}^{-3})$	1.641	1.637
$\mu(\text{mm}^{-1})$	1.846	1.751
Goodness-of-fit, $S$	1.119	1.754
Final $R$ indices [ $I \geq 2\sigma(I)$ ] <sup>a</sup>	$R_I = 0.0185$ $wR_2 = 0.0468$	$R_I = 0.0213$ $wR_2 = 0.0539$
$R$ indices (all data) <sup>b</sup>	$R_I = 0.0188$ $wR_2 = 0.0470$	$R_I = 0.0219$ $wR_2 = 0.0542$

$$^a R_I = \Sigma(|F_o| - |F_c|) / \Sigma|F_c| \quad ^b wR_2 = \{\Sigma[w(F_o^2 - F_c^2)_2] / \Sigma[w(F_o^2)_2]\}^{0.5}$$

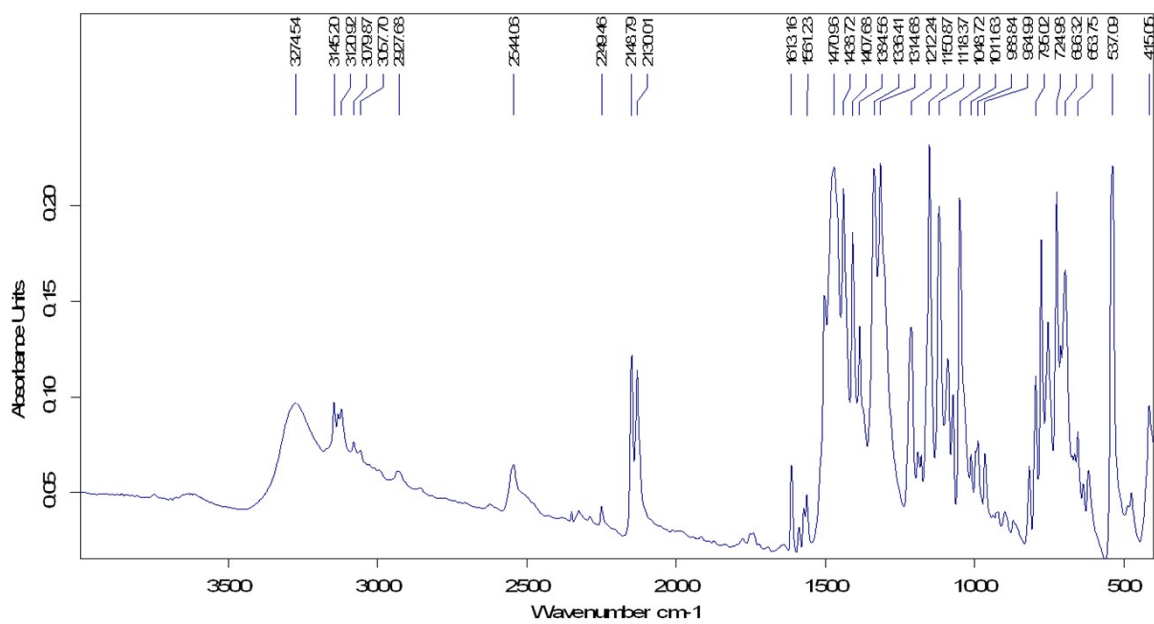
