Supporting Information

Contrasting Impact of Coordination Polyhedra and Site Symmetry on the Electronic Energy Levels in Nine-coordinated Eu(III) and Sm(III) Crystals Structures Determined from Single Crystal Luminescence Spectra

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This is the supporting information for the article, showing the additionally measured emission and excitation spectra, time-resolved emission decay profiles, crystallographic information, and PXRD. Additionally, Boltzmann population calculations, Voight fitting of spectra, and arguments for the population analysis of the emission and excitation spectra resulting in the deconvoluted electronic energy levels for the Sm^{3+} systems.

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1.1.1.1 Picture of $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Crystals

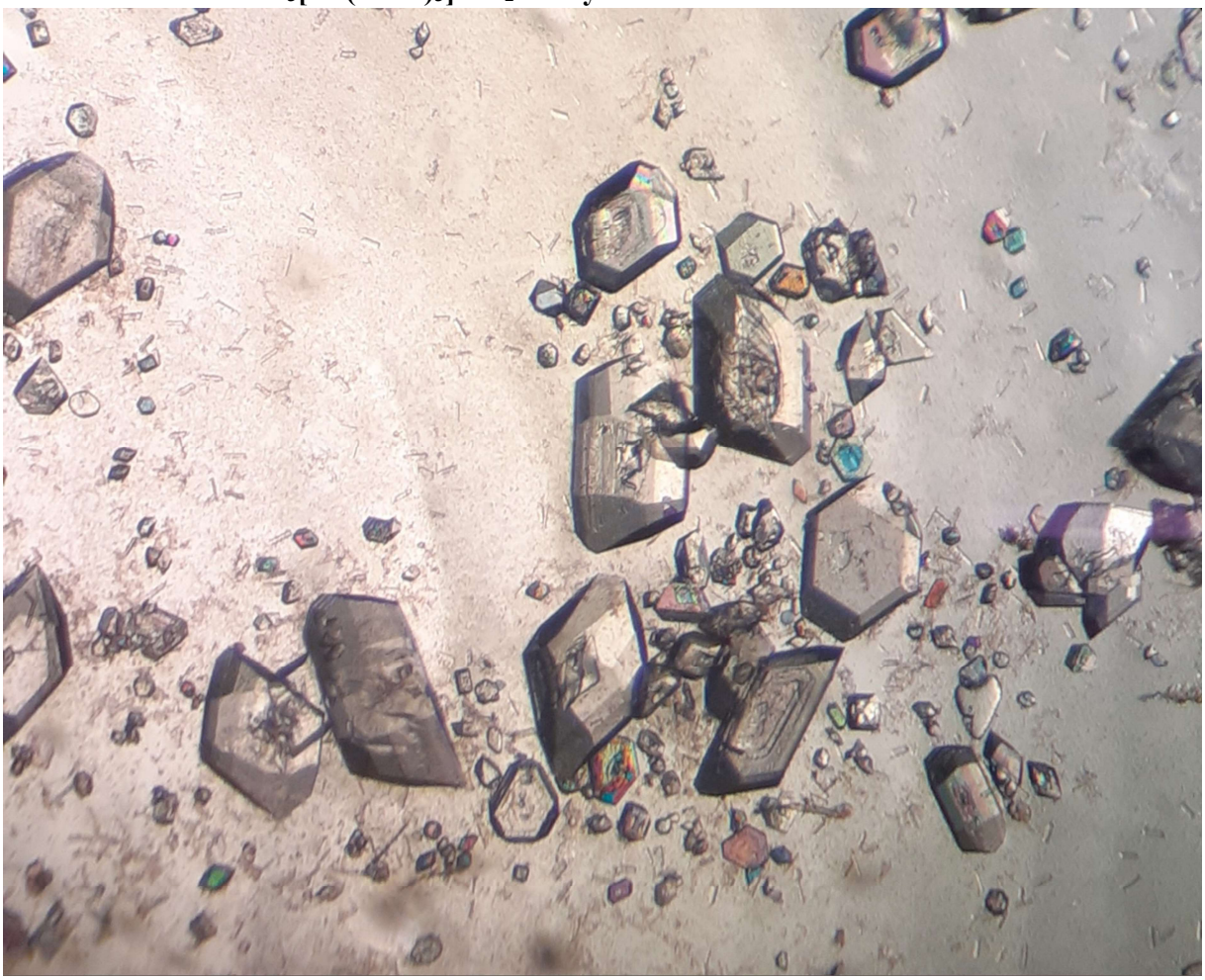


Figure S 1: Pictures of $Na_3[Eu(ODA)_3]\cdot 8H_2O$ made following the description in the experimental section. The crystals have a difference in size, but all of the crystal were found to be clear, light, and colourless with a prism structure. All crystals were observed to have the same phase. The complex crystallises in the monoclinic *C2/c* space group.

1.1.1.2 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Crystal Structure

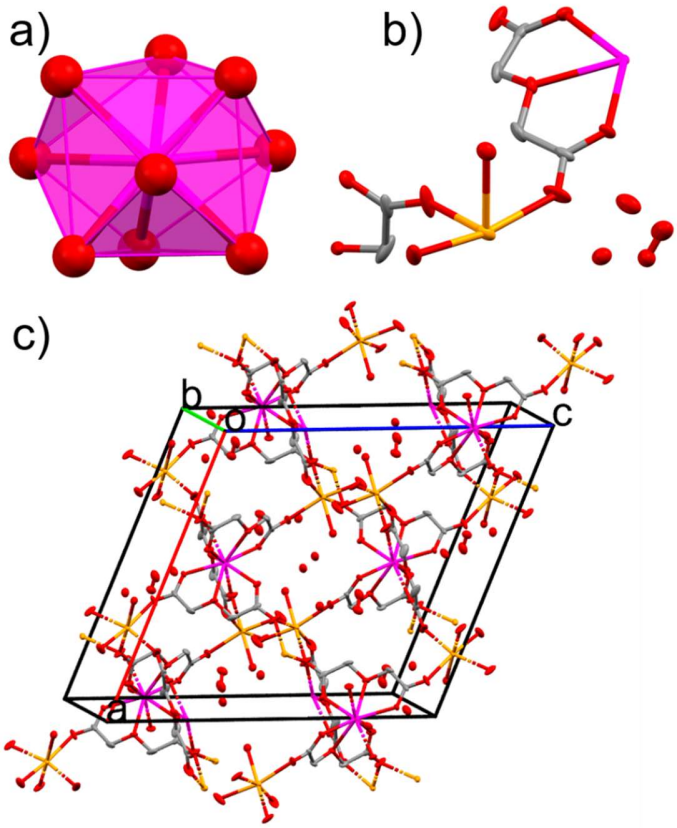


Figure S 2: a) Polyhedral depicting coordination around the Eu^{3+} ion in $Na_3[Eu(ODA)_3]\cdot 8H_2O$. **b)** The asymmetric unit for $Na_3[Eu(ODA)_3]\cdot 8H_2O$. **c)** The unit cell for $Na_3[Eu(ODA)_3]\cdot 8H_2O$. Colour code: Eu = pink, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.1.1.3 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Crystallographic Information

Table S 1: Crystal data and structure refinement for $Na_3[Eu(ODA)_3]\cdot 8H_2O$.

Crystal data	
Empirical formula	$C_{12}H_{27}EuNa_3O_{23}$
Formula weight	760.26
Temperature/K	120
Crystal system	monoclinic
Space group	C2/c
a/Å	17.520(3)

b/Å	8.3804(13)
c/Å	19.059(3)
α/°	90
β/°	111.350(4)
γ/°	90
Volume/Å^3	2606.2(7)
Z	4
ρ_{calc}g/cm^3	1.922
μ/mm^{-1}	2.555
F(000)	1492.0
Crystal size/mm^3	0.18 × 0.174 × 0.11
Radiation	MoKα (λ = 0.71073)
Data collection	
2Θ range for data collection/°	4.59 to 63.012
Index ranges	-25 ≤ h ≤ 25, -12 ≤ k ≤ 12, -27 ≤ l ≤ 28
Reflections collected	29301
Independent reflections	4349 [R_{int} = 0.0518, R_{sigma} = 0.0301]
Refinement	
Data/restraints/parameters	4349/6/202
Goodness-of-fit on F^2	1.297
Final R indexes [I>=2σ (I)]	R_1 = 0.0378, wR_2 = 0.1082
Final R indexes [all data]	R_1 = 0.0388, wR_2 = 0.1086
Largest diff. peak/hole / e Å^{-3}	2.58/-3.37

1.1.2 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Experimental and Crystallographic Information

1.1.2.1 Picture of $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Crystals

Figure S 3: Pictures of $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ made following the description in the experimental section. The crystals have a difference in size, but all of the crystal were found to be clear, light, and colourless with a prism structure. All crystals were observed to have the same phase. The complex crystallises in the orthorhombic $C222_1$ space group.

1.1.2.2 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Crystal Structure

The crystal created in the experimental section was found to be a twin, and the structure could not be determined. However, the Bravais lattice and unit cell was found to agree with the previously reported structure by by Brayshaw *et al*.[1] and the crystal was then used for single crystal luminescence measurements.

1.1.2.3 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Crystallographic Information

Table S 2: Crystal data and structure refinement for $Cs_3[Eu(DPA)_3]\cdot 9H_2O$.

Crystal data	
Empirical formula	$C_{20}Cs_2EuN_3Na_2O_{21}$
Formula weight	1081.99
Temperature/K	296.15
Crystal system	orthorhombic
Space group	$C222_1$
a/Å	18.0233(9)
b/Å	10.0116(5)
c/Å	18.5298(9)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3343.6(3)
Z	4
ρ_{calc}g/cm^3	2.149
μ/mm^{-1}	4.135
F(000)	2016.0
Crystal size/mm^3	? × ? × ?
Radiation	MoKα (λ = 0.71073)
Refinement	
2Θ range for data collection/°	4.396 to 51.34
Index ranges	-21 ≤ h ≤ 21, -12 ≤ k ≤ 12, -21 ≤ l ≤ 22
Reflections collected	18157
Independent reflections	3175 [R_{int} = 0.0319, R_{sigma} = 0.0226]

1.1.3 Na[Eu(DOTA)H_2O]·4H_2O Experimental and Crystallographic Information

1.1.3.1 Picture of Na[Eu(DOTA)H_2O]·4H_2O Crystals

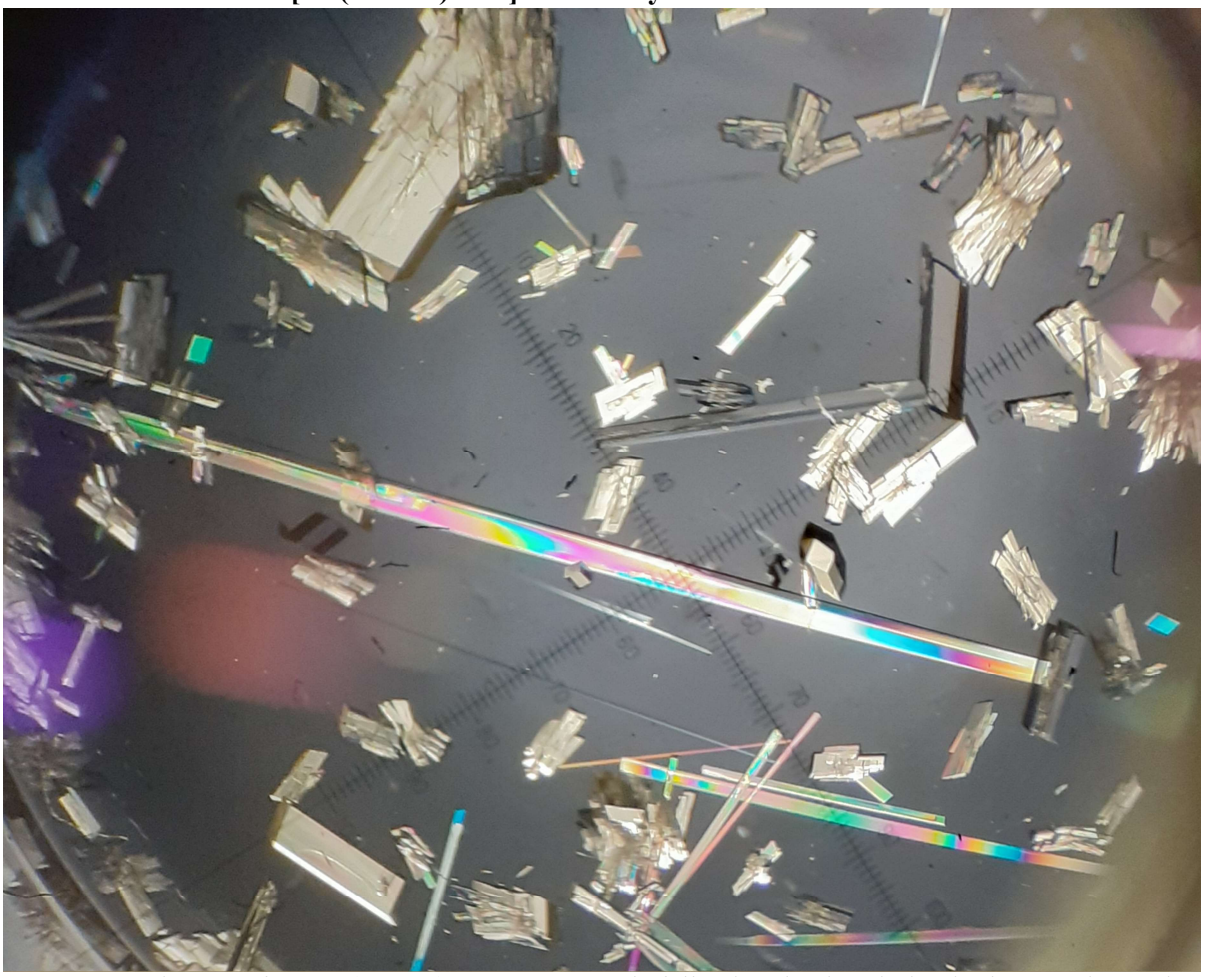


Figure S 4: Pictures of Na[Eu(DOTA)H_2O]·4H_2O made following the description in the experimental section. The crystals have a difference in size, but all of the crystal were found to be clear, light, and colourless with a prism structure. All crystals were observed to have the same phase. The complex crystallises in the triclinic $P\bar{1}$ space group.

