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SUPPLEMENTARY MATERIAL

Structural Systematics of Lanthanide(III) Picrate Solvates: Neutral, Mononuclear $Ln(pic)_3(dimethylsulfoxide)_3$ Arrays

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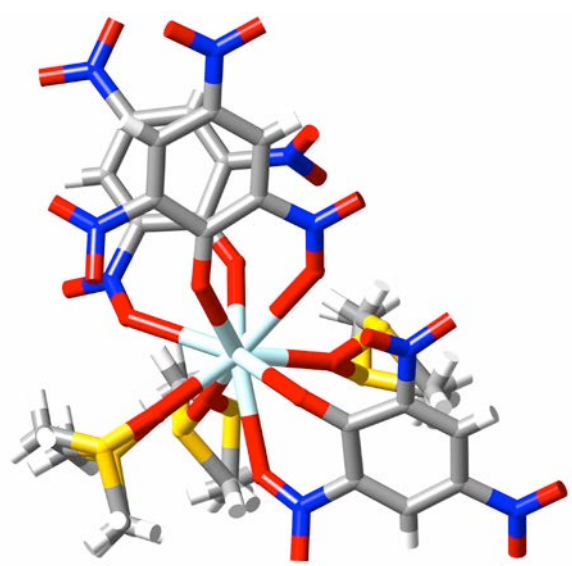
A. X-ray structures of the complex molecules

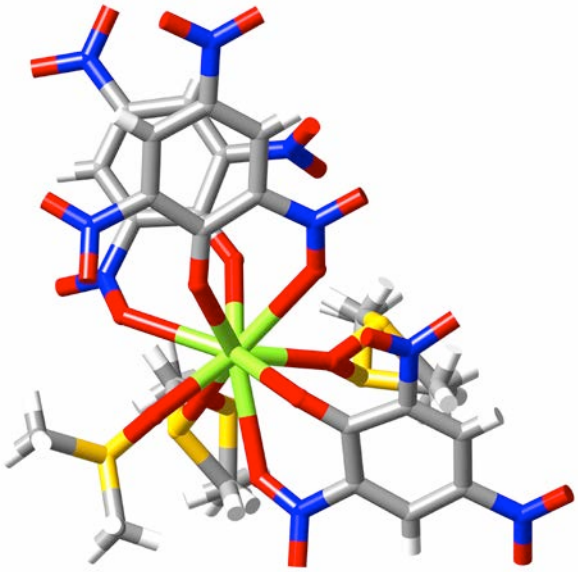
B. Hirshfeld surface diagrams

C. Tables of selected geometrical parameters

Figure S1 Structure of the molecules present in the monoclinic, *C*2/c, form of *mer*-[Ln(pic)$_3$(dmso)$_3$]. Stick representations, viewed down *c*. Disordered components are shown as if each site is fully occupied. The molecules are chiral but both enantiomers are present in the lattice.



Ln = La



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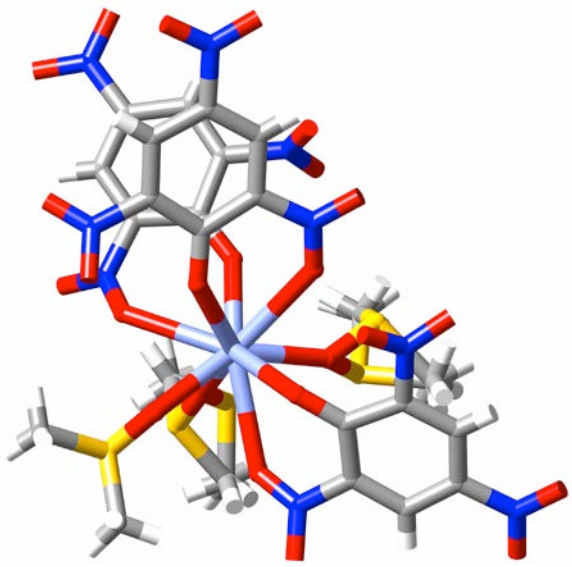