## References

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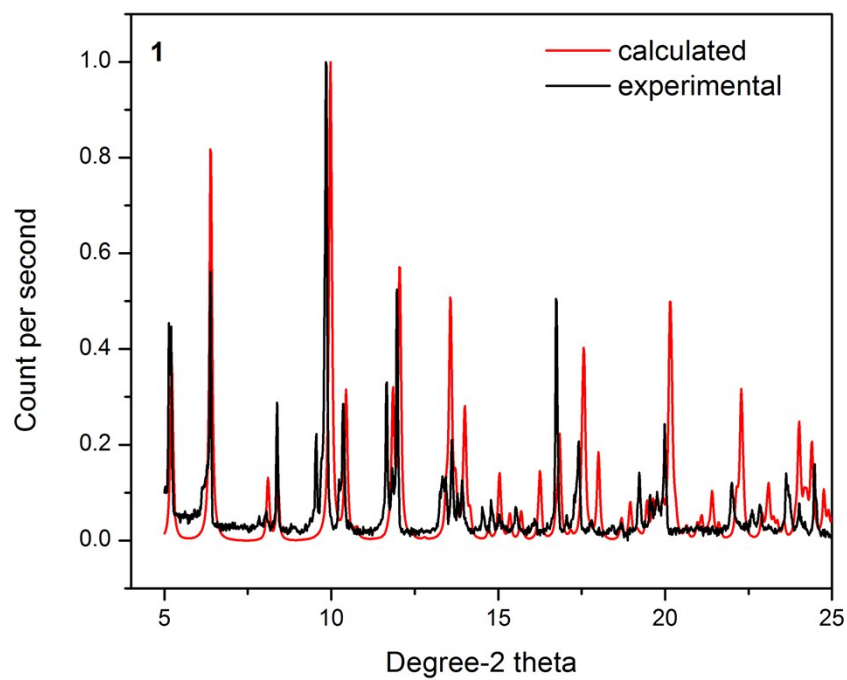
2. (a) O. Schott, J. Ferrando-Soria, A. Bentama, S.-E. Stiriba, J. Pasán, C. Ruiz-Pérez, M. Andruh, F. Lloret and M. Julve, *Inorg. Chim. Acta*, 2011, **376**, 358; (b) K. A. Reeder, E. V. Dose and L. J. Wilson, *Inorg. Chem.*, 1978, **17**, 1071.
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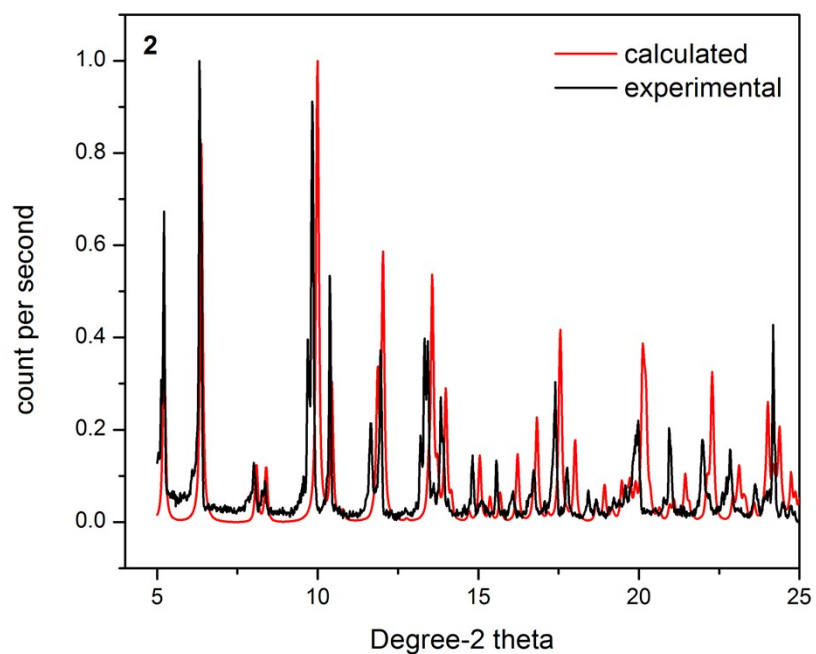
**Fig. S1.** FTIR spectrum of compound 1.