1.1.3.2 Na[Eu(DOTA)H_2O]·4H_2O Crystal Structure

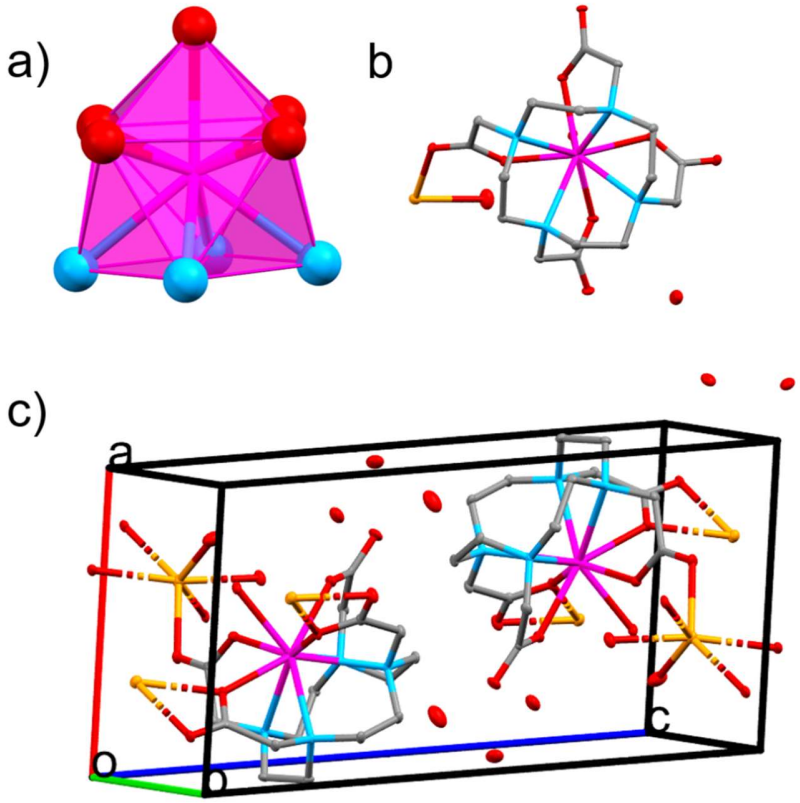


Figure S 5: a) Polyhedral depicting coordination around the Eu^{3+} ion in Na[Eu(DOTA)H_2O]·4H_2O. **b)** The asymmetric unit for Na[Eu(DOTA)H_2O]·4H_2O. **c)** The unit cell for Na[Eu(DOTA)H_2O]·4H_2O. Colour code: Eu = pink, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.1.3.3 Na[Eu(DOTA)H_2O]·4H_2O Crystallographic Information

Table S 3: Crystal data and structure refinement for Na[Eu(DOTA)H_2O]·4H_2O.

Crystal data	
Empirical formula	$C_{16}H_{34}EuN_4NaO_{13}$
Formula weight	665.42
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	8.6270(5)

b/Å	9.1258(6)
c/Å	15.6209(9)
α/°	82.982(2)
β/°	85.085(2)
γ/°	81.209(3)
Volume/Å^3	1203.44(13)
Z	2
ρ_{calc}g/cm^3	1.836
μ/mm^{-1}	2.696
F(000)	672.0
Crystal size/mm^3	0.205 × 0.14 × 0.06
Radiation	MoKα (λ = 0.71073)
Refinement	
2Θ range for data collection/°	4.544 to 61.012
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -22 ≤ l ≤ 22
Reflections collected	57415
Independent reflections	7345 [R_{int} = 0.0667, R_{sigma} = 0.0401]
Refinement	
Data/restraints/parameters	7345/2/343
Goodness-of-fit on F^2	1.049
Final R indexes [I > = 2σ (I)]	R_1 = 0.0250, wR_2 = 0.0467
Final R indexes [all data]	R_1 = 0.0341, wR_2 = 0.0489
Largest diff. peak/hole / e Å^{-3}	0.92/-0.93

1.1.4 $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ Experimental and Crystallographic Information

1.1.4.1 $Na[Eu(EDTA)(H_2O)_3]\cdot 4H_2O$ Picture of Crystals

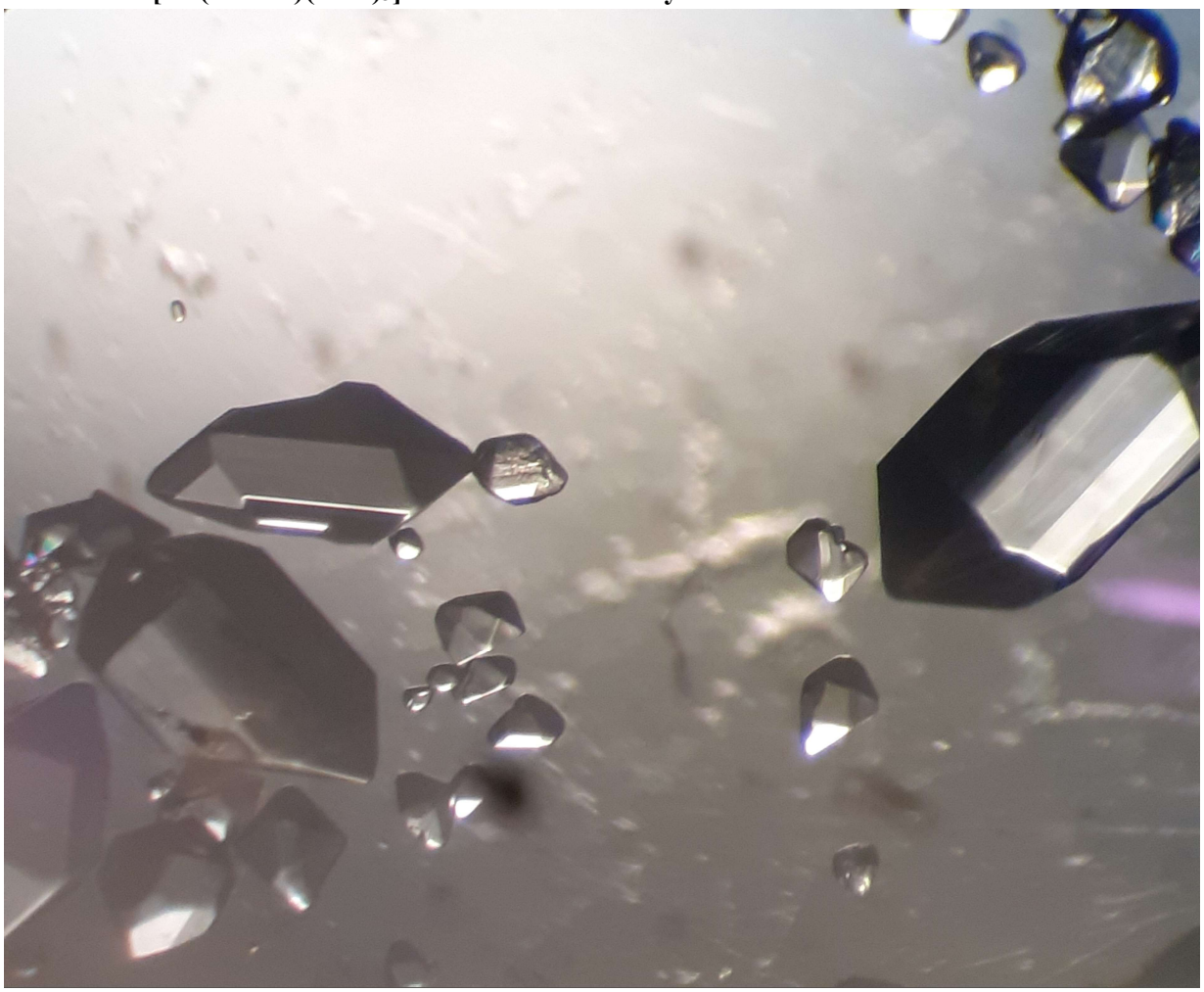


Figure S 6: Pictures of $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ made following the description in the experimental section. The crystals have a difference in size, but all of the crystal were found to be clear, light, and colourless with a prism structure. All crystals were observed to have the same phase. The complex crystallises in the orthorhombic *Fdd2* space group.

1.1.4.2 Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O Crystal Structure

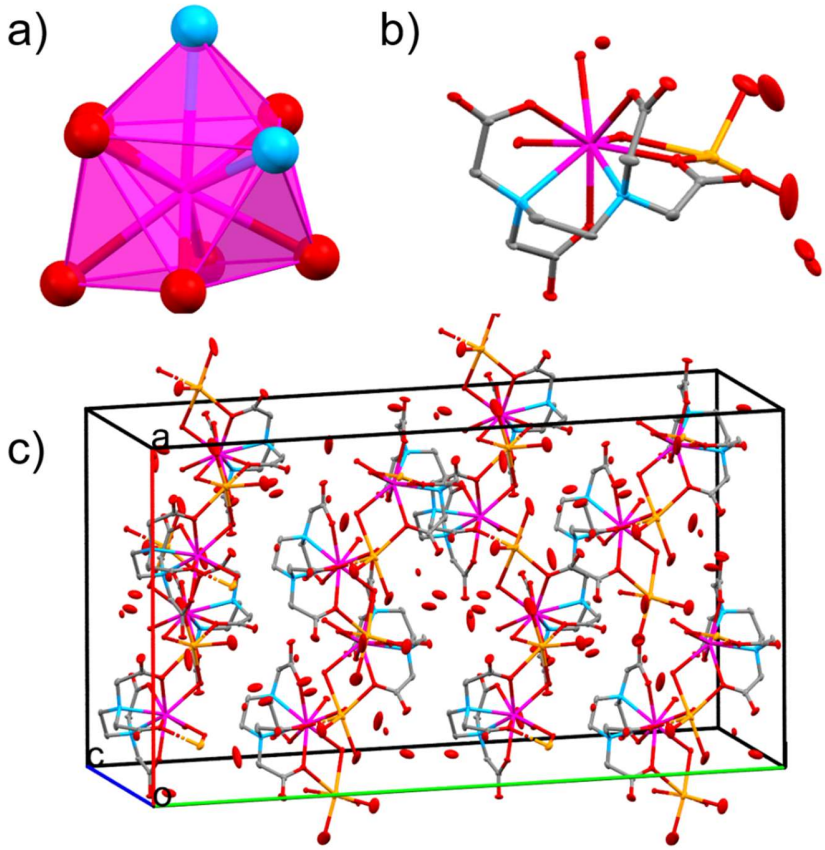


Figure S 7: a) Polyhedral depicting coordination around the Eu^{3+} ion in Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O. **b)** The asymmetric unit for Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O. **c)** The unit cell for Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O. Colour code: Eu = pink, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.1.4.3 Na[Eu(EDTA)(H_2O)$_3$]·5H_2O Crystallographic Information

Table S 4: Crystal data and structure refinement for Na[Eu(EDTA)(H_2O)$_3$]·5H_2O.

