Supporting Information

Table S1. Bond lengths (Å) and bond angles (°) in coordination environment of Th^{IV} atoms in crystal structures $(H_5O_2)[Th(DMF)_5(H_2O)]_2[Fe(CN)_6]_3$ (**1**) and $[Th(DMF)_4(H_2O)_3][Fe(CN)_6](NO_3)\cdot 2H_2O$ (**2**).

1		**2**	
Th1–O1	2.418(4)	Th1–O1	2.441(6)
Th1–O2	2.440(4)	Th1–O2	2.415(7)
Th1–O3	2.404(4)	Th1–O3	2.391(4)
Th1–O4	2.394(4)	Th1–O1*w*	2.514(6)
Th1–O5	2.409(4)	Th1–O2*w*	2.473(4)
Th1–O1*w*	2.464(3)	Th1–N4	2.575(5)
Th1–N6	2.583(4)		
Th1–N11*a*	2.589(4)		
Th1–N12	2.578(5)		
N6–Th1–N11*a*	68.97(14)	N4–Th1–N4*b*	122.6(3)
N12–Th1–N11*a*	120.51(16)	O1*w*–Th1–N4*b*	118.68(13)
O1*w*–Th1–N11*a*	120.22(15)		
O1*w*–Th1–N12	119.24(15)		

Symmetry code: (*a*) 1 – *x*, 2 – *y*, 2 – *z* ; (*b*) *x*, 1/2 – *y*, *z*.

Table S2. Interatomic distances (Å) in coordination environment of Fe^{III} atoms (only symmetrically independent distances are presented).

Compound 1		**Compound 2**	
Fe1–C16	1.935(5)	Fe1–C9	1.917(6)
Fe1–C17	1.953(6)	Fe1–C10	1.950(7)
Fe1–C18	1.928(5)	Fe1–C11	1.943(7)
Fe1–C19	1.929(6)		
Fe1–C20	1.937(6)		
Fe1–C21	1.922(5)		
Fe2–C22	1.923(5)		
Fe2–C23	1.944(6)		
Fe2–C24	1.955(6)		

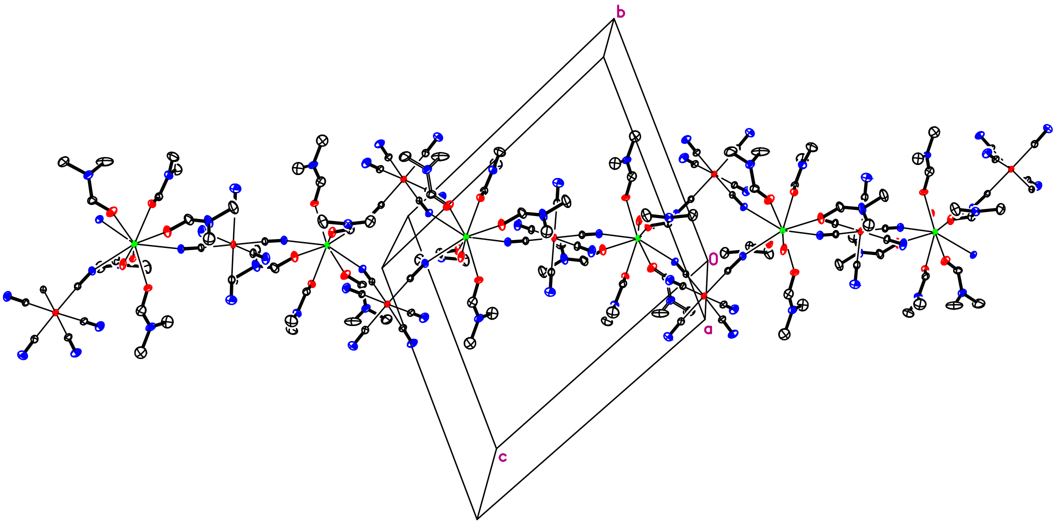


Figure S1. Infinite anionic chain in crystals of $(H_5O_2)[Th(DMF)_5(H_2O)]_2[Fe(CN)_6]_3$ (**1**). Hydrogen atoms are omitted for clarity.