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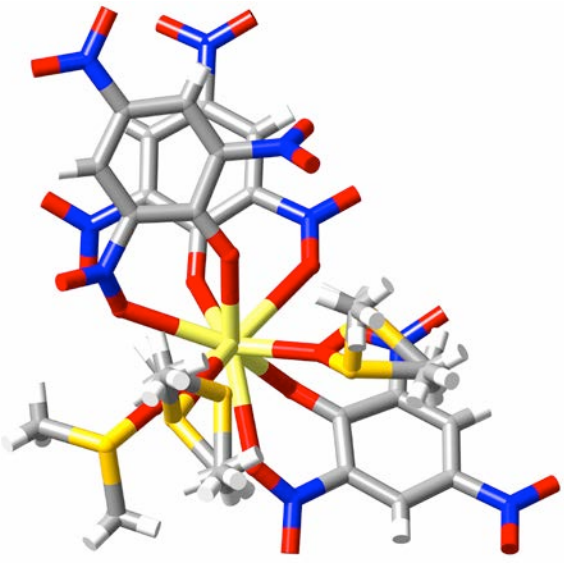

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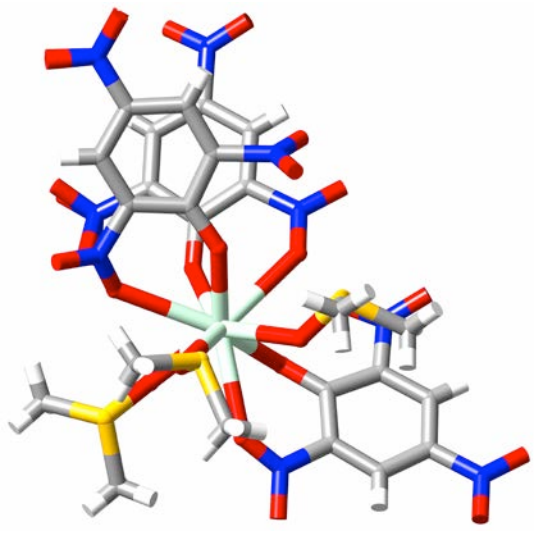
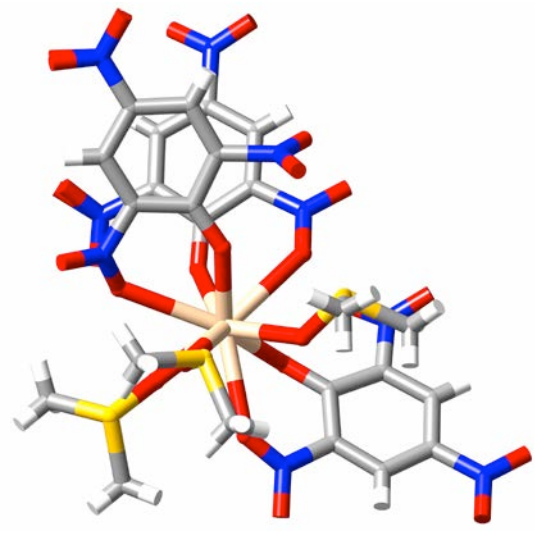
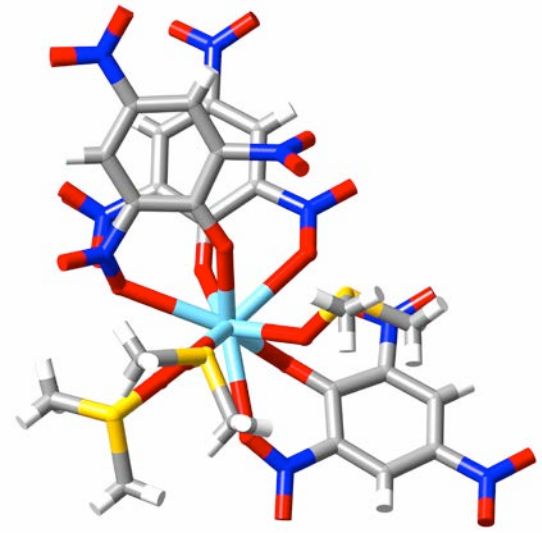