Crystal data	
Empirical formula	$C_{10}H_{28}EuN_2NaO_{16}$
Formula weight	607.29
Temperature/K	100
Crystal system	orthorhombic
Space group	Fdd2
a/Å	19.3808(9)
b/Å	35.2814(17)
c/Å	12.0315(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8226.9(7)
Z	16
ρ_{calc}g/cm^3	1.938
μ/mm^{-1}	3.151
F(000)	4752.0
Crystal size/mm^3	0.606 × 0.522 × 0.434
Radiation	MoKα (λ = 0.71073)
Data collection	
2Θ range for data collection/°	4.148 to 61.994
Index ranges	-27 ≤ h ≤ 28, -50 ≤ k ≤ 51, -17 ≤ l ≤ 17
Reflections collected	35327
Independent reflections	6527 [R_{int} = 0.0431, R_{sigma} = 0.0328]

Refinement	
Data/restraints/parameters	6527/21/325
Goodness-of-fit on F^2	1.049
Final R indexes [I>=2σ (I)]	R_1 = 0.0193, wR_2 = 0.0461
Final R indexes [all data]	R_1 = 0.0199, wR_2 = 0.0464
Largest diff. peak/hole / e $Å^{-3}$	1.13/-1.88
Flack parameter	0.018(10)

1.2 Sm^{3+} Compounds Crystallographic Information

1.2.1 $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Experimental and Crystallographic Information

1.2.1.1 Picture of $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Crystals

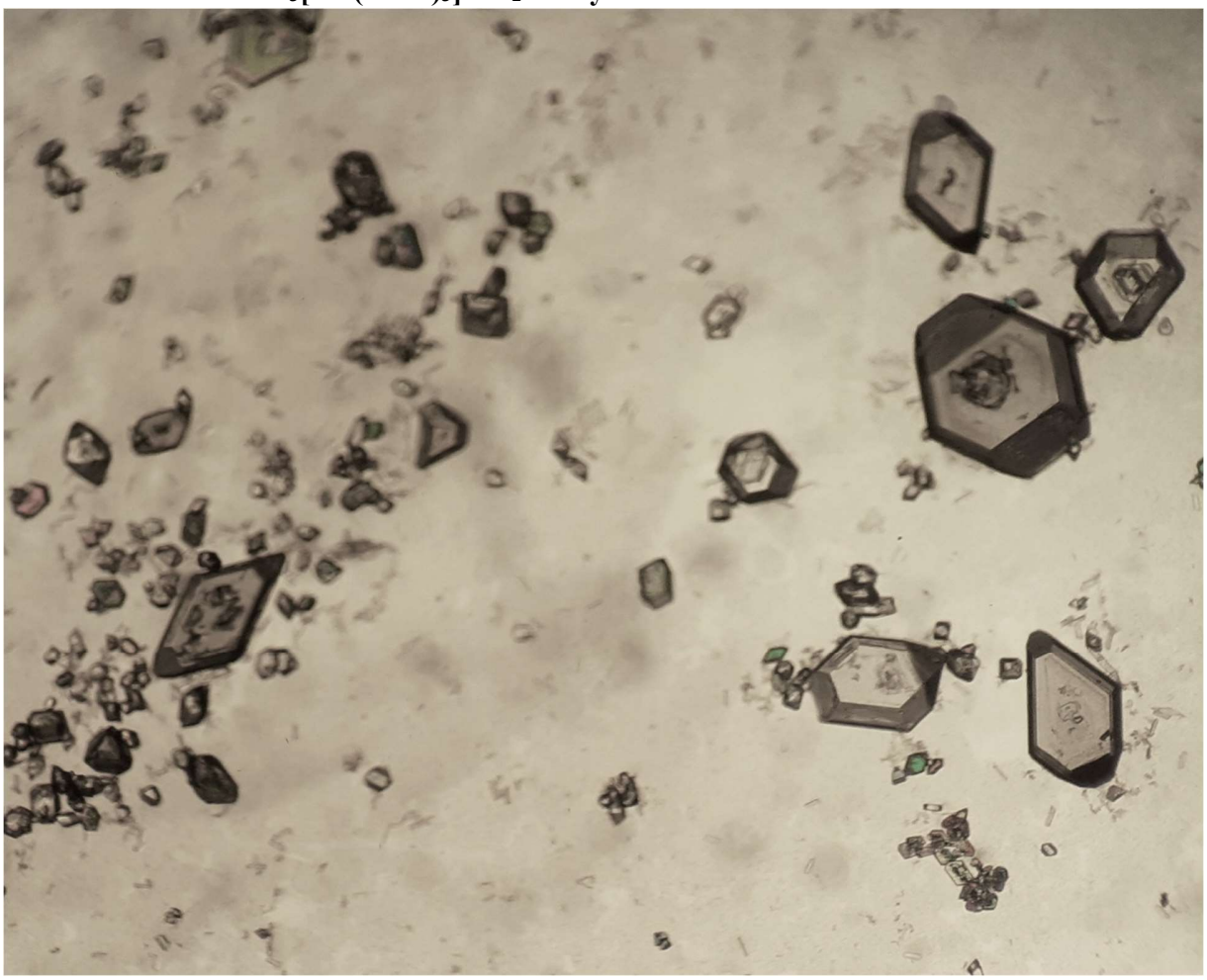


Figure S 8: Pictures of $Na_3[Sm(ODA)_3]\cdot 7H_2O$ made following the description in the experimental section. The crystals have a difference in size, but all of the crystal were found to be clear, light, and colourless with a prism structure. All crystals were observed to have the same phase. The complex crystallises in the monoclinic *Cc* space group.

1.2.1.2 $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Crystal Structure

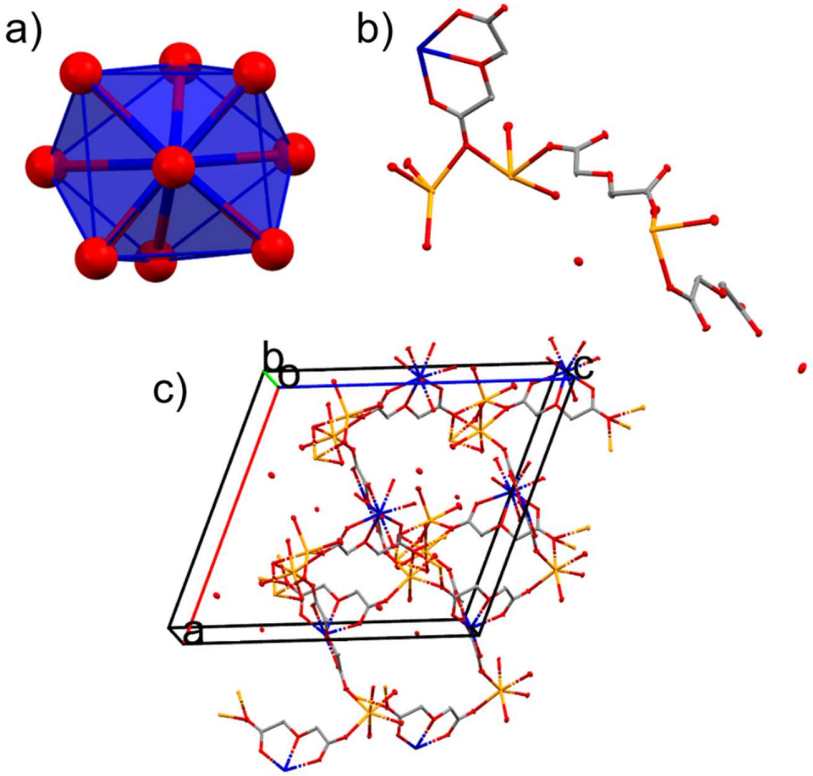


Figure S 9: a) Polyhedral depicting coordination around the Sm^{3+} ion in $Na_3[Sm(ODA)_3]\cdot 7H_2O$. **b)** The asymmetric unit for $Na_3[Sm(ODA)_3]\cdot 7H_2O$. **c)** The unit cell for $Na_3[Sm(ODA)_3]\cdot 7H_2O$. Colour code: Sm = dark blue, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.2.1.3 $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Crystallographic Information

Table S 5: Crystal data and structure refinement for $Na_3[Sm(ODA)_3]\cdot 7H_2O$.

Crystal data	
Empirical formula	$C_{12}H_{28}Na_3O_{23}Sm$
Formula weight	759.66
Temperature/K	100
Crystal system	monoclinic
Space group	Cc
a/Å	17.5900(13)
b/Å	8.3808(6)

c/Å	19.0418(16)
α/°	90
β/°	111.266(3)
γ/°	90
Volume/Å^3	2616.0(4)
Z	8
ρ_{calc}g/cm^3	1.929
μ/mm^{-1}	2.393
F(000)	1516.0
Crystal size/mm^3	0.416 × 0.324 × 0.202
Radiation	MoKα (λ = 0.71073)
Data collection	
2Θ range for data collection/°	4.59 to 68.674
Index ranges	-26 ≤ h ≤ 27, -13 ≤ k ≤ 13, -30 ≤ l ≤ 30
Reflections collected	46134
Independent reflections	10560 [R_{int} = 0.0428, R_{sigma} = 0.0434]
Refinement	
Data/restraints/parameters	10560/3/371
Goodness-of-fit on F^2	1.063
Final R indexes [I>=2σ (I)]	R_1 = 0.0228, wR_2 = 0.0448
Final R indexes [all data]	R_1 = 0.0273, wR_2 = 0.0461
Largest diff. peak/hole / e Å^{-3}	0.44/-0.61
Flack parameter	0.032(7)

1.2.2 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Experimental and Crystallographic Information

1.2.2.1 Picture of $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Crystals

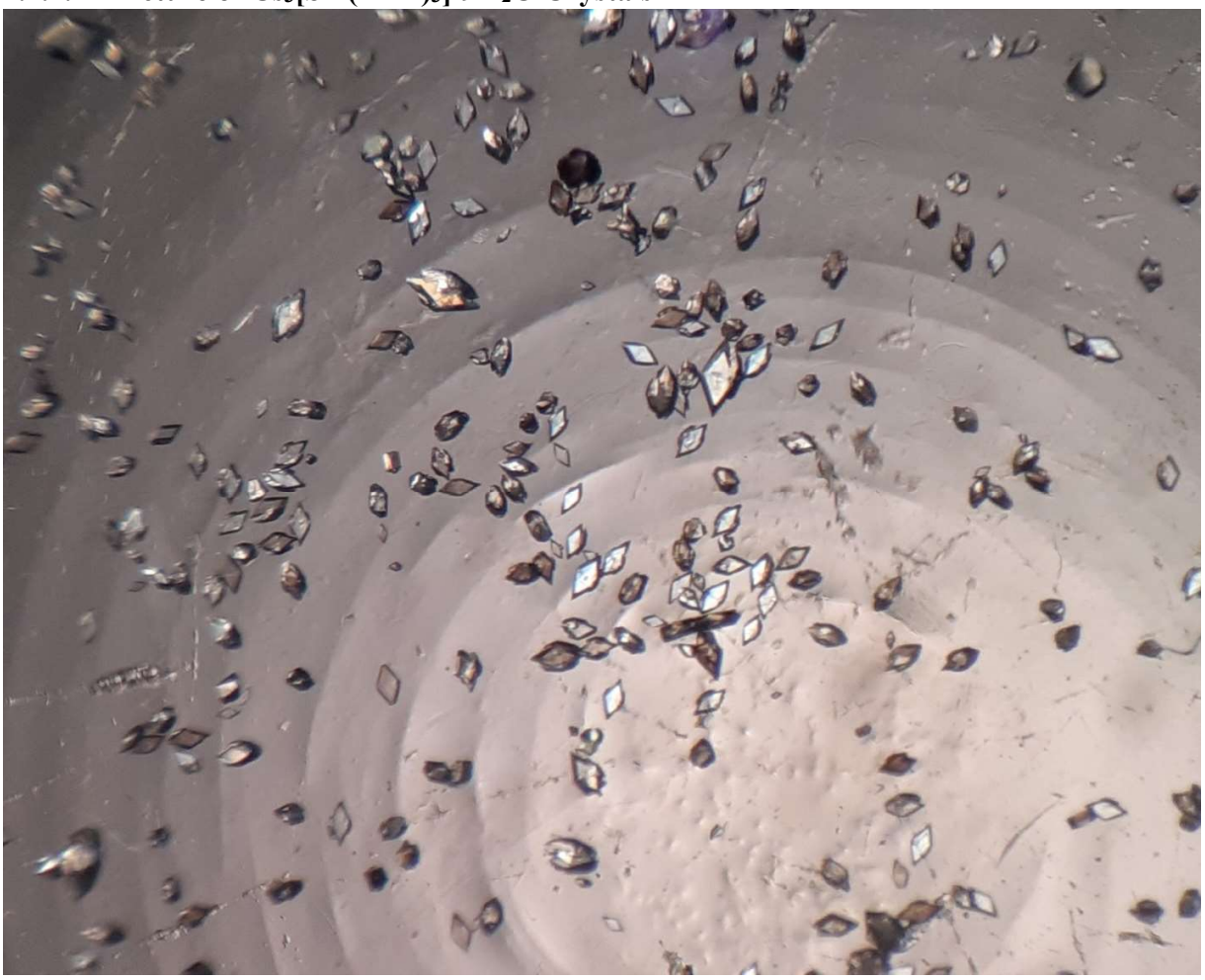


Figure S 10: Pictures of $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ made following the description in the experimental section. The crystals have a difference in size, but all of the crystal were found to be clear, light, and colourless with a prism structure. All crystals were observed to have the same phase. The complex crystallises in the orthorhombic $C222_1$ space group.