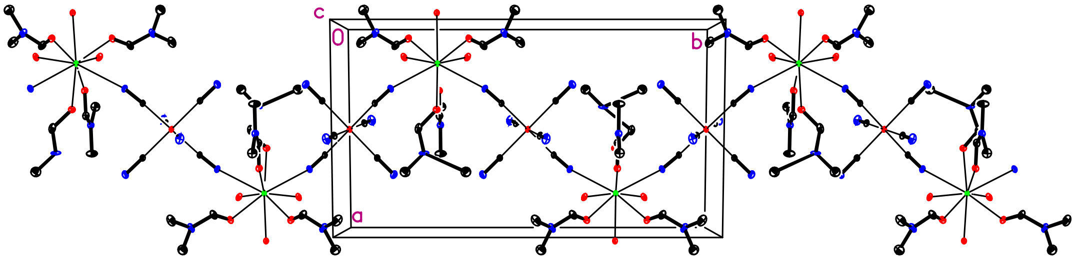


Figure S2. Infinite cationic chain in crystals of $[Th(DMF)_4(H_2O)_3][Fe(CN)_6](NO_3)\cdot 2H_2O$ (**2**). Hydrogen atoms are omitted for clarity.

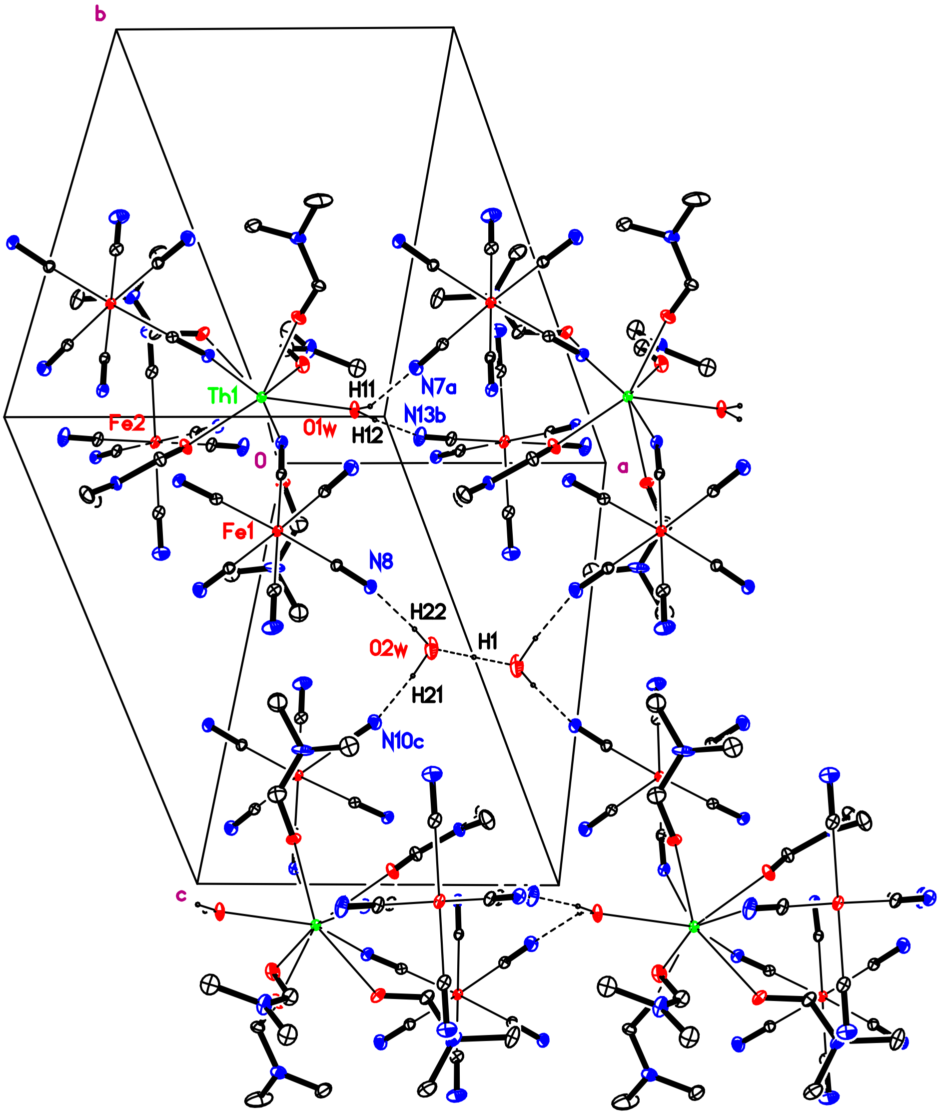