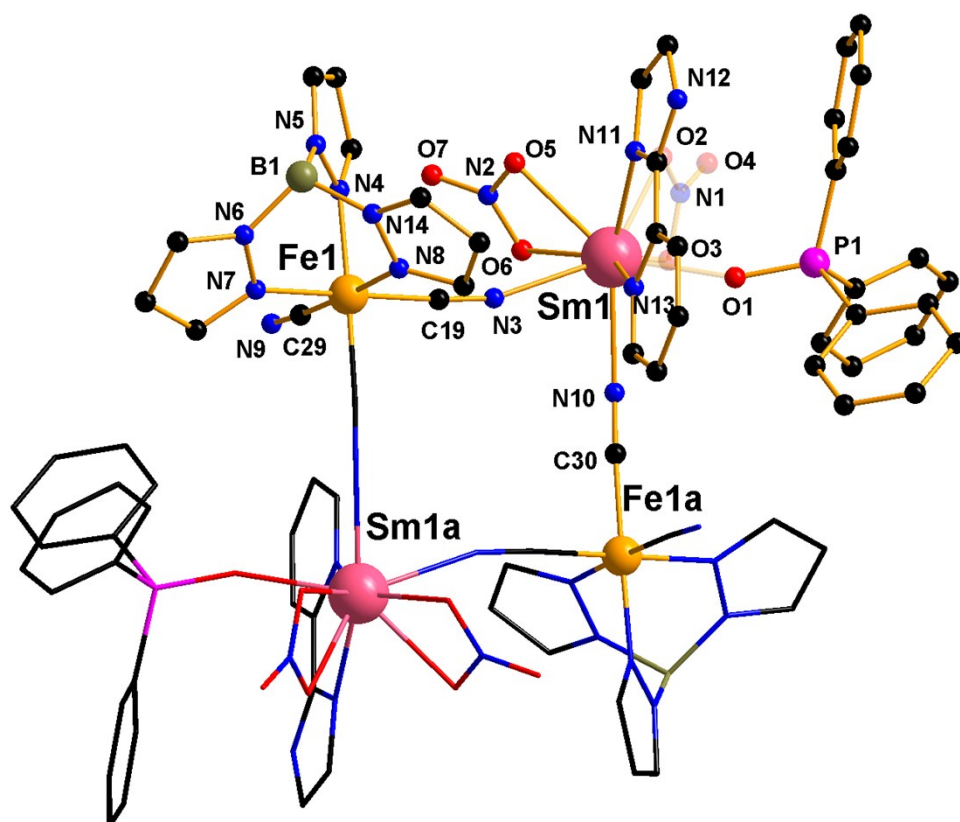
**Fig. S2.** FTIR spectrum of compound 2.



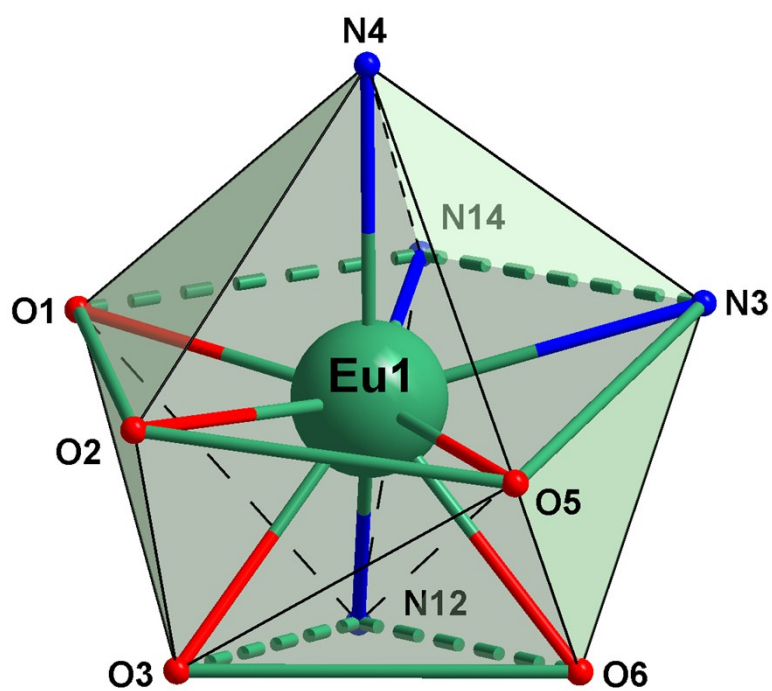
**Figure S3.** Experimental and calculated powder X-ray diffractograms at room temperature for compound **1**.