1.2.2.2 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Crystal Structure

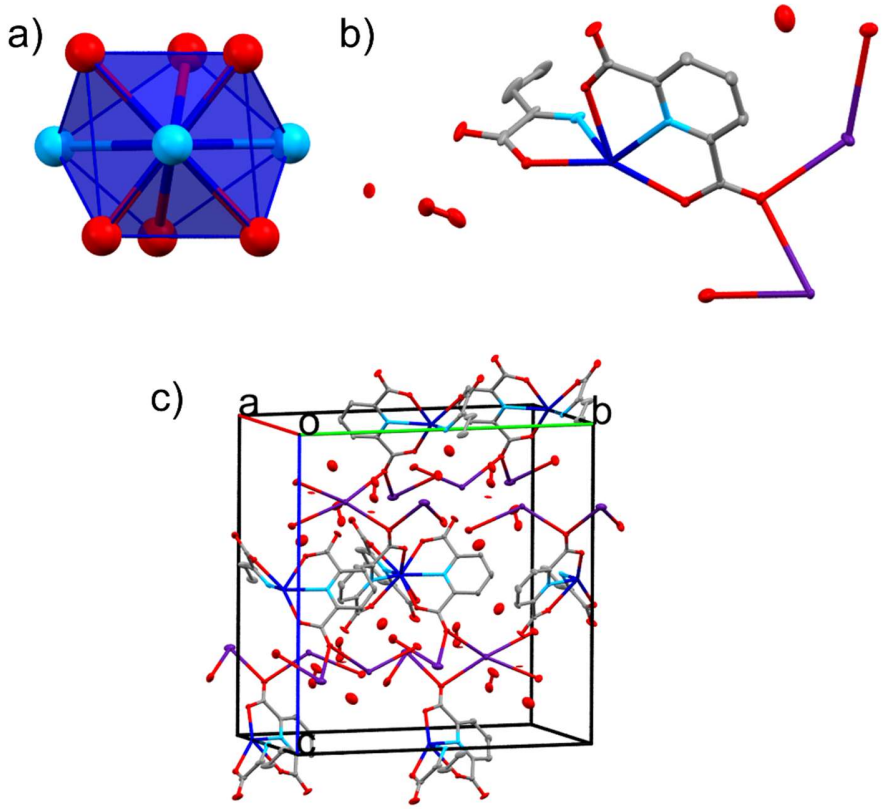


Figure S 11: a) Polyhedral depicting coordination around the Sm^{3+} ion in $Cs_3[Sm(DPA)_3]\cdot 9H_2O$. **b)** The asymmetric unit for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$. **c)** The unit cell for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$. Colour code: Sm = dark blue, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.2.2.3 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Crystallographic Information

Table S 6: Crystal data and structure refinement for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$.

Crystal data	
Empirical formula	$C_{21}H_{23}Cs_3N_3O_{21}Sm$
Formula weight	1202.50
Temperature/K	100
Crystal system	orthorhombic
Space group	$C222_1$
a/Å	10.0017(13)

b/Å	18.033(3)
c/Å	18.530(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3342.1(8)
Z	4
ρ_{calc}g/cm^3	2.398
μ/mm^{-1}	5.068
F(000)	2268.0
Crystal size/mm^3	0.162 × 0.127 × 0.071
Radiation	MoKα (λ = 0.71073)
Data collection	
2Θ range for data collection/°	4.396 to 72.66
Index ranges	-16 ≤ h ≤ 16, -30 ≤ k ≤ 30, -30 ≤ l ≤ 30
Reflections collected	64847
Independent reflections	8116 [R_{int} = 0.0502, R_{sigma} = 0.0283]
Refinement	
Data/restraints/parameters	8116/15/257
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0244, wR_2 = 0.0617
Final R indexes [all data]	R_1 = 0.0284, wR_2 = 0.0637
Largest diff. peak/hole / e Å^{-3}	2.35/-2.02
Flack parameter	0.132(16)

1.2.3 Na[Sm(DOTA)H_2O]·4H_2O Experimental and Crystallographic Information

1.2.3.1 Picture of Na[Sm(DOTA)H_2O]·4H_2O Crystals

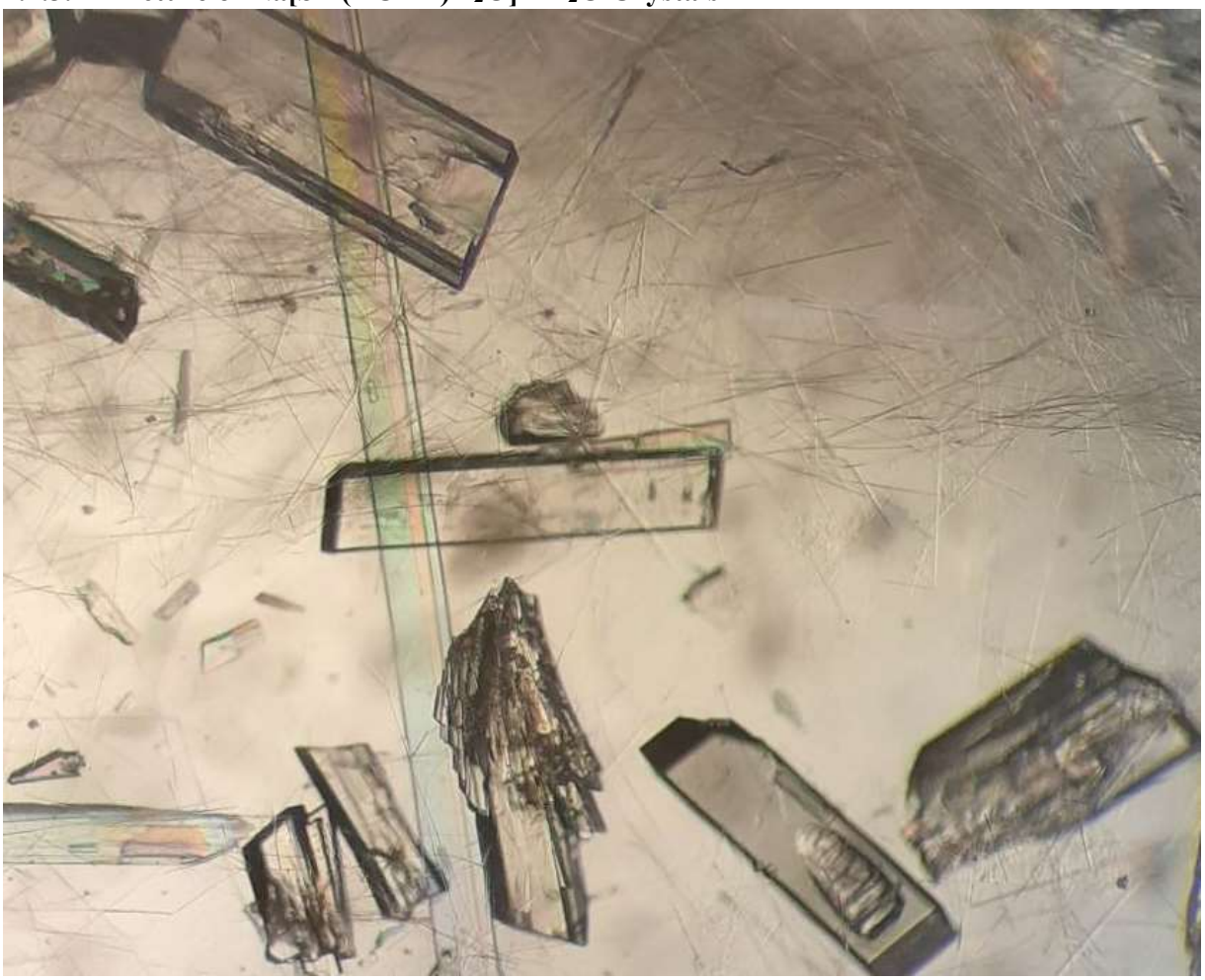


Figure S 12: Pictures of Na[Sm(DOTA)H_2O]·4H_2O made following the description in the experimental section. The crystals have a difference in size, but all the crystal were found to be clear, light, and colourless with an irregular structure. All crystals were observed to have the same phase. The complex crystallises in the triclinic $P\bar{1}$ space group.

1.2.3.2 Na[Sm(DOTA)H_2O]·4H_2O Crystal Structure

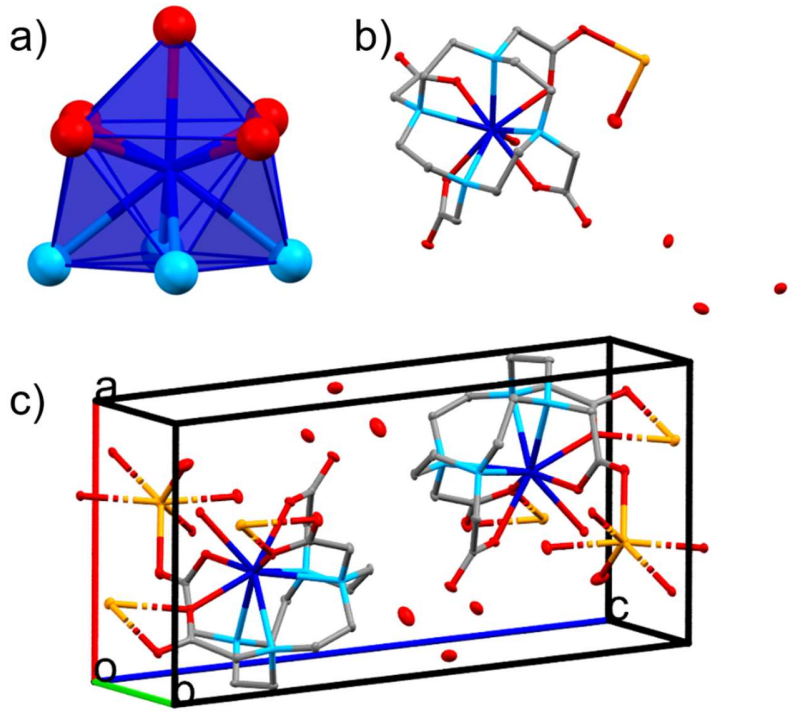


Figure S 13: a) Polyhedral depicting coordination around the Sm^{3+} ion in Na[Sm(DOTA)H_2O]·4H_2O. **b)** The asymmetric unit for Na[Sm(DOTA)H_2O]·4H_2O. **c)** The unit cell for Na[Sm(DOTA)H_2O]·4H_2O. Colour code: Sm = dark blue, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.2.3.3 Na[Sm(DOTA)H_2O]·4H_2O Crystallographic Information

Table S 7: Crystal data and structure refinement for Na[Sm(DOTA)(H_2O)]·5H_2O.

Crystal data	
Empirical formula	$C_{16}H_{34}N_4NaO_{13}Sm$
Formula weight	663.81
Temperature/K	100
Crystal system	triclinic
Space group	P-1
a/Å	8.6233(8)
b/Å	9.1615(8)
c/Å	15.6526(14)

α/°	82.938(3)
β/°	84.975(3)
γ/°	80.994(3)
Volume/Å^3	1209.13(19)
Z	2
ρ_{calc}g/cm^3	1.823
μ/mm^{-1}	2.518
F(000)	670.0
Crystal size/mm^3	0.291 × 0.134 × 0.083
Radiation	MoKα (λ = 0.71073)
Data collection	
2Θ range for data collection/°	4.53 to 64.06
Index ranges	-12 ≤ h ≤ 12, -13 ≤ k ≤ 13, -23 ≤ l ≤ 23
Reflections collected	59699
Independent reflections	8427 [R_{int} = 0.0513, R_{sigma} = 0.0305]
Refinement	
Data/restraints/parameters	8427/0/332
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0200, wR_2 = 0.0435
Final R indexes [all data]	R_1 = 0.0249, wR_2 = 0.0450
Largest diff. peak/hole / e Å^{-3}	0.79/-0.56

1.2.4 $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ Experimental and Crystallographic Information