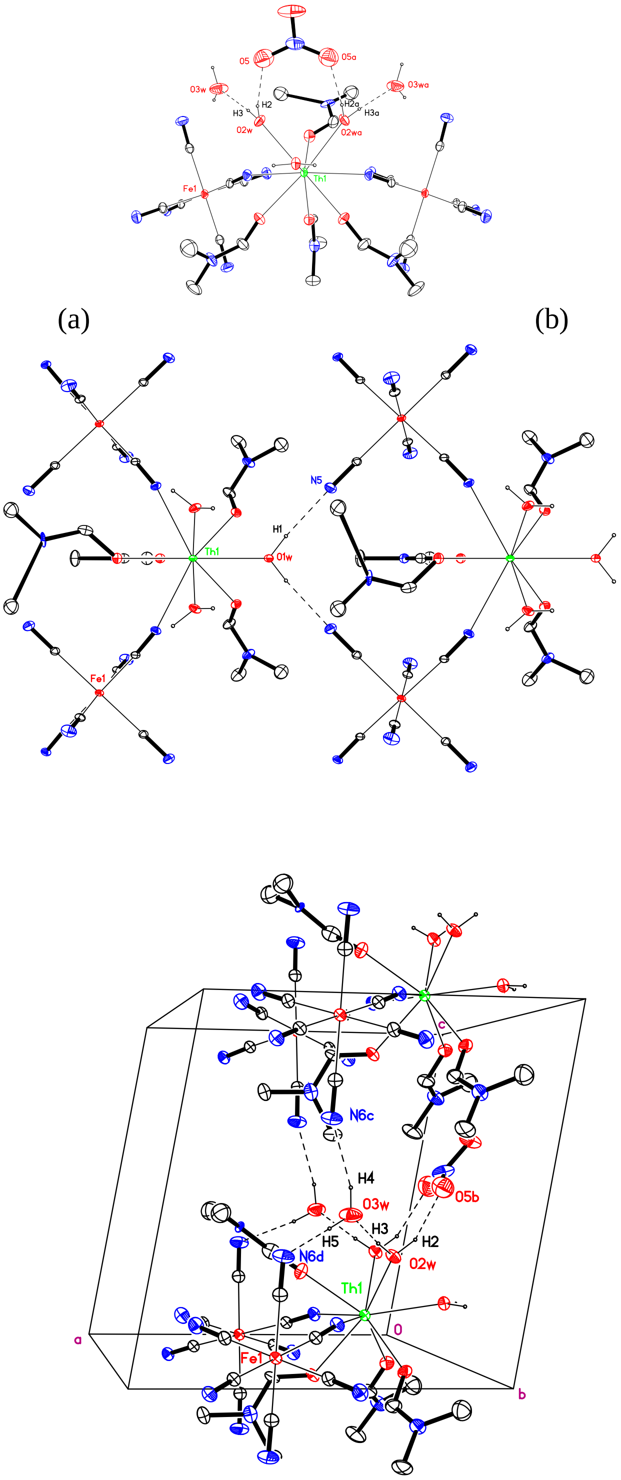


Figure S3. Hydrogen bonding in crystal structure **1**. Symmetry codes are the same as in **Table S3**.

Table S3. Hydrogen bonds for compound **1**.