Ln = Gd



Ln = Dy



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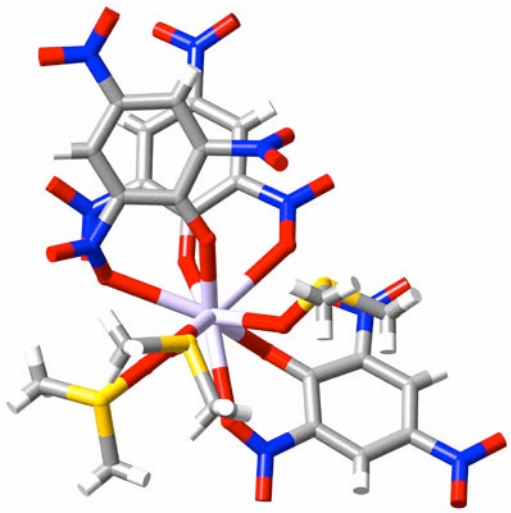
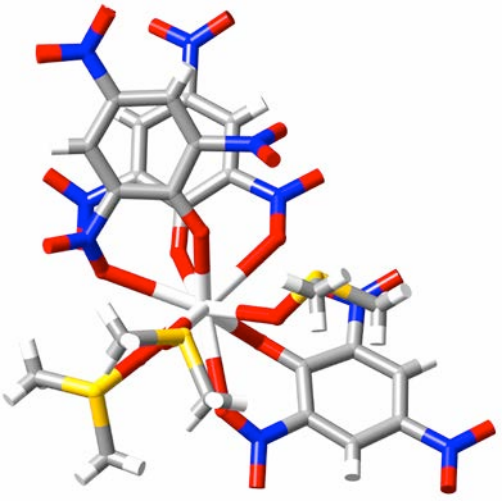
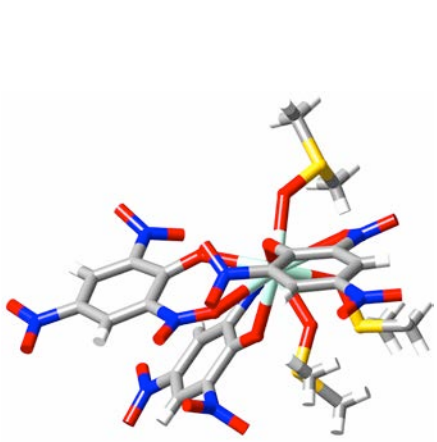


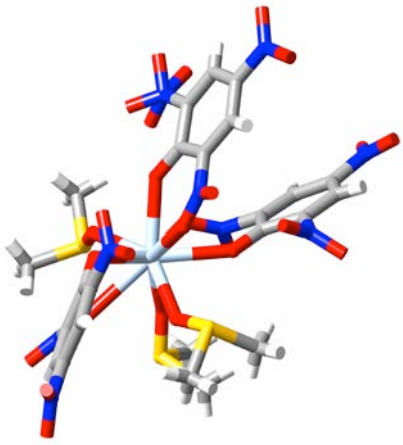
Ln = Lu



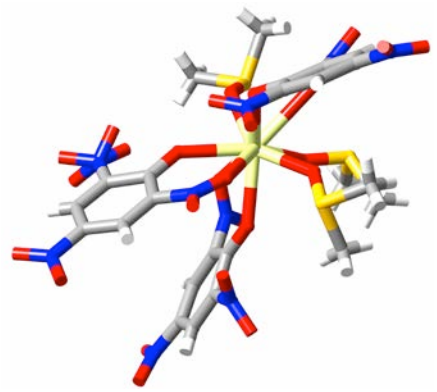
Ln = Y

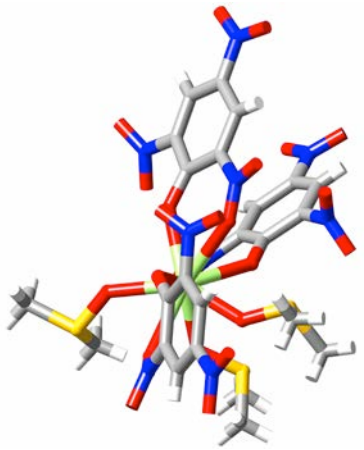
Figure S2 Molecules present in the triclinic, $P\bar{1}$, form of *mer*-[Ln(pic)$_3$(dmso)$_3$]. Stick representations, viewed down *c*. Disordered components are shown as if each site is fully occupied. The two inequivalent molecules are chiral but both enantiomers of each are present in the lattice.