1.2.4.1 Picture of $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ Crystals

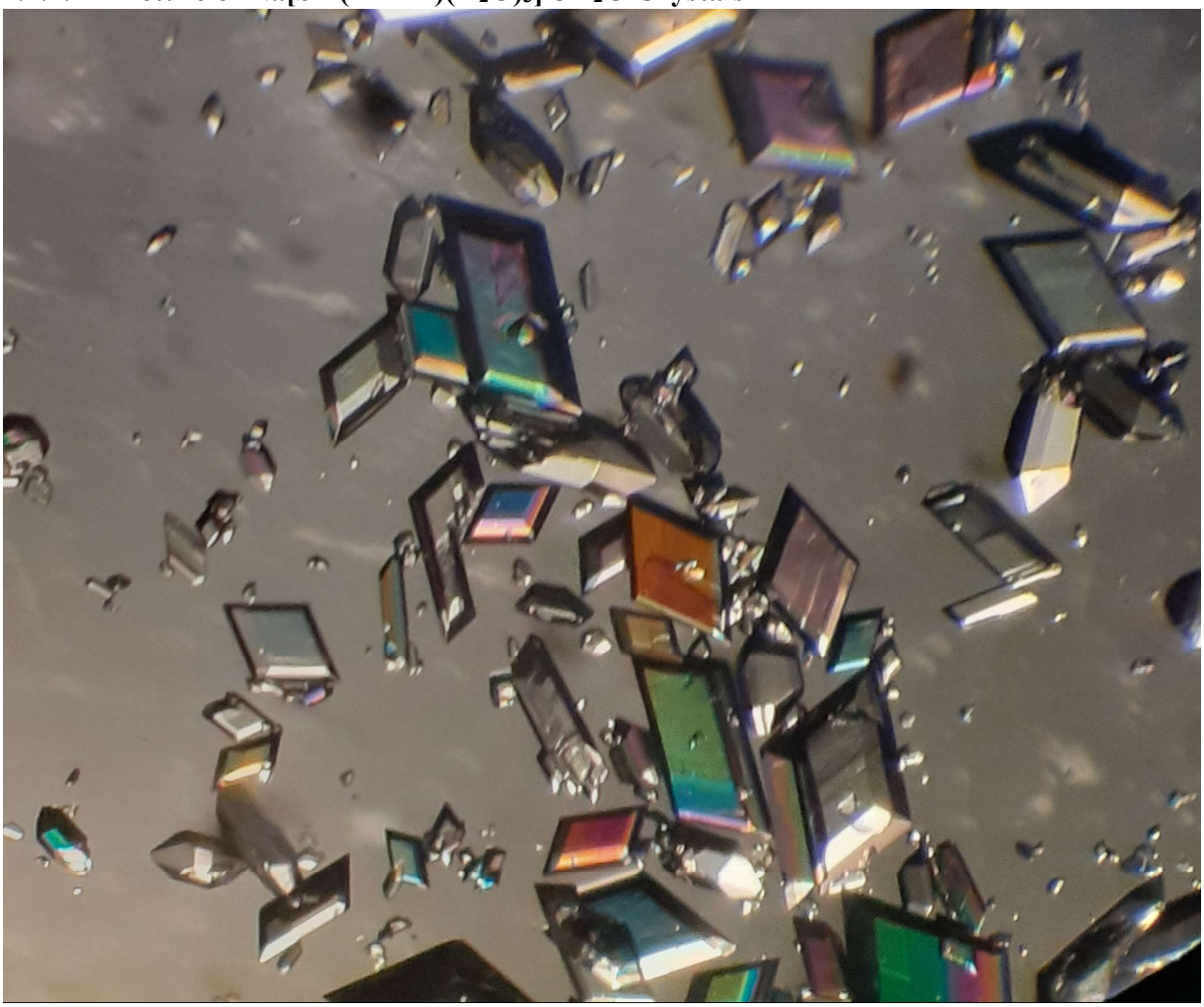


Figure S 14: Pictures of $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ made following the description in the experimental section. All of the crystal were found to be clear, light, and colourless with a rhombohedral structure. All crystals were observed to have the same phase. The complex crystallises in the orthorhombic *Fdd2* space group.

1.2.4.2 Na[Sm(EDTA)(H_2O)$_3$]·5H_2O Crystal Structure

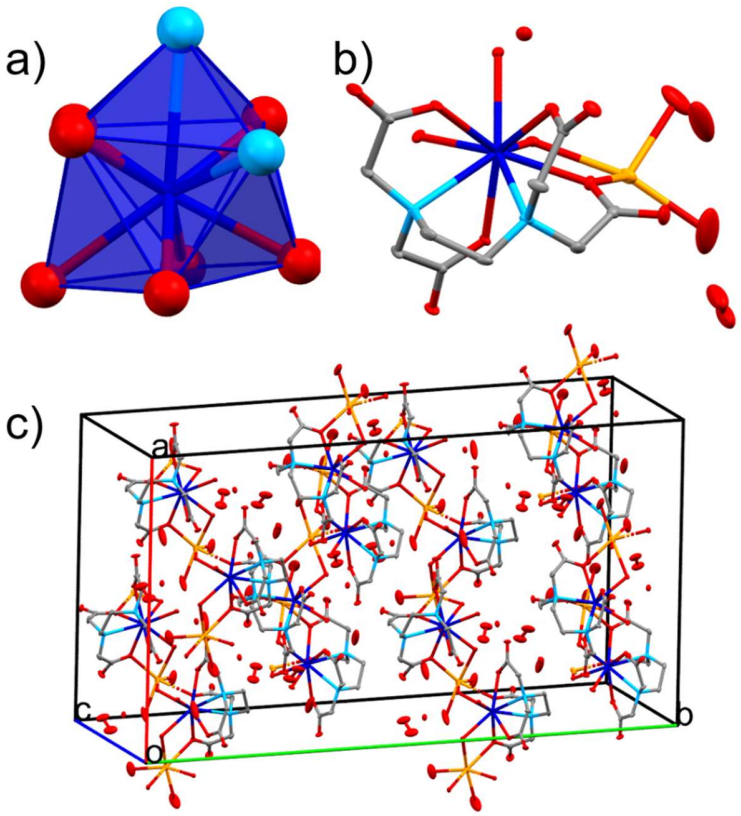


Figure S 15: a) Polyhedral depicting coordination around the Sm^{3+} ion in Na[Sm(EDTA)(H_2O)$_3$]·5H_2O. **b)** The asymmetric unit for Na[Sm(EDTA)(H_2O)$_3$]·5H_2O. **c)** The unit cell for Na[Sm(EDTA)(H_2O)$_3$]·5H_2O. Colour code: Sm = dark blue, N = light blue, C = blue, O = red and Na = orange. Hydrogen atoms omitted for clarity. Thermal ellipsoids are 50% probability.

1.2.4.3 Na[Sm(EDTA)(H_2O)$_3$]·5H_2O Crystallographic Information

Table S 8: Crystal data and structure refinement for Na[Sm(EDTA)(H_2O)$_3$]·5H_2O.

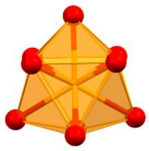
Crystal data	
Empirical formula	$C_{10}H_{28}N_2NaO_{16}Sm$
Formula weight	605.68
Temperature/K	100
Crystal system	orthorhombic
Space group	Fdd2
a/Å	19.459(3)

b/Å	35.397(6)
c/Å	12.032(2)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	8288(2)
Z	16
ρ_{calc}g/cm^3	1.935
μ/mm^{-1}	2.936
F(000)	4829.0
Crystal size/mm^3	0.576 × 0.308 × 0.122
Radiation	MoKα (λ = 0.71073)
Data collection	
2Θ range for data collection/°	4.142 to 69.942
Index ranges	-31 ≤ h ≤ 31, -56 ≤ k ≤ 56, -19 ≤ l ≤ 19
Reflections collected	42482
Independent reflections	8972 [R_{int} = 0.0458, R_{sigma} = 0.0418]
Refinement	
Data/restraints/parameters	8972/5/333
Goodness-of-fit on F^2	1.013
Final R indexes [I>=2σ (I)]	R_1 = 0.0236, wR_2 = 0.0505
Final R indexes [all data]	R_1 = 0.0268, wR_2 = 0.0516
Largest diff. peak/hole / e Å^{-3}	1.57/-1.03
Flack parameter	0.024(10)

2 Symmetry Deviation Values

2.1 Symmetry Deviation Values for Ideal Nine-coordinated Structures

Table S 9: Symmetry deviation values, σ_{ideal}, for comparison of ideal nine-coordinated structures. Values were calculated using AlignIt.[2]

						
	cSAP	**TTP**	**MFF**	**HOOP**	**TCup**	**HBPy**
cSAP	0	0.97	13.51	20.15	16.71	26.83
TTP		0	9.63	14.12	19.26	23.25
MUFF			0	14.61	20.40	24.92
HOOP				0	19.79	14.49
TCup					0	21.52
HBPy						0

2.2 Symmetry Deviation Values for the Eu^{3+} and Sm^{3+} Compounds

2.2.1 Symmetry Deviation Values for the Eu^{3+} Compounds

Table S 10: Symmetry deviation values, σ_{ideal}, for the Eu^{3+} complexes.

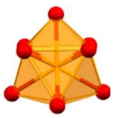
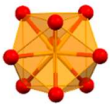
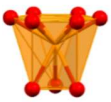
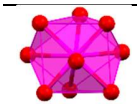
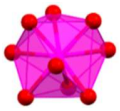
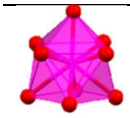
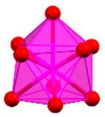
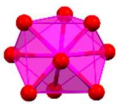
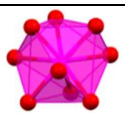
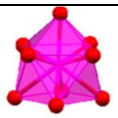
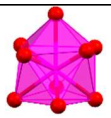
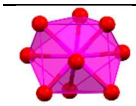
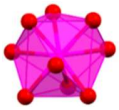
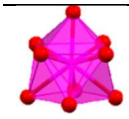
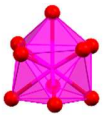
		 cSAP	 TTP	 MFF	 HOOP	 TCup	 HBPy
	**$Na_3[Eu(ODA)_3]\cdot 8H_2O$**	1.26	**0.76**	11.55	19.94	18.33	24.65
	**$Cs_3[Eu(DPA)_3]\cdot 9H_2O$**	1.87	**0.89**	9.88	14.84	18.96	23.85
	**$Na[Eu(DOTA)(H_2O)]\cdot 4H_2O$**	**0.38**	1.48	14.32	20.21	18.41	26.25
	**$Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$**	**0.63**	0.96	14.35	18.78	17.03	25.31

Table S 11: Symmetry deviation values, σ_{ideal}, for the Eu^{3+} complexes.

					
		$Na_3[Eu(ODA)_3]\cdot 8H_2O$	**$Cs_3[Eu(DPA)_3]\cdot 9H_2O$**	**$Na[Eu(DOTA)(H_2O)]\cdot 4H_2O$**	**$Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$**
	**$Na_3[Eu(ODA)_3]\cdot 8H_2O$**	-	-	-	-
	**$Cs_3[Eu(DPA)_3]\cdot 9H_2O$**	0.19	-	-	-
	**$Na[Eu(DOTA)(H_2O)]\cdot 4H_2O$**	1.15	1.97	-	-
	**$Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$**	1.73	1.29	1.07	-

2.2.2 Symmetry Deviation Values for the Sm^{3+} Compounds

Table S 12: Symmetry deviation values, σ_{ideal}, for the Sm^{3+} complexes.

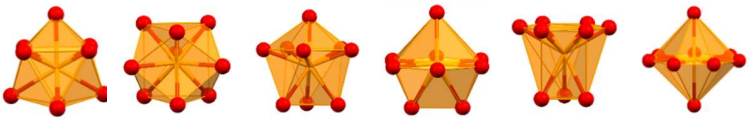
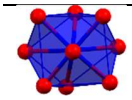
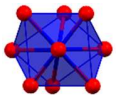
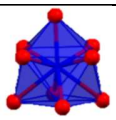
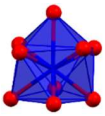
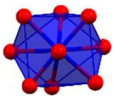
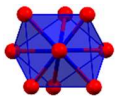
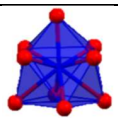
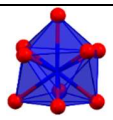
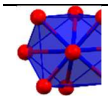
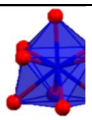
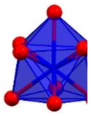
							
		cSAP	**TTP**	**MFF**	**HOOP**	**TCup**	**HBPy**
	**$Na_3[Sm(ODA)_3]\cdot 7H_2O$**	1.40	**0.87**	11.49	16.54	18.81	23.94
	**$Cs_3[Sm(DPA)_3]\cdot 9H_2O$**	1.92	**0.96**	11.19	20.24	19.35	24.12
	**$Na[Sm(DOTA)(H_2O)]\cdot 4H_2O$**	**0.39**	1.49	13.63	21.10	17.77	26.14
	**$Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$**	**0.64**	0.99	13.97	18.55	18.24	25.34

Table S 13: Symmetry deviation values, σ_{ideal}, for the Sm^{3+} complexes.