D–H···A	**D–H, Å**	**H···A, Å**	**D···A, Å**	**DHA, deg**	**Symmetry code**
O1*w*–H11···N7*a*	0.83(2)	2.03(4)	2.799(6)	154(6)	2 – *x*, 2 – *y*, 2 – *z*
O1*w*–H12···N13*b*	0.834(19)	1.94(2)	2.776(7)	174(6)	1 + *x*, *y*, *z*
O2*w*–H21···N10*c*	0.84(2)	1.80(3)	2.637(8)	172(11)	1 – *x*, 1 – *y*, 2 – *z*
O2*w*–H22···N8	0.84(2)	1.81(4)	2.616(8)	161(11)	



(a) (b)

(c)

Figure S4. Hydrogen bonding in crystal structure **2**. Hydrogen bonds with O1*w* link the chains along the *a* axis **(a)**. Hydrogen bonds with O2*w* as a H donor link the nitrate anion and water molecule of crystallization O3*w* **(b)**. Hydrogen bonds with O3*w* connect two adjacent cationic chains through O*w*–H···N interaction **(c)**. Symmetry codes are the same as in **Table S4**.

Table S4. Hydrogen bonds for compound **2**.

D–H···A	**D–H, Å**	**H···A, Å**	**D···A, Å**	**DHA, deg**	**Symmetry code**
O1*w*–H1···N5*a*	0.853(19)	2.02(3)	2.865(8)	169(6)	*x* – 2, 3/2 – *y*, *z*
O2*w*–H2···O5*b*	0.84(2)	1.87(4)	2.660(10)	155(7)	*x* – 2, *y*, *z*
O2*w*–H3··O3*w*	0.85(2)	1.87(3)	2.715(8)	172(8)	
O3*w*–H4···N6*c*	0.84(2)	2.10(5)	2.900(9)	159(11)	*x*, *y*, *z* + 1
O3*w*–H5···N6*d*	0.85(2)	2.37(5)	3.175(10)	159(11)	1 – *x*, 1 – *y*, –*z*

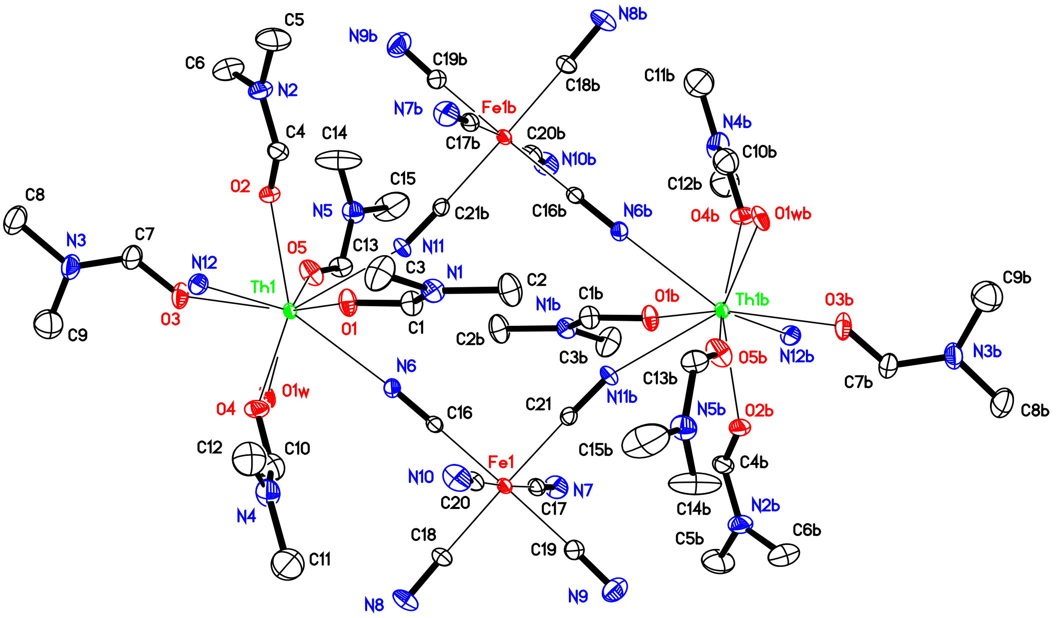


Figure S5. The centrosymmetric tetranuclear fragment in anionic chain **1** (H atoms omitted, 20% ellipsoids). Symmetry code: (*b*) 1 – *x*, 2 – *y*, 2 – *z*.