**Figure S4.** Experimental and calculated powder X-ray diffractograms at room temperature for compound **2**.

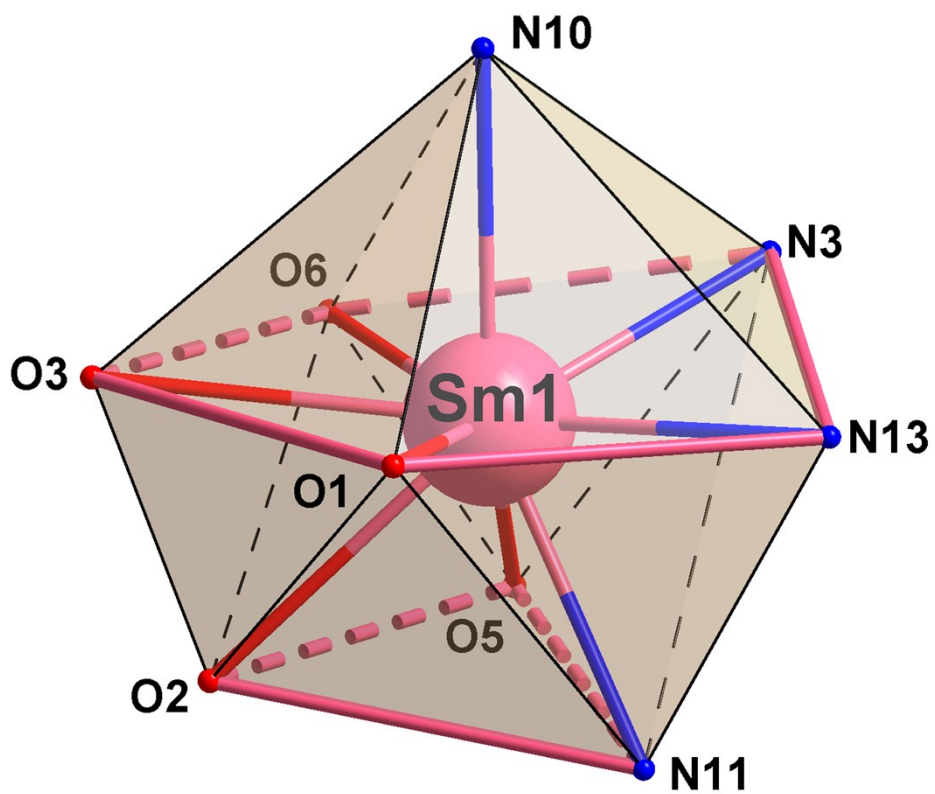


**Figure S5.** View of the square units in **2** together with the atom numbering scheme (the molecular fragment generated by the inversion symmetry operation is represented as wires and sticks) [Symmetry code: (a) =  $1-x, 1-y, 1-z$ ].