	 **$Na_3[Sm(ODA)_3]\cdot 7H_2O$**	 **$Cs_3[Sm(DPA)_3]\cdot 9H_2O$**	 **$Na[Sm(DOTA)(H_2O)]\cdot 4H_2O$**	 **$Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$**
 **$Na_3[Sm(ODA)_3]\cdot 7H_2O$**	-			
 **$Cs_3[Sm(DPA)_3]\cdot 9H_2O$**	0.25	-		
 **$Na[Sm(DOTA)(H_2O)]\cdot 4H_2O$**	0.85	1.62	-	
 **$Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$**	0.85	1.33	0.73	-

3 PXRD

3.1 PXRD Eu^{3+} Compounds

3.1.1 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ PXRD

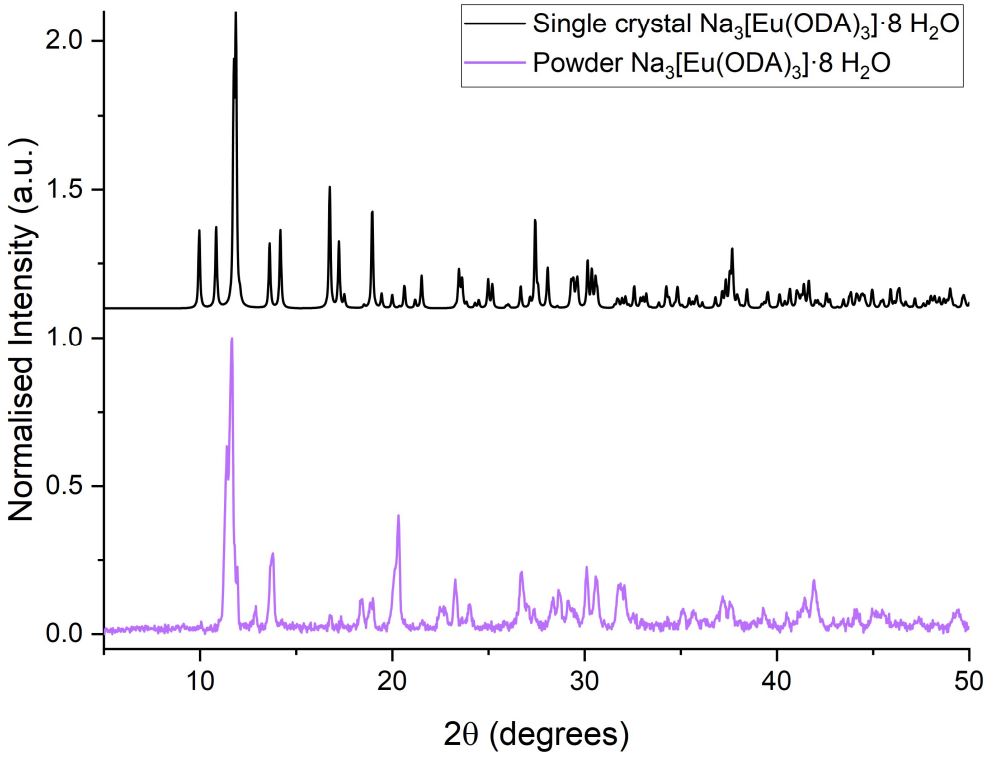


Figure S 16: PXRD for $Na_3[Eu(ODA)_3]\cdot 8H_2O$. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The purple diffractogram is simulated from the structure determined for the single crystal.

3.1.2 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ PXRD

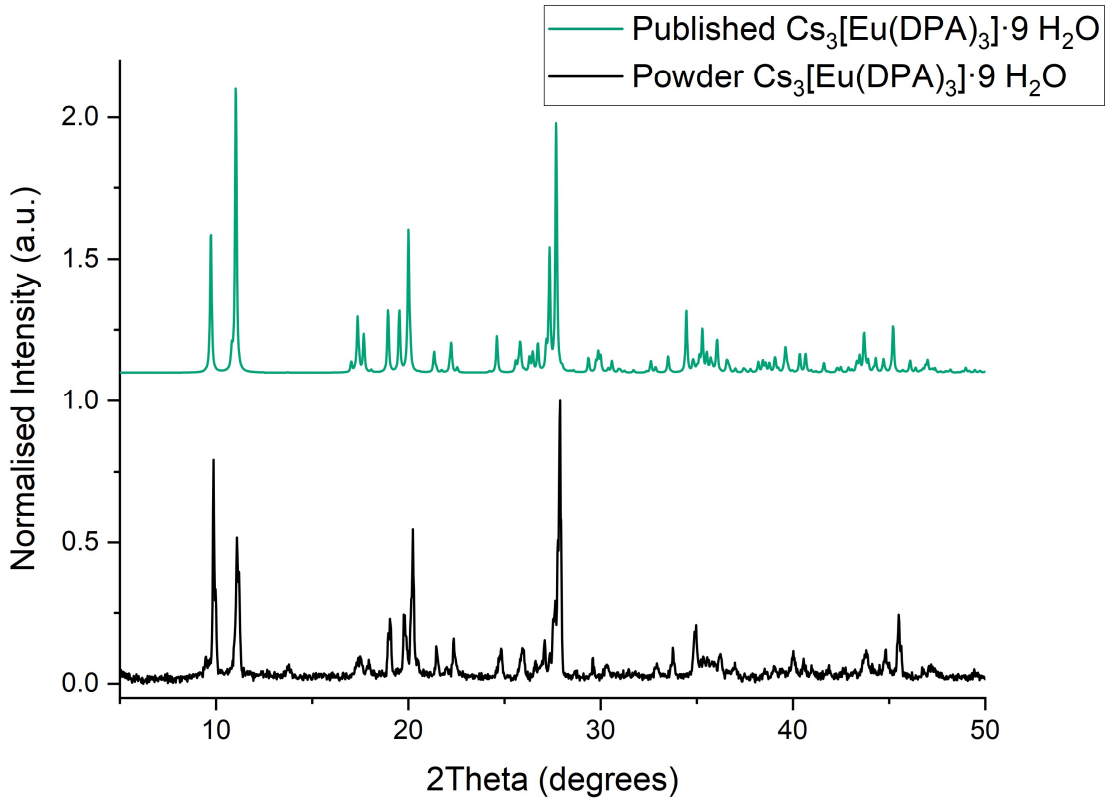


Figure S 17: PXRD for $Na_3[Eu(DPA)_3]\cdot 9H_2O$. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The green diffractogram is simulated from the published structure by Brayshaw *et al.*[1] as the crystal created in the experimental section was found to be a twin, and the structure could not be determined.

3.1.3 Na[Eu(DOTA)H_2O]·4H_2O PXRD

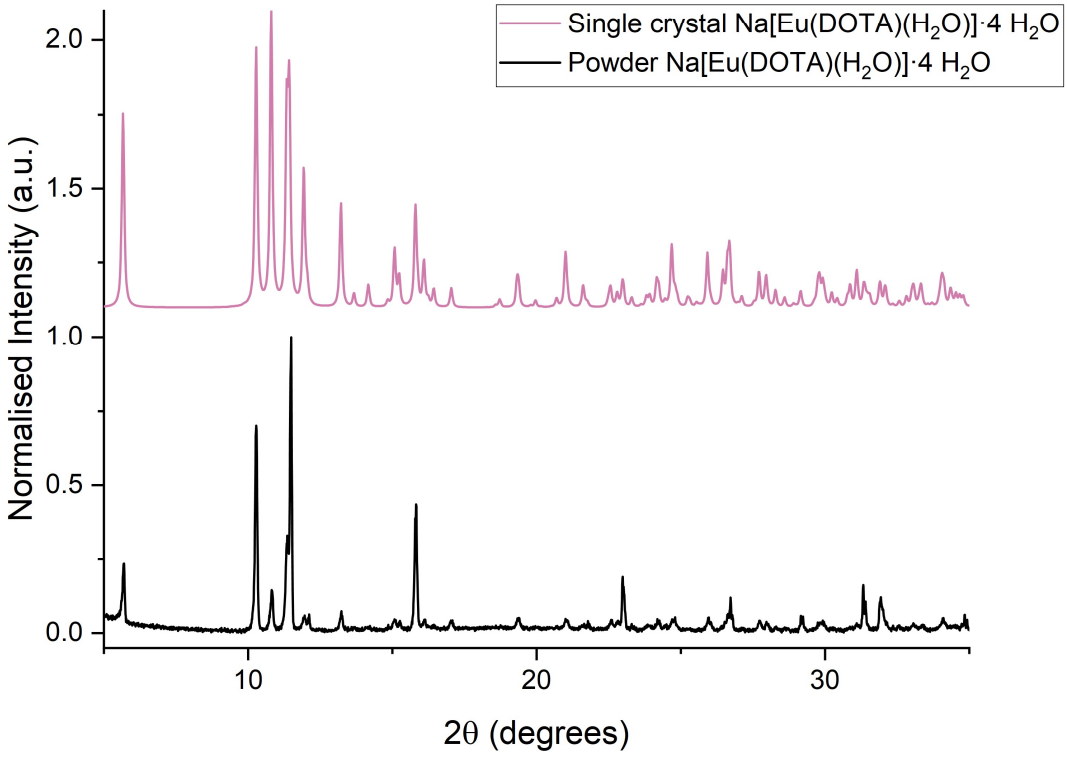


Figure S 18: PXRD for Na[Eu(DOTA)H_2O]·4H_2O. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The pink diffractogram is simulated from the structure determined for the single crystal.

3.1.4 Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O PXRD

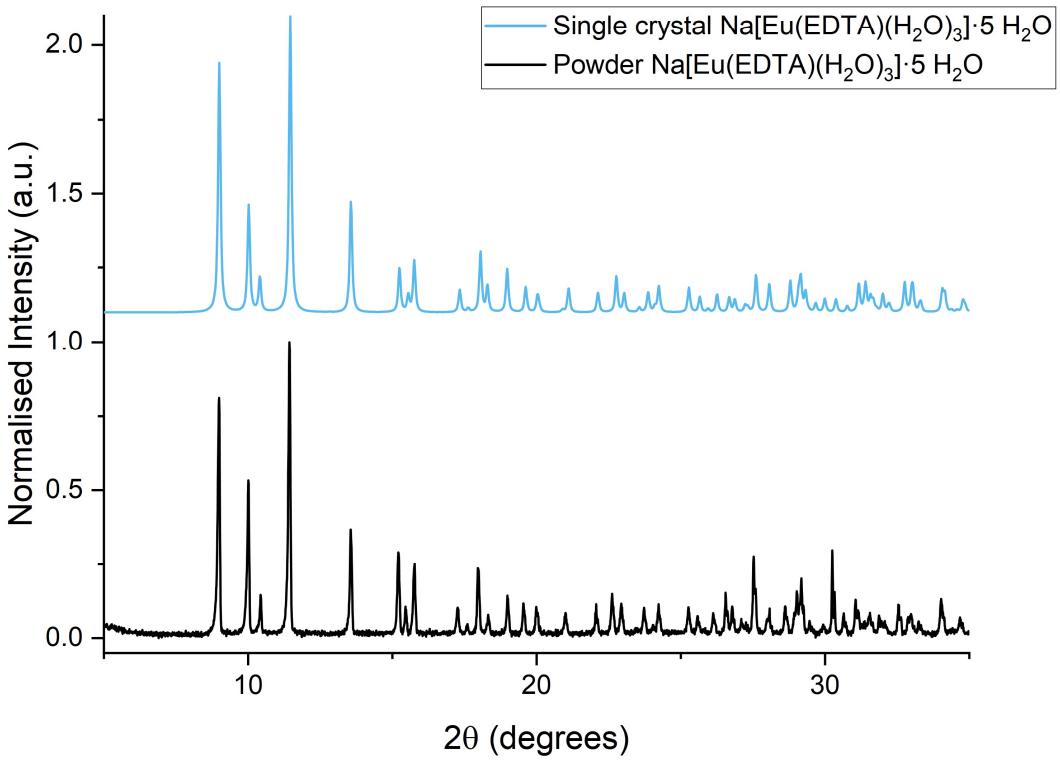


Figure S 19: PXRD for Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The light blue diffractogram is simulated from the structure determined for the single crystal.

3.2 PXRD Sm^{3+} Compounds

3.2.1 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ PXRD

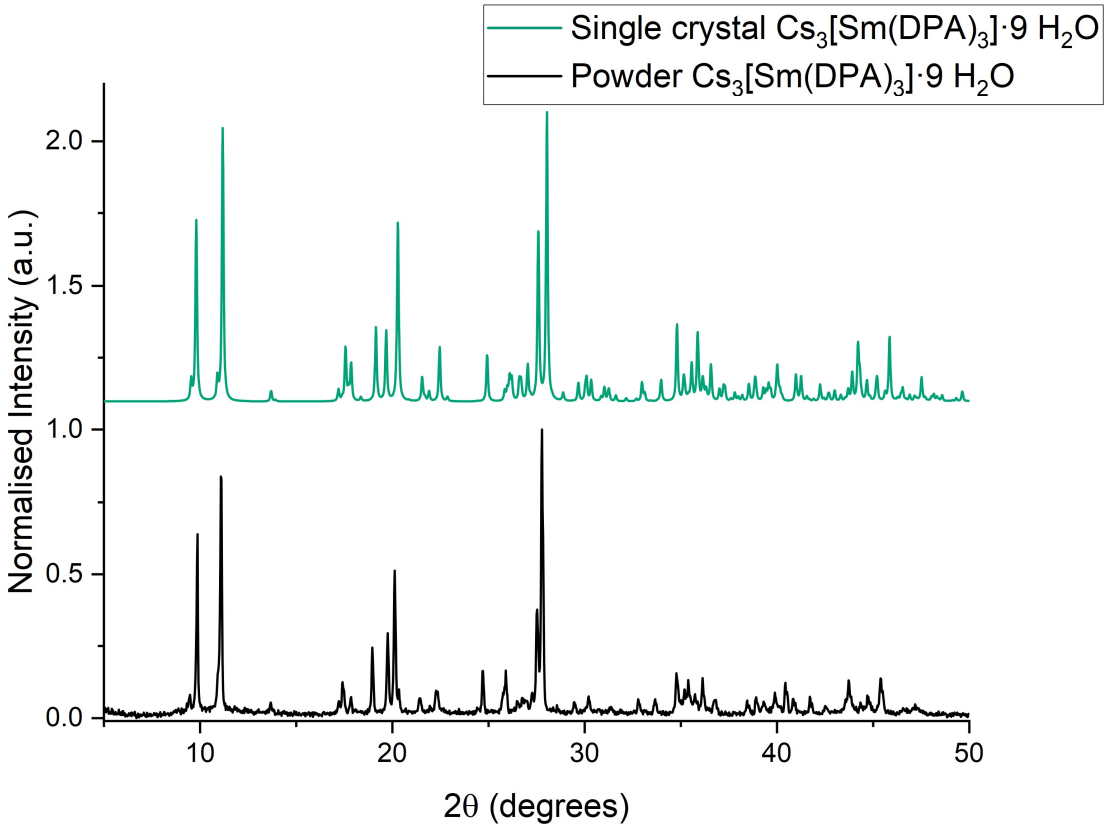


Figure S 20: PXRD for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The light blue diffractogram is simulated from the structure determined for the single crystal.