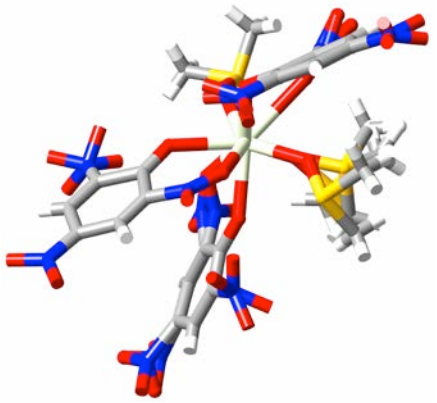


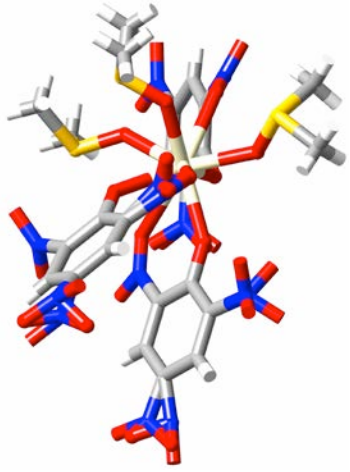
Ln = La molecule 1 molecule 2





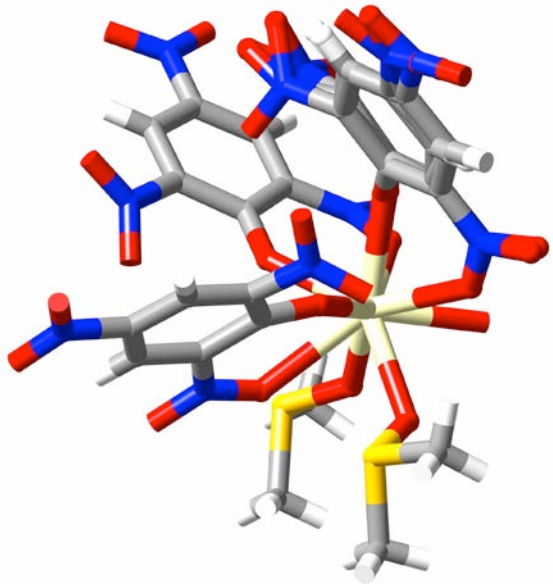
Ln = Pr molecule 1 molecule 2



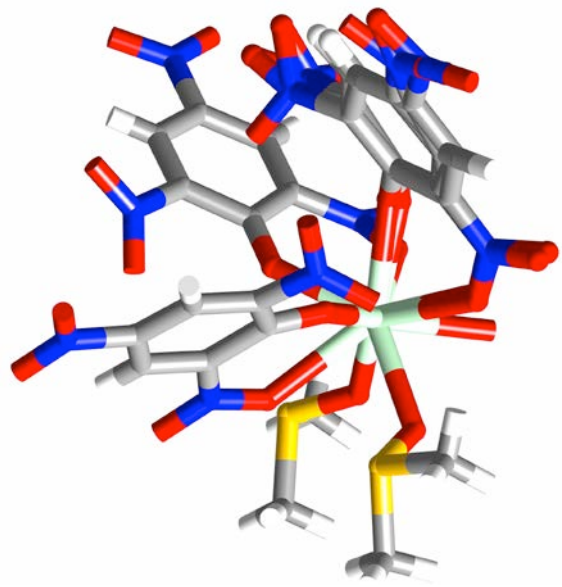


Ln = Sm molecule 1 molecule 2

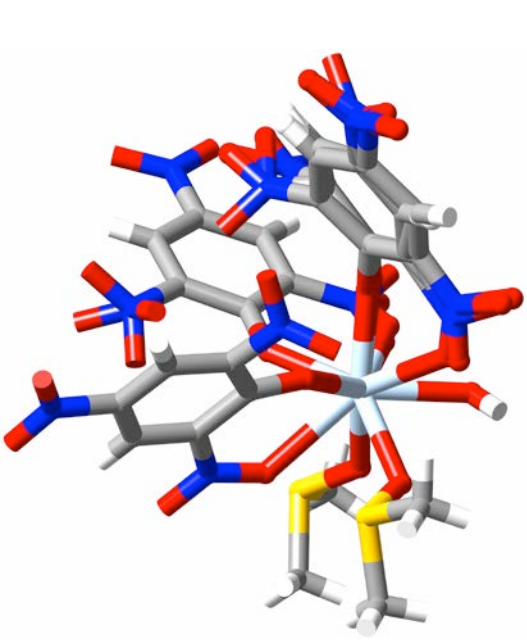
Figure S3 Molecules present in the triclinic, $P\bar{1}$, form of *fac*-[Ln(pic)$_3$(OH$_2$)(dmso)$_2$]. Stick representations, viewed down *b*. Disordered components are shown as if each site is fully occupied. The molecules are chiral but both enantiomers of each are present in the lattice.