**Figure S6.** Muffin-like coordination polyhedron of the europium(III) ion in **1**.



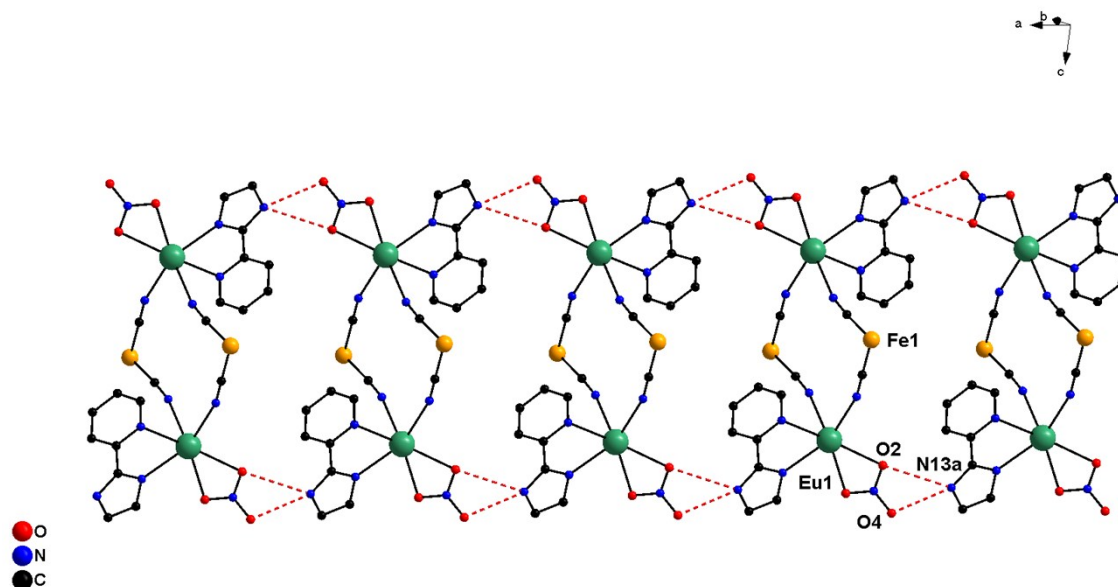


**Figure S7.** Muffin-like coordination polyhedron for the samarium(III) ion in **2**.

**Table S2.** Summary of SHAPE analysis for the [LnN<sub>4</sub>O<sub>5</sub>] fragments in **1** and **2** [Ln = Eu(**1**) and Sm (**2**)].

CN = 9 <sup>b</sup>	Eu(III)	Sm(III)
EP-9	34.383	34.404
OPY-9	22.475	22.436
HBPY-9	18.154	18.094
JTC-9	15.452	15.527
JCCU-9	8.840	8.853
CCU-9	7.696	7.696
JCSAPR-9	2.899	2.975
CSAPR-9	2.057	2.124
JTCTPR-9	3.700	3.807
TCTPR-9	2.855	2.944
JTDIC-9	12.968	12.851
HH-9	11.739	11.725
<b>MFF-9</b>	<b>1.282</b>	<b>1.298</b>

<sup>a</sup>The listed values correspond to the deviation between the ideal and real coordination polyhedra, the lowest values being given in bold. <sup>b</sup>EP-9, *D*<sub>9h</sub>, enneagon; OPY-9, *C*<sub>8v</sub>, octagonal pyramid; HBPY-9, *D*<sub>7h</sub>, heptagonal bipyramid; JTC-9, *C*<sub>3v</sub>, Johnson triangular cupola J3; JCCU-9, *C*<sub>4v</sub>, capped cube J8; CCU-9, *C*<sub>4v</sub>, spherical-relaxed capped cube; JCSAPR-9, *C*<sub>4v</sub>, capped square antiprism; CSAPR-9, *C*<sub>4v</sub>, spherical capped square antiprism; JTCTPR-9, *D*<sub>3h</sub>, tricapped trigonal prism J51; TCTPR-9, *D*<sub>3h</sub>, spherical tricapped trigonal prism; JTDIC-9, *C*<sub>3v</sub>, tridiminished icosahedron; HH-9, *C*<sub>2v</sub>, hula-hoop; MFF-9, *C*<sub>s</sub>, muffin.