3.2.2 Na[Sm(DOTA)H_2O]·4H_2O PXRD

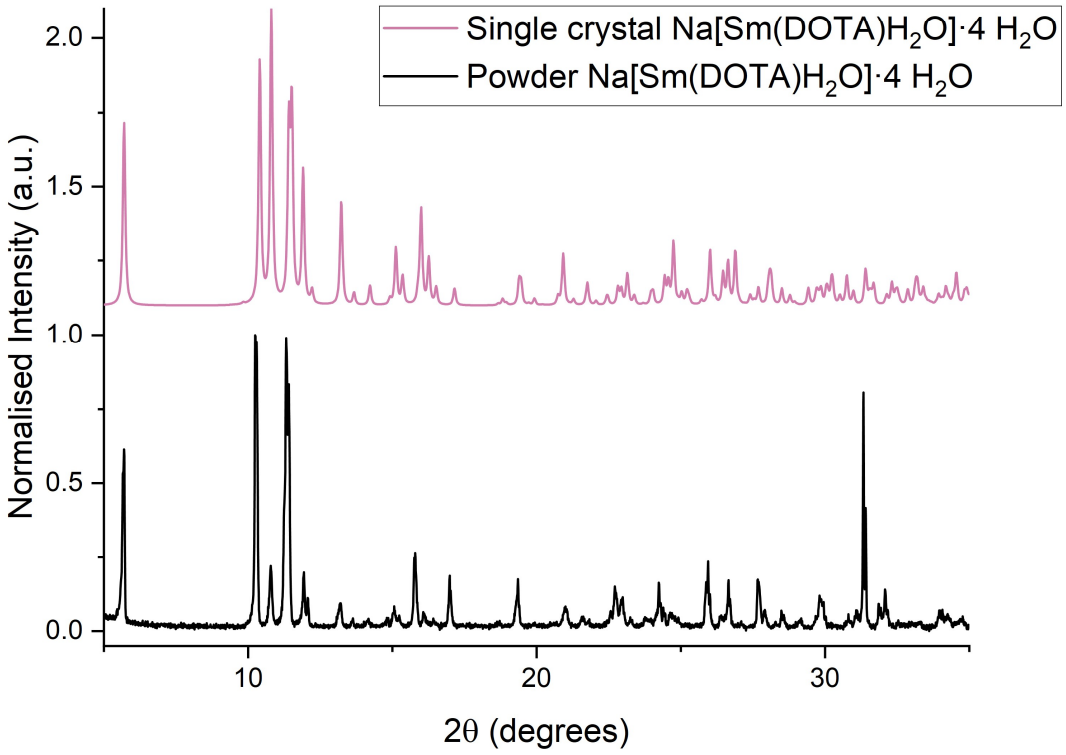


Figure S 21: PXRD for Na[Sm(DOTA)H_2O]·4H_2O. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The light blue diffractogram is simulated from the structure determined for the single crystal.

3.2.3 Na[Sm(EDTA)H$_2$O]·5H$_2$O PXRD

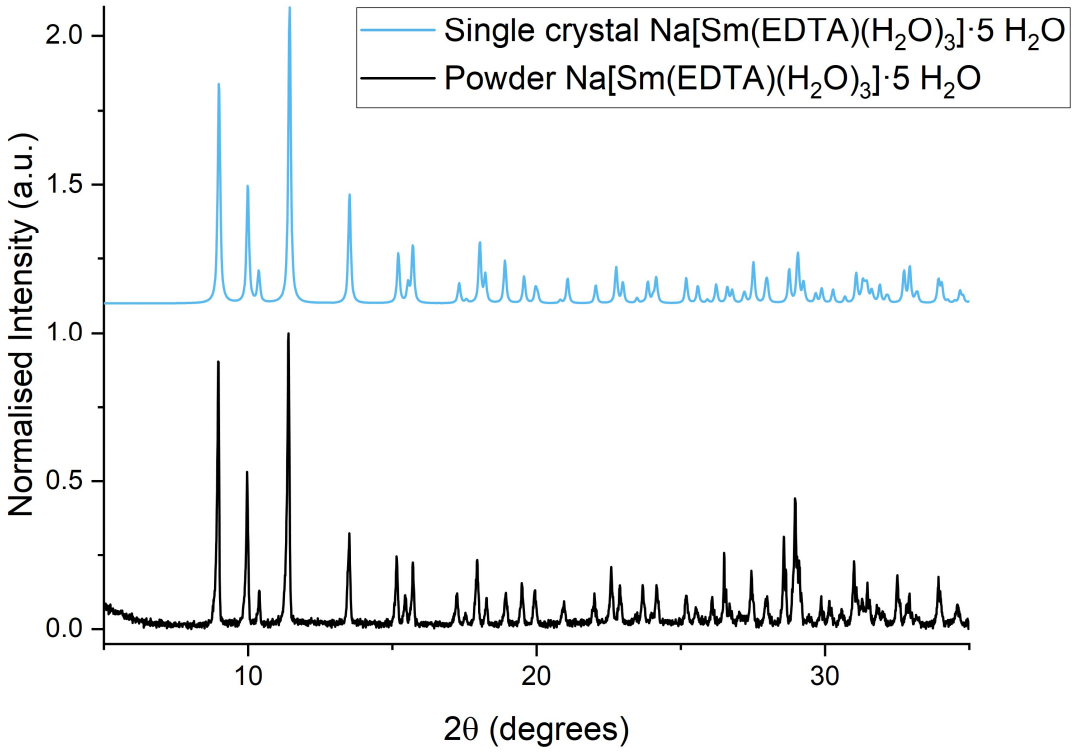


Figure S 22: PXRD for Na[Sm(EDTA)(H$_2$O)$_3$]·5H$_2$O. The black diffractogram is recorded for the powder made from crystals crushed to a powder. The light blue diffractogram is simulated from the structure determined for the single crystal.

4 Spectroscopy Data

4.1 Experimental Setup for Solid State Single Crystal Luminescence

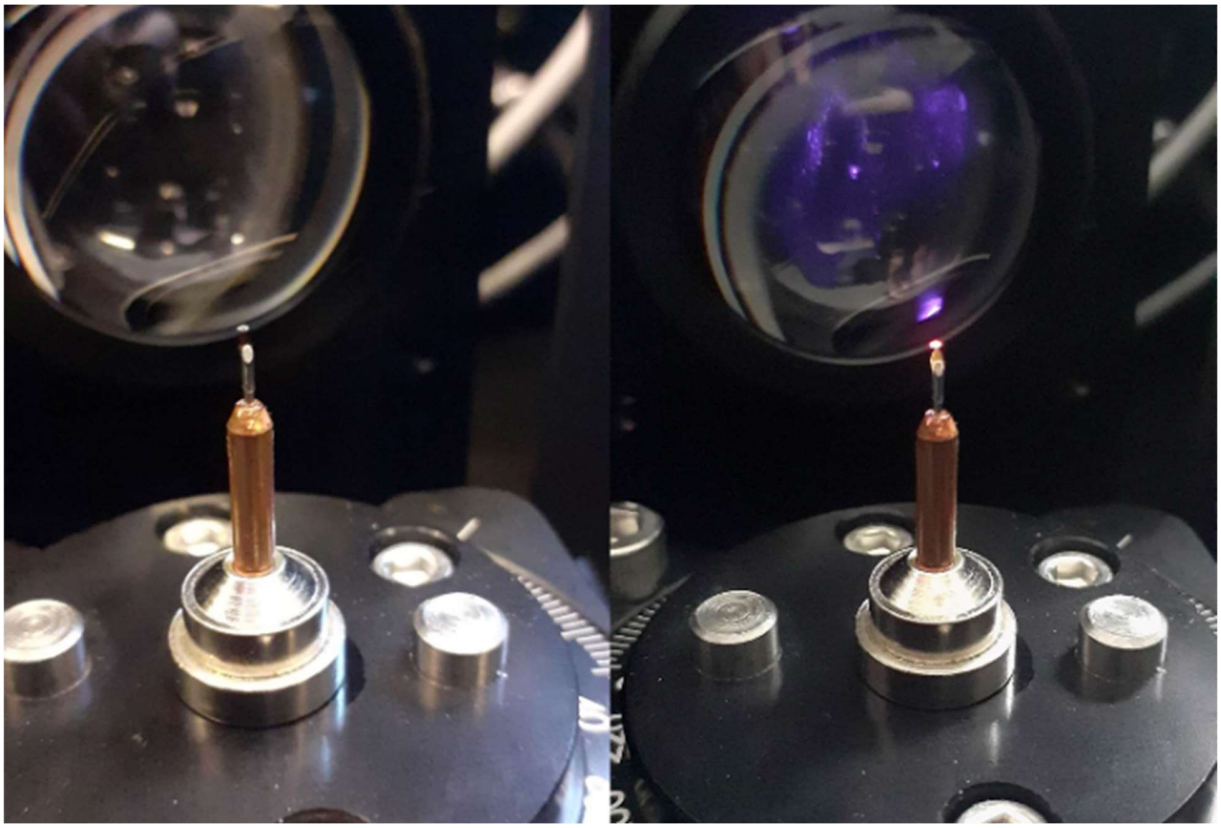


Figure S 23: Solid-state single crystal emission setup using a crystal mounting loop. Emission was measured at 293 K. The picture shows a $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ crystal. The picture to the right show excitation at 394 nm.

4.2 Spectroscopy Data for Eu^{3+} Compounds

4.2.1 Luminescence Lifetimes for Eu^{3+} Compounds

Table S 14: Luminescence lifetimes of the Eu^{3+} complexes for crystals ground to a powder in 2-methyltetrahydrofuran at 77 K.

Complex	τ_{obs} (µs)
$Na_3[Eu(ODA)_3]\cdot 8H_2O$	2860.21
$Cs_3[Eu(DPA)_3]\cdot 9H_2O$	1697.99
$Na[Eu(DOTA)(H_2O)]\cdot 4H_2O$	731.06
$Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$	364.10

Table S 15: Luminescence lifetimes of the Eu^{3+} complexes for single crystals at 293 K.

Complex	τ_{obs} (µs)
$Na_3[Eu(ODA)_3]\cdot 8H_2O$	1965.36
$Cs_3[Eu(DPA)_3]\cdot 9H_2O$	1415.91
$Na[Eu(DOTA)(H_2O)]\cdot 4H_2O$	748.44
$Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$	355.38

4.2.2 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Spectra

4.2.2.1 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Emission Spectra

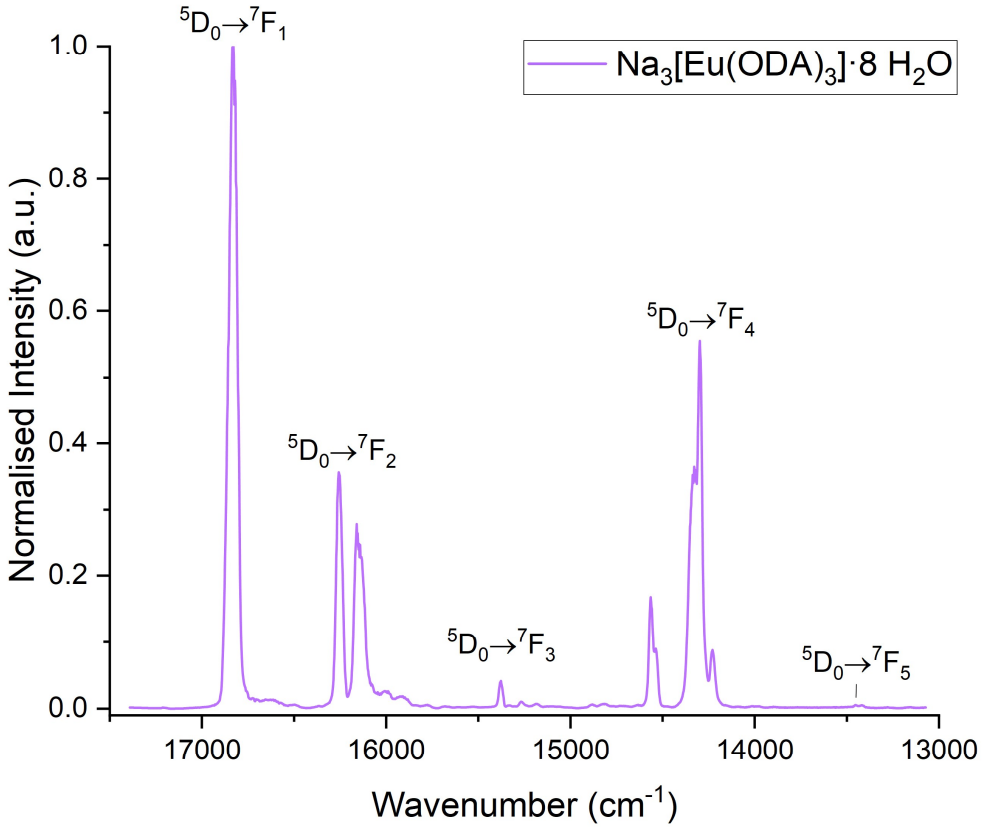


Figure S 24: Normalised emission spectrum (excitation at 394 nm) for $Na_3[Eu(ODA)_3]\cdot 8H_2O$ in 2-methyltetrahydrofuran glass at 77 K.