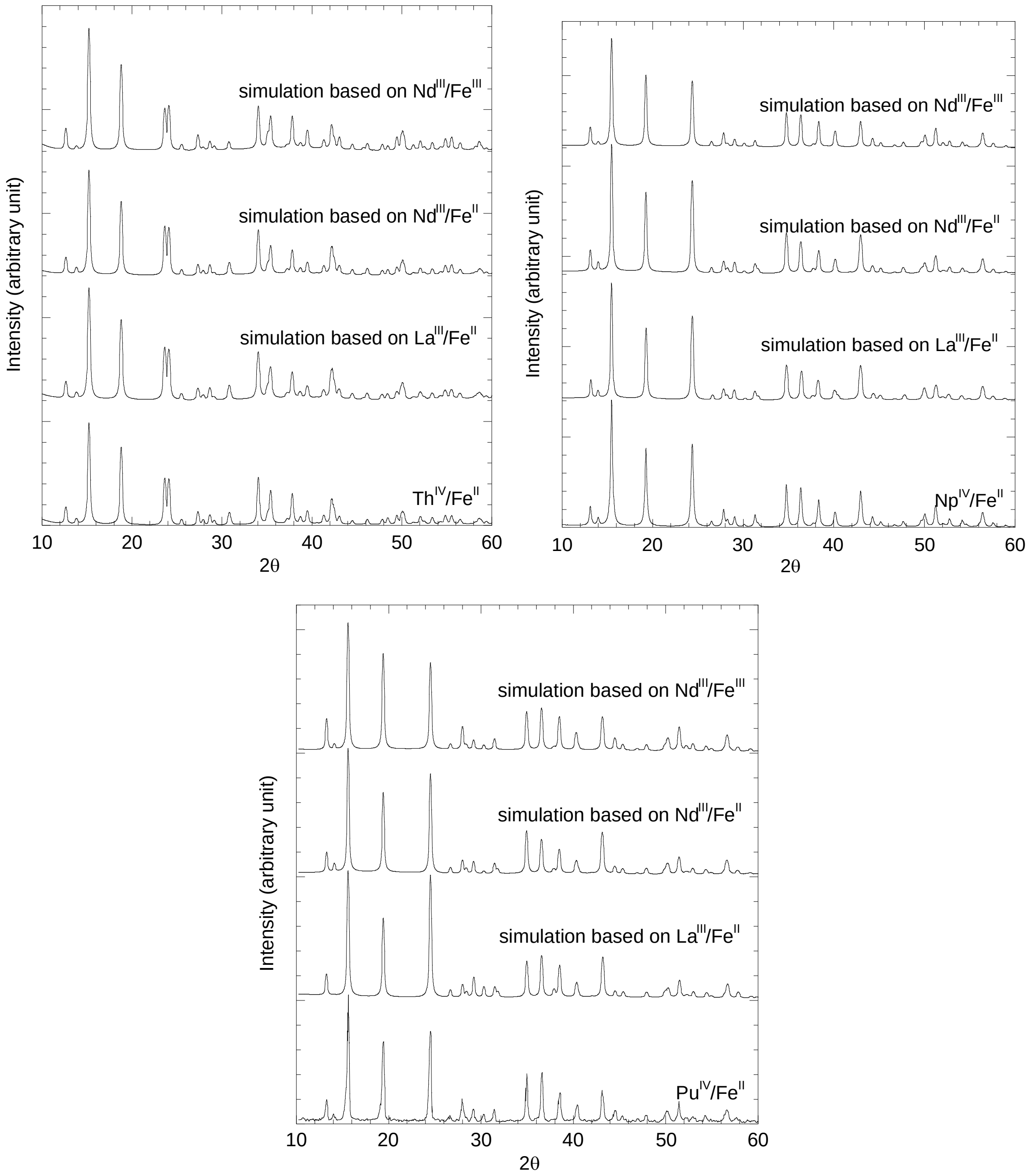


Figure S6. Comparison between simulated powder XRD spectrum based on $KLa^{III}Fe^{II}(CN)_6\cdot4H_2O$, $KNd^{III}Fe^{II}(CN)_6\cdot4H_2O$ and $Nd^{III}Fe^{III}(CN)_6\cdot5H_2O$ structures and the experimental powder pattern from actinide ferrocyanides (S6 a: Th; S6 b: Np; S6 c: Pu).