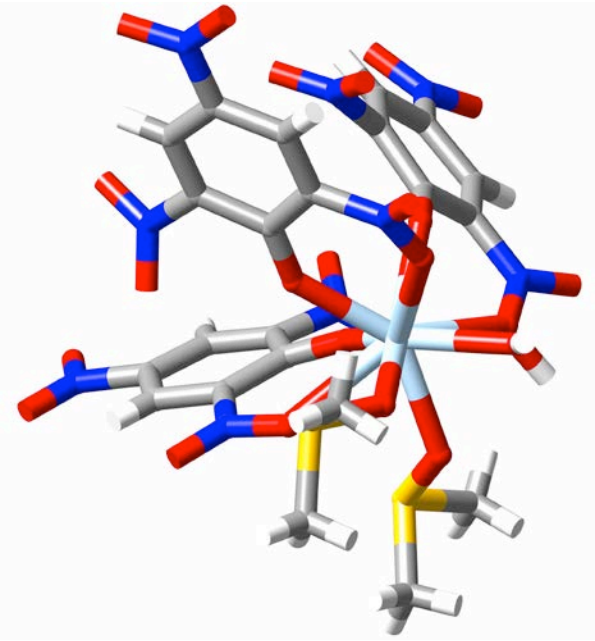
Ln = Sm



Ln = Gd



Ln = Lu, 300 K



Ln = Lu, 170 K

Figure S5 Projections down *b*, with the *c* axis vertical of portions of the lattices of the triclinic (upper) and monoclinic (lower) forms of *mer*-[La(pic)$_3$(dmso)$_3$]. For clarity, hydrogen atoms and lesser components of disorder are not shown. Inequivalent La atoms of the triclinic form are shown in two shades of blue.