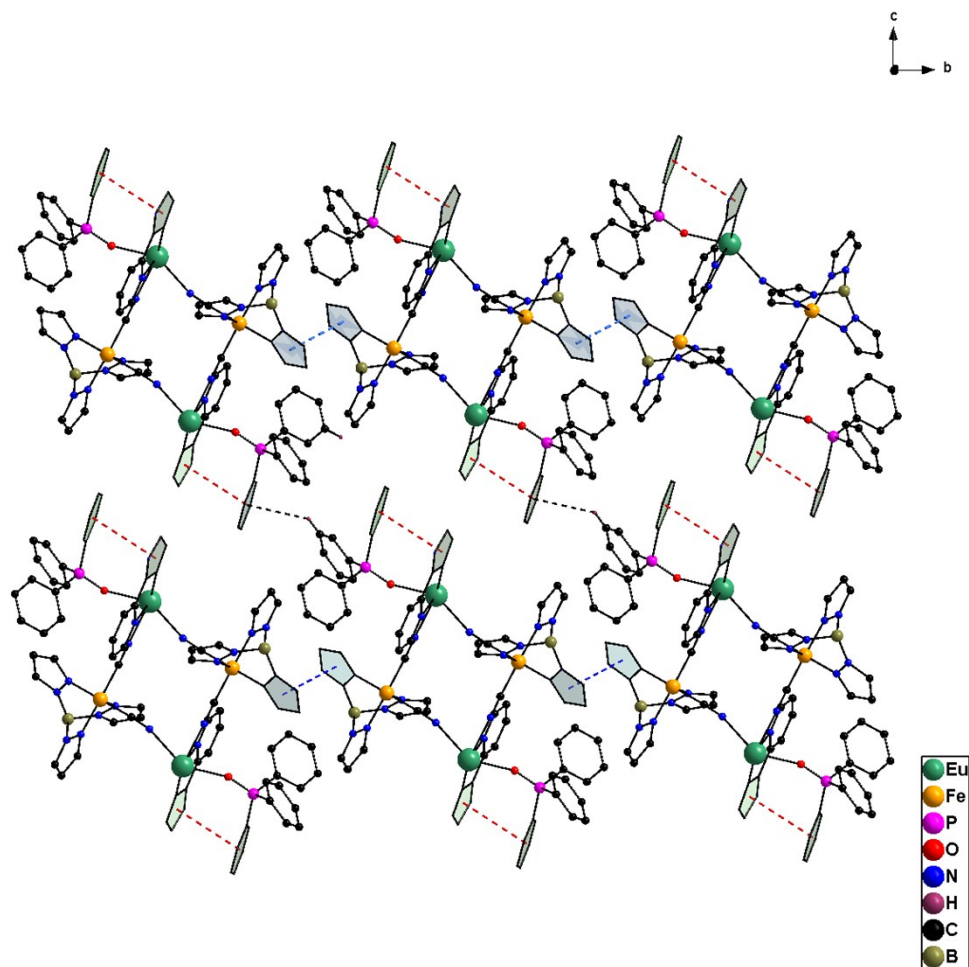


**Figure S8.** Detail of the packing diagram for **1** showing the supramolecular chains formed through hydrogen bonds, after an axis parallel to the crystallographic *a* axis [the triphenylphosphine oxide groups, two nitrate groups as well as the pyrazolyl rings of the  $(\{\text{HB}(\text{pz})_3\}^-)$  ligands were omitted for the sake of clarity]. Symmetry code: (a) =  $-1+x, y, z$ .