Table S5. Best-fit EXAFS parameters for compound **Th^{IV}/Fe^{III}/DMF (1)** and comparison with XRD results. σ^2 is the Debye-Waller factor, S_0^2 is the global amplitude factor, Δe_0 is the energy shift parameter in eV, r is the quality factor of the fit in R space (cumulating on Fe K-edge spectra and An L$_{III}$-edges), ε is the average noise of the spectrum, *QF* is the quality factor. All the mentioned coordination numbers (CN) have been fixed at 6 cyano ligands for the Fe cation and 3 bridged cyano ligands, 1 water molecule and 5 DMF ligands for thorium. Th-N-C distances are given in average of the 3 set of distances in the 3 cyano bridges and The Th-DMF as an average of the 5 Th-DMF distances obtained by XRD. Uncertainties are in italics in parentheses.The Debye-Waller factor for parameter d_{C-N} is obtained from single scattering path Fe-N (see experimental section).

	Th^{IV}/Fe^{III}/DMF EXAFS	**Th^{IV}/Fe^{III}/DMF XRD**
CN	6	6
***d*Fe-C (Å)**	1.93*(1)*	1.937*(5)*
σ^2 (Å^2)	0.0031	
CN	6	6
***d*C-N (Å)**	1.13*(1)*	1.145*(5)*
σ^2 (Å^2)	0.0090	
CN	1	1
***d*An-O$_w$ (Å)**	2.49*(3)*	2.464*(5)*
σ^2 (Å^2)	0.0021	
CN	5	5
***d*An-O$_{DMF}$ (Å)**	2.41*(3)*	2.413*(4)*
σ^2 (Å^2)	*0.0032*	
CN	3	3
***d*An-N (Å)**	2.61*(6)*	2.583*(4)*
σ^2 (Å^2)	*0.014*	
An: S_0^2, Δe_0, ε	1.1, 7.2eV 0.0019	
Fe: S_0^2, Δe_0, ε	0.6, -4.8 eV 0.0012	
***r* (%)**	1.2	
QF	4.12	

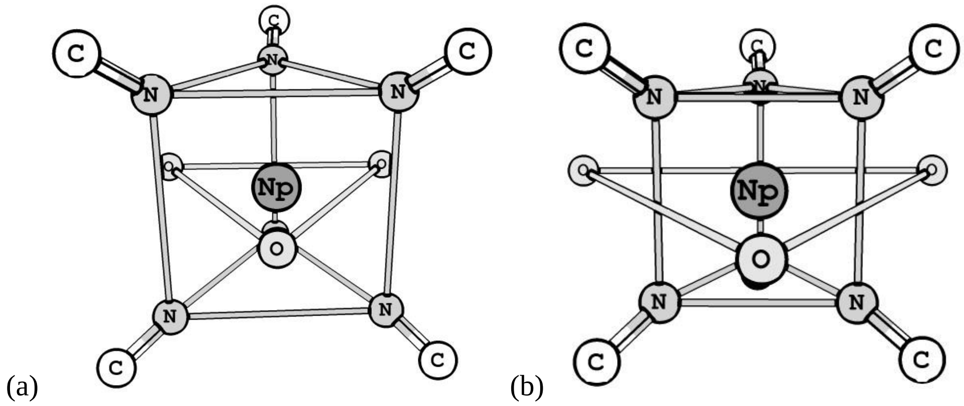


Figure S7. Comparison of two $\{Np(NC)_6(OH_2)_3\}$ clusters in a trigonal tricapped geometry. (a) is the concave prism $d_{\text{An-O}} < d_{\text{An-CN}}$ and (b) is the convex prism $d_{\text{An-O}} > d_{\text{An-CN}}$.