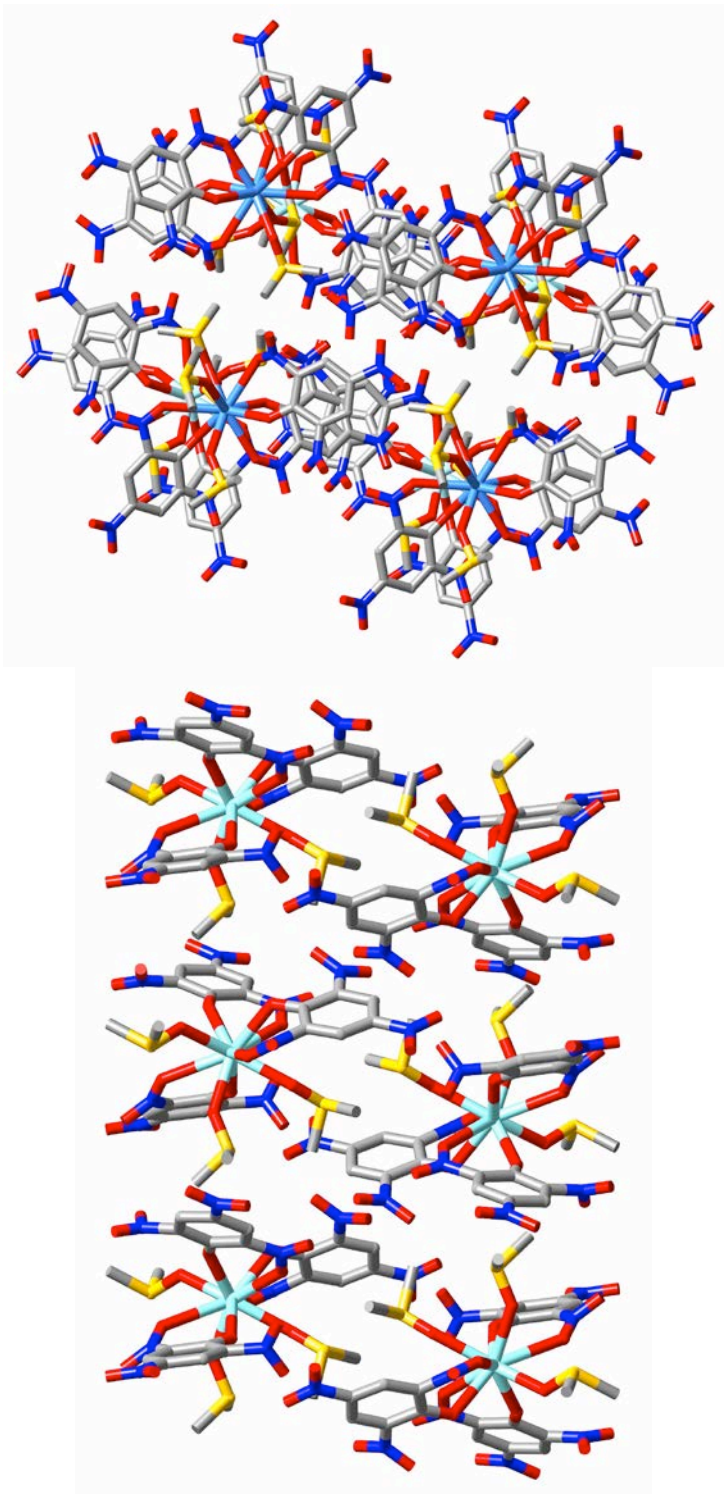
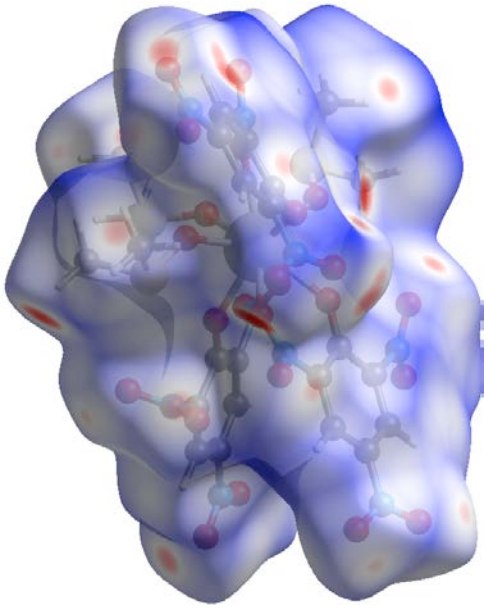
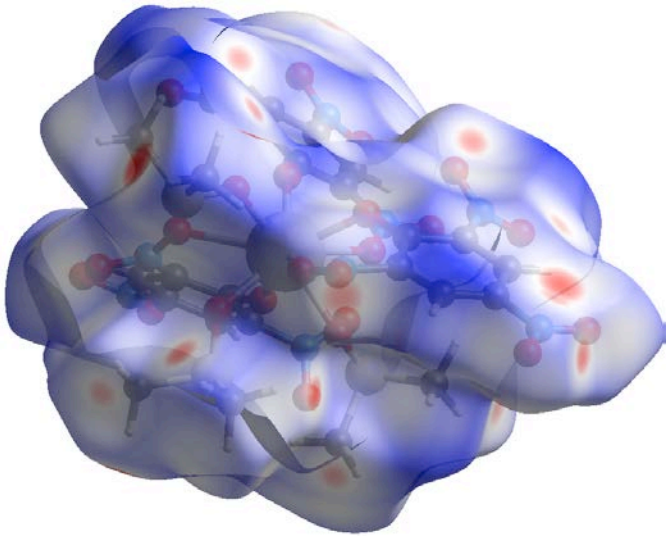


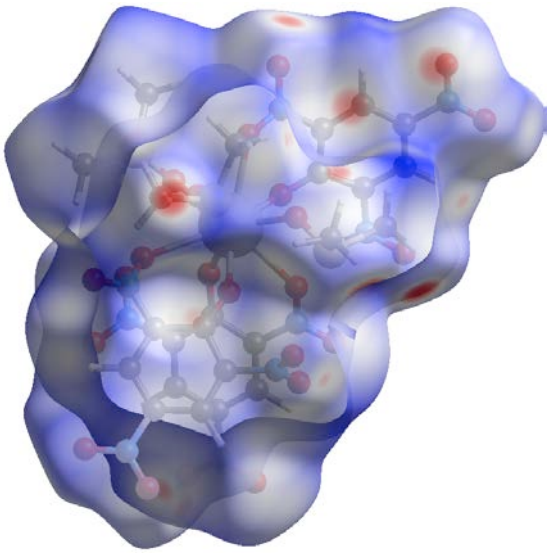
Figure S5 The Hirshfeld surface, "transparent" d_{norm} representation from CrystalExplorer, viewed down *a*, *b* and *c*, for monoclinic, *C*2/c form, *mer*-[Y(pic)$_3$(dmso)$_3$]. Red regions indicate points where interaction with external atoms exceed dispersion.