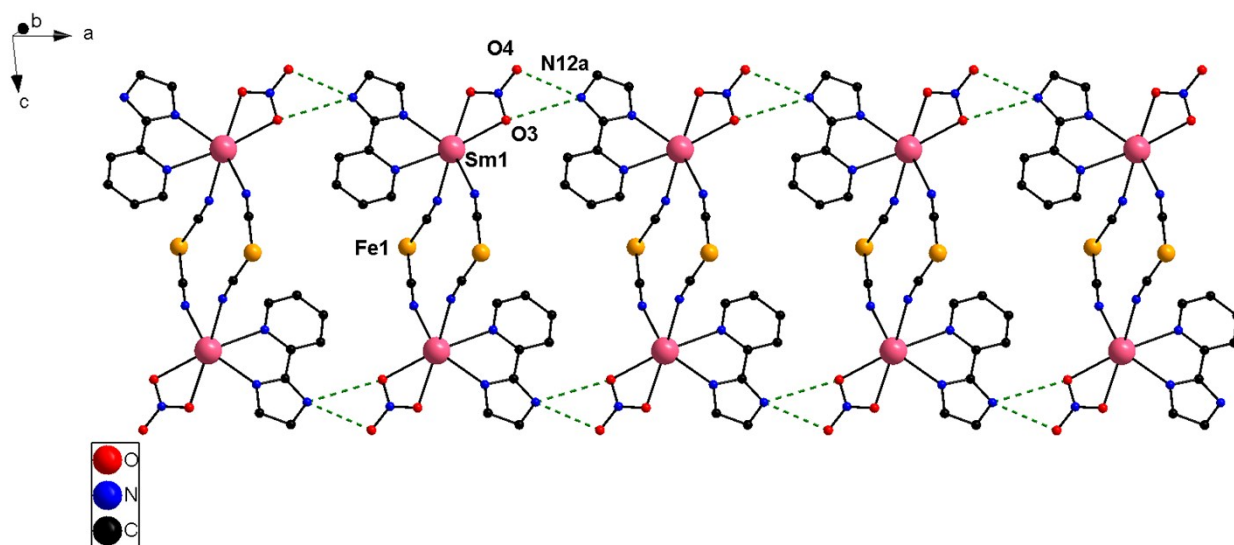
**Table S3.** Selected intermolecular contacts (Å) for **1**\*

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	Angle D-H...A
N13-H13 <sup>a</sup> ...O2	0.82(4)	2.60(4)	3.315(3)	148(3)
N13-H13 <sup>a</sup> ...O4	0.82(4)	2.21(4)	2.876(3)	139(3)

\*Symmetry code: (a) =  $-1+x, y, z$ .