down *a*



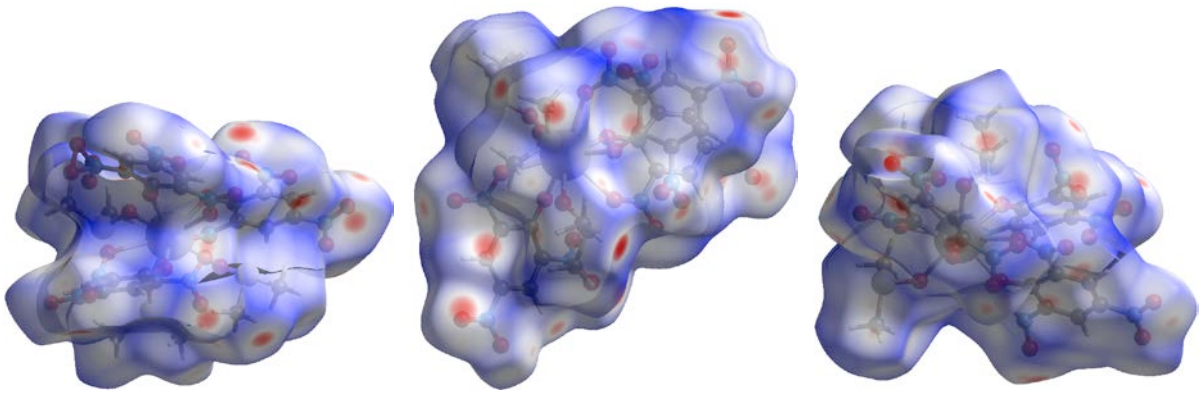
down *b*



down *c*

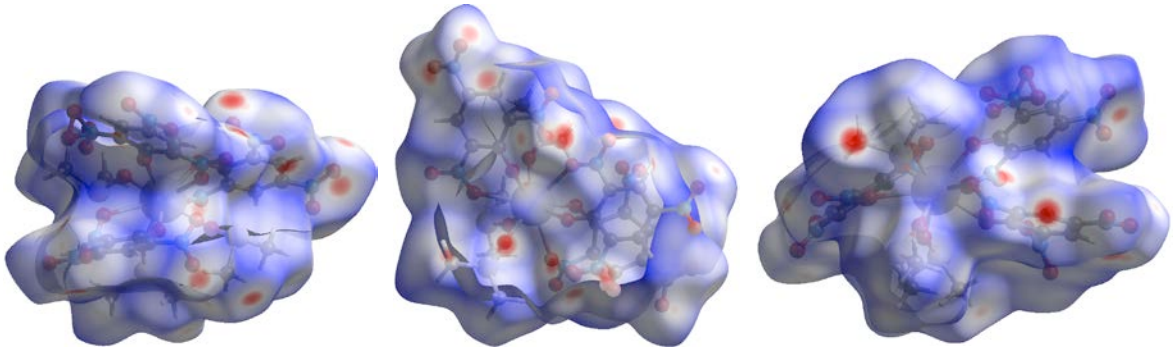
Figure S6 The Hirshfeld surface, "transparent" d_{norm} representation from CrystalExplorer, viewed down *a*, *b* and *c*, for the two inequivalent molecules present in the lattice of the triclinic $P\bar{1}$ form of *mer*-[La(pic)$_3$(dmso)$_3$]. Red regions indicate points where interaction with external atoms exceed dispersion.

For La1:



down *a* down *b* down *c*

For La2:



down *a* down *b* down *c*

Table S1
Some selected Ln-O bond lengths, *mer*-[Ln(dmso-*O*)$_3$(pic-*O*,*O*′)$_3$], 300 K

Phase	Monoclinic			Triclinic			
Ln	La	Lu	Y	(mol. 1) La	(mol. 2)	(mol. 1) Pr	(mol. 2)
Distances (Å)							
Ln-O(11)	2.442(3)	2.248(2)	2.292(4)	2.450(4)	2.458(4)	2.407(3)	2.431(3)
Ln-O(121)	2.755(4)	2.792(2)	2.771(4)	2.740(5)	2.798(4)	2.729(3)	2.798(3)
Ln-O(21)	2.417(3)	2.211(2)	2.263(4)	2.453(4)	2.440(5)	2.435(3)	2.399(3)
Ln-O(221)	2.758(4)	2.712(2)	2.699(4)	2.774(4)	2.676(5)	2.765(3)	2.660(3)
Ln-O(31)	2.450(3)	2.250(2)	2.290(4)	2.450(4)	2.436(4)	2.415(3)	2.407(3)
Ln-O(321)	2.786(4)	2.663(2)	2.651(4)	2.702(4)	2.762(3)	2.687(3)	2.757(3)
Ln-O(01)	2.419(3)	2.243(2)	2.272(4)	2.452(4)	2.448(4)	2.431(3)	2.416(3)
Ln-O(02)	2.414(4)	2.247(2)	2.291(4)	2.456(4)	2.426(4)	2.433(3)	2.399(4)
Ln-O(03)	2.413(3)	2.246(2)	2.291(4)	2.453(4)	2.462(4)	2.425(3)	2.434(3)