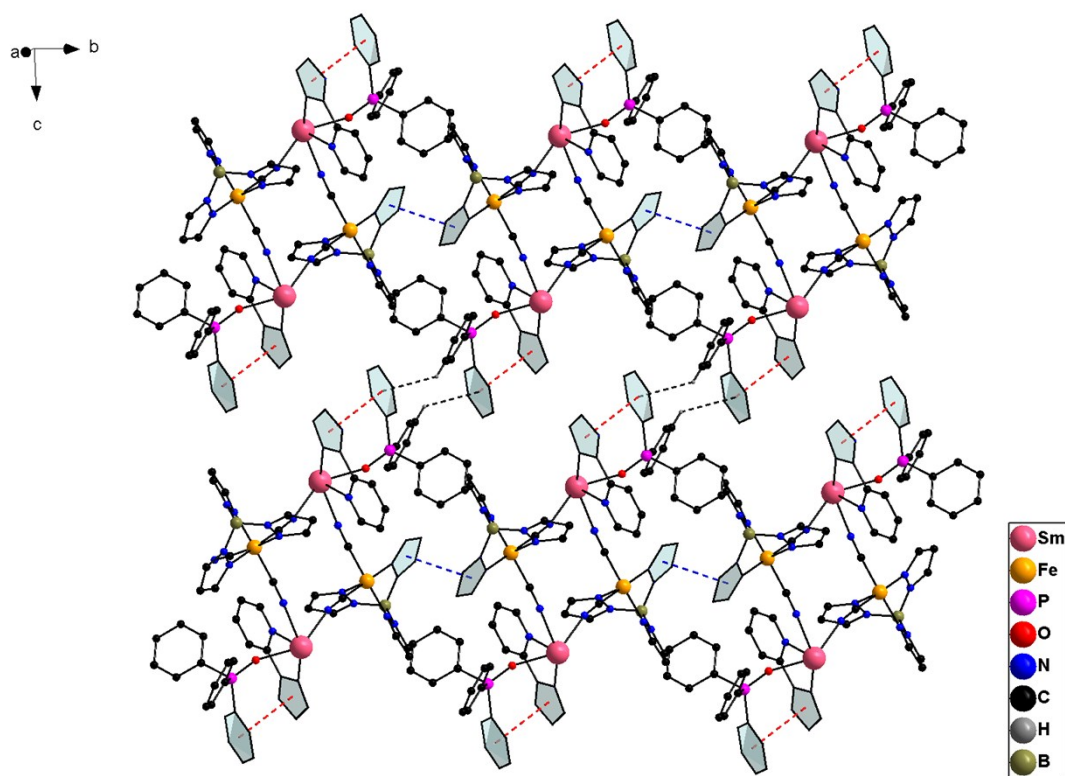


**Figure S9.** Detail of the packing diagram for **1** in the crystallographic *bc* plane, showing the intra- (red-dashed line) and intermolecular  $\pi\cdots\pi$  (blue dashed lines) and C-H $\cdots\pi$  (black dashed lines) stacking interactions established between pyrazolyl, imidazole and phenyl rings of pyim,  $\{\text{HB}(\text{pz})_3\}^-$  and  $\text{PPh}_3\text{O}$  ligands. The values of the centroid-centroid distances are ca. 3.60 (pyrazolyl-pyrazolyl rings), 3.82 (phenyl-imidazolyl rings) and 3.16 Å (C-H<sub>phenyl</sub>-phenyl ring), with the angles between the normal to the ring and the centroid-centroid vector being ca. 11.90 (pyrazolyl-pyrazolyl rings), 11.13/16.70 (phenyl-imidazolyl rings) and ca. 8.30° (C-H<sub>phenyl</sub>-phenyl ring). The nitrate groups were removed for the sake of clarity.



**Figure S10.** Detail of the packing diagram in **2** showing the hydrogen-bonded ladder-like chains formed along the *a* axis. The triphenylphosphine oxide groups, two nitrate groups as well as the pyrazolyl rings of the  $\{\text{HB}(\text{pz})_3\}^-$  ligands were omitted for the sake of clarity [Symmetry code: (a) =  $x, y, -1+z$ ; (b) =  $x, y, 1+z$ ].

Selected intermolecular contacts ( $\text{\AA}$ ) for **2**<sup>\*,&</sup>:  $\text{O3}\cdots\text{N12a} = 3.246 \text{ \AA}$  and  $\text{O4}\cdots\text{N12a} = 2.879 \text{ \AA}$ . \*Symmetry code: (a) =  $1+x, y, z$ . & The hydrogen atoms from the  $\text{N-H}_{\text{pyim}}$  molecules could not be assigned.



**Figure S11.** View of the crystal packing of **2** in the *bc* plane showing the supramolecular layers formed through  $\pi\cdots\pi$  (red and blue dashed lines) and C-H $\cdots\pi$  (black dashed lines) intra- and intermolecular interactions employing imidazole, pyrazolyl and phenyl rings from pyim,  $\{\text{HB}(\text{pz})_3\}^-$  and  $\text{PPh}_3\text{O}$  ligands. The centroid-centroid distance is ca. 3.82 (intramolecular imidazole-phenyl rings), 3.60 (pyrazolyl-pyrazolyl rings) and 3.15 Å (pyrazolyl-phenyl rings). The angles between the normal to the ring and the centroid-centroid vector is ca. 12.11 (pyrazolyl-pyrazolyl), 11.16/16.75 (intramolecular pyrazolyl-phenyl) and 8.33° (phenyl-phenyl). The nitrate ligands were removed for the sake of clarity.