Table S2
Some selected Ln-O bond lengths/Å, *fac*-[Ln(dmso-*O*)$_3$(OH$_2$)(pic-*O*,*O*′)$_2$]

	Sm (153 K)	Lu (170 K)
Bond		
Ln-O(11)	2.304(1)	2.213(3)
Ln-O(121)	2.568(2)	2.501(3)
Ln-O(21)	2.342(1)	2.234(3)
Ln-O(221)	2.580(2)	2.591(3)
Ln-O(31)	2.34(2)	2.217(3)
Ln-O(321)	2.634(1)	2.658(3)
Ln-O(1)	2.412(1)	2.300(3)
Ln-O(01)	2.437(1)	2.325(3)
Ln-O(02)	2.438(1)	2.333(3)

For Sm only the bond lengths involving the major component of the disordered array are given. O(1) is the water molecule oxygen.

Table S3
Selected picrate and dmso parameters, [Ln(pic-*O*,*O*′)$_3$(dmso)$_3$]

Phase	Monoclinic			Triclinic				Hydrated	
Ln	La*	Lu	Y	(mol. 1) La	(mol. 2)	(mol. 1) Pr	(mol. 2)	Sm†	Lu (170 K)
Phenoxide distances (Å)									
O(11)-C(11)	1.257(6)	1.274(3)	1.269(7)	1.259(7)	1.265(7)	1.269(4)	1.260(5)	1.261(2)	1.268(5)
O(21)-C(21)	1.265(6)	1.274(3)	1.276(7)	1.284(7)	1.270(8)	1.274(5)	1.279(5)	1.265(2)	1.271(5)
O(31)-C(31)	1.265(5)	1.269(3)	1.281(7)	1.270(7)	1.278(7)	1.280(4)	1.278(4)	1.26(2)	1.266(5)
C_6 (phenyl) Interplanar dihedral angles (°)									
1/2	33.74(2)	34.76(13)	34.2(3)	29.4(2)	38.7(2)	30.57(15)	38.7(2)	72.62(7)	74.2(2)
1/3	40.3(2)	44.35(12)	43.4(2)	43.4(2)	43.0(2)	44.49(15)	42.6(2)	57.9(2)	60.7(2)
2/3	20.4(2)	24.41(13)	23.6(3)	19.3(2)	24.5(2)	20.62(15)	24.2(2)	62.8(2)	62.4(2)
Inter-centroid distances (Å)									
1/2	4.53_5	4.40_4	4.41_7	4.2_1	4.79_1	4.25_1	4.77_8	6.83_3	6.61_7
1/3	9.00_8	8.80_6	8.82_3	8.87_2	9.07_9	8.87_5	9.07_5	6.41_1	6.24_0
2/3	7.87_9	7.61_3	7.65_8	8.00_4	7.87_1	7.96_8	7.86_8	5.33_7	5.23_0
Sulfoxide distances (Å)									
O(01)-S(01)	1.531(4)	1.528(2)	1.527(4)	1.534(4)	1.517(5)	1.533(3)	1.530(3)	1.527(2)	1.525(3)
O(02)-S(02)	1.465(6)	1.527(2)	1.524(4)	1.525(4)	1.517(6)	1.533(3)	1.530(3)	1.539(14)	1.539(3)
O(03)-S(03)	1.474(4)	1.528(2)	1.530(4)	1.526(4)	1.523(4)	1.531(3)	1.523(3)		

* Values for disordered components (Ln = La): sulfoxide distances O(01')-S(01') = 1.48(2), O(02')-S(02') = 1.426(5), O(03')-S(03') = 1.456(9) Å.
† Values for disordered components (Ln = Sm): phenoxide distance O(31')-C(31')= 1.26(2) Å; The inter-planar dihedral angle between C_6 'phenyl' rings 3' and 1, 2 is 63.2(2), 55.9(2)°. The distances between C_6 'phenyl' centroids 3'-1, 2 is 6.695, 5.329 Å.