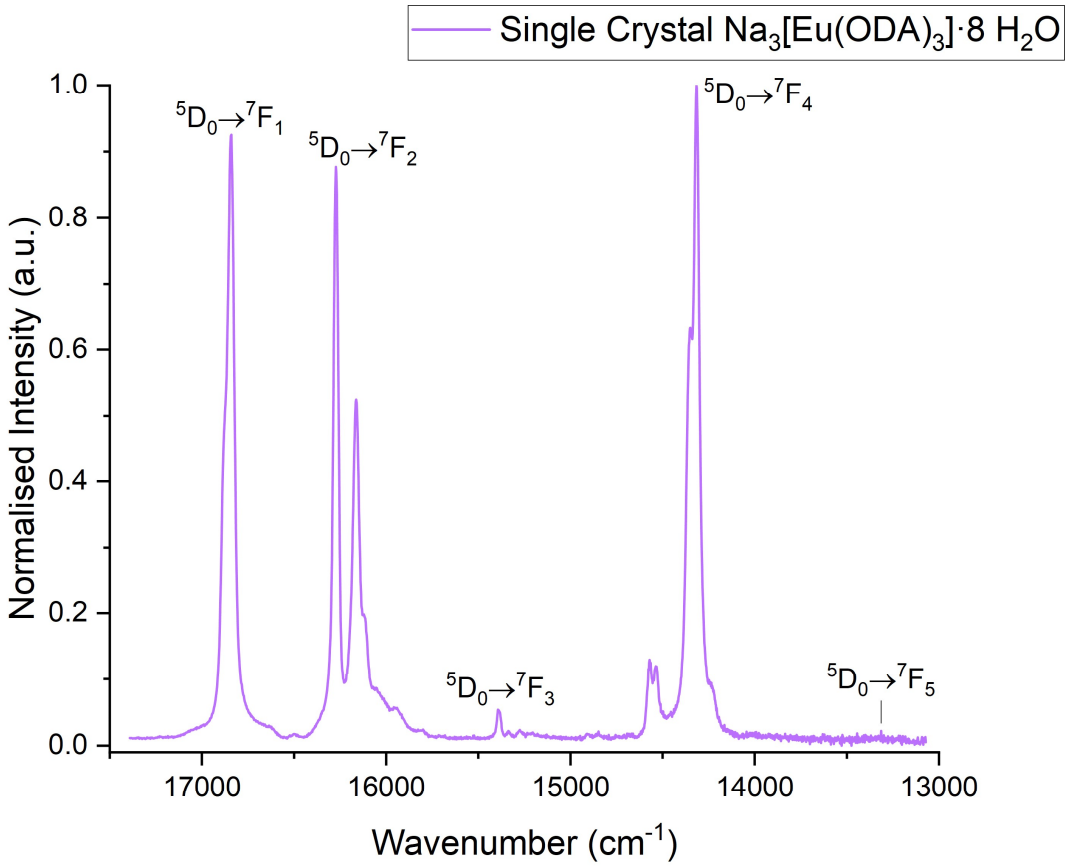


Figure S 25: Normalised emission spectrum (excitation at 394 nm) for single crystal $Na_3[Eu(ODA)_3]\cdot 8H_2O$ at 293 K.

4.2.2.2 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Excitation Spectra

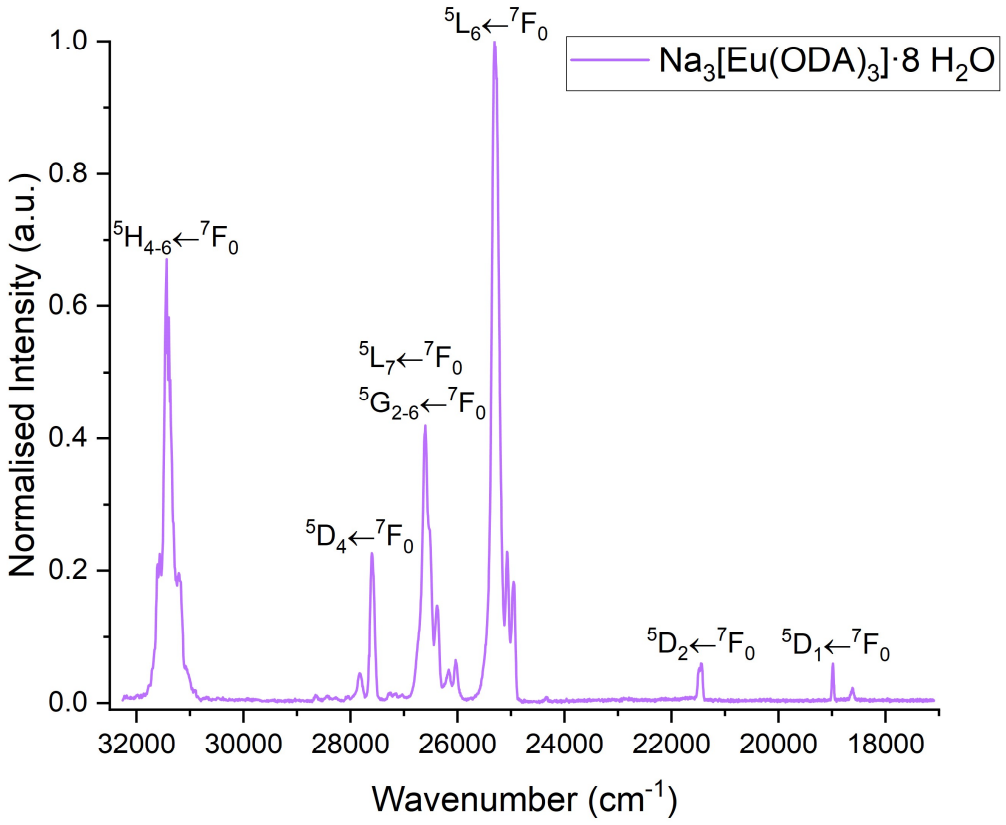


Figure S 26: Normalised excitation spectra (emission at 614 nm) for $Na_3[Eu(ODA)_3]\cdot 8H_2O$ in 2-methyltetrahydrofuran glass at 77 K.

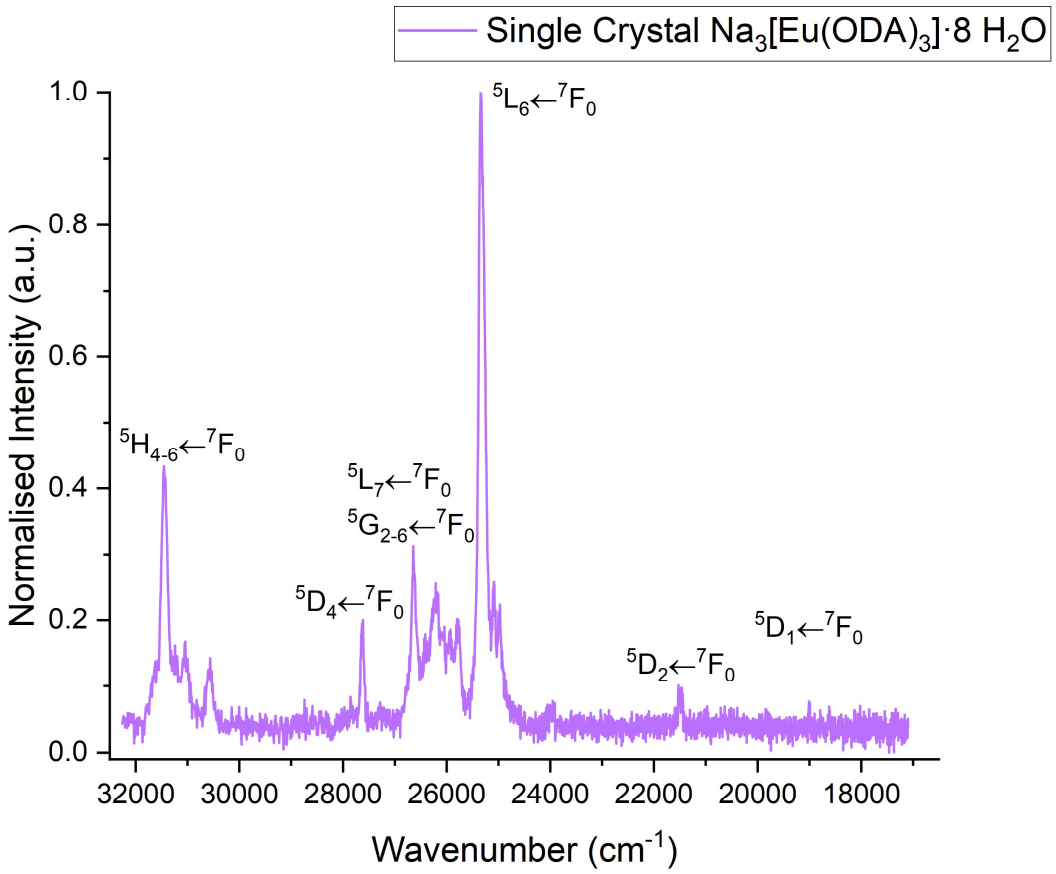


Figure S 27: Normalised excitation spectra (emission at 614 nm) for single crystal $Na_3[Eu(ODA)_3]\cdot 8H_2O$ at 293 K.

4.2.2.3 $Na_3[Eu(ODA)_3]\cdot 8H_2O$ Luminescence Lifetimes

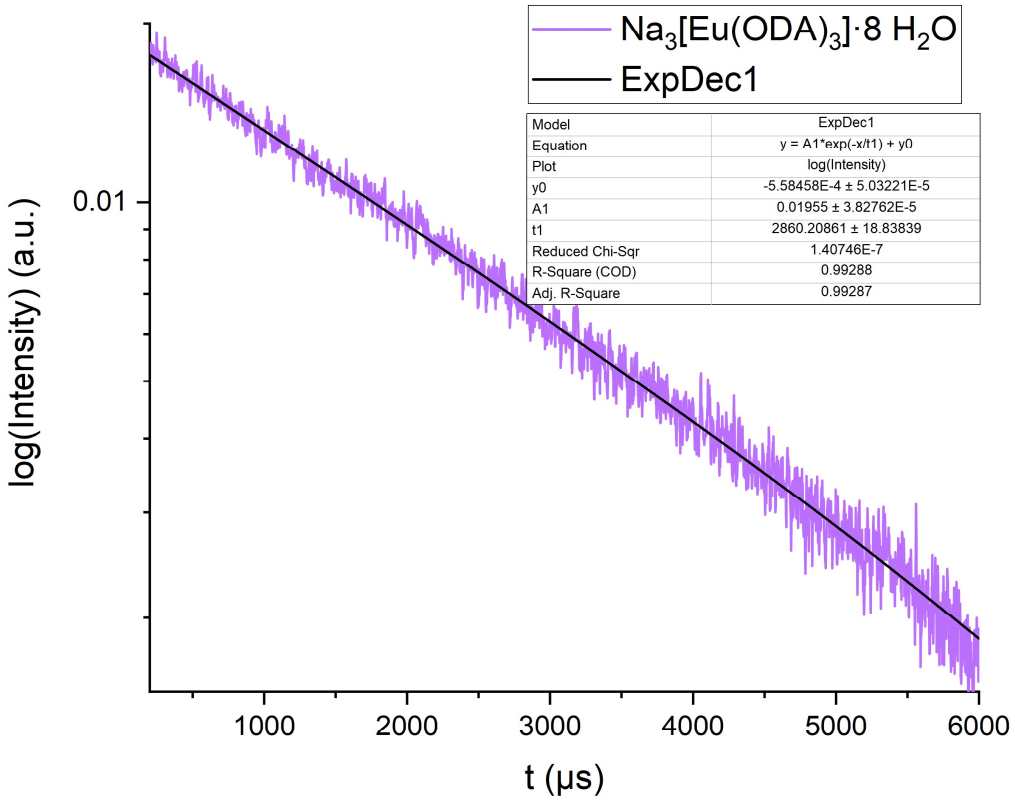


Figure S 28: $Na_3[Eu(ODA)_3]\cdot 8H_2O$ luminescence lifetime in 2-methyltetrahydrofuran glass at 77 K. Fitted using OriginPro's ExpDec1 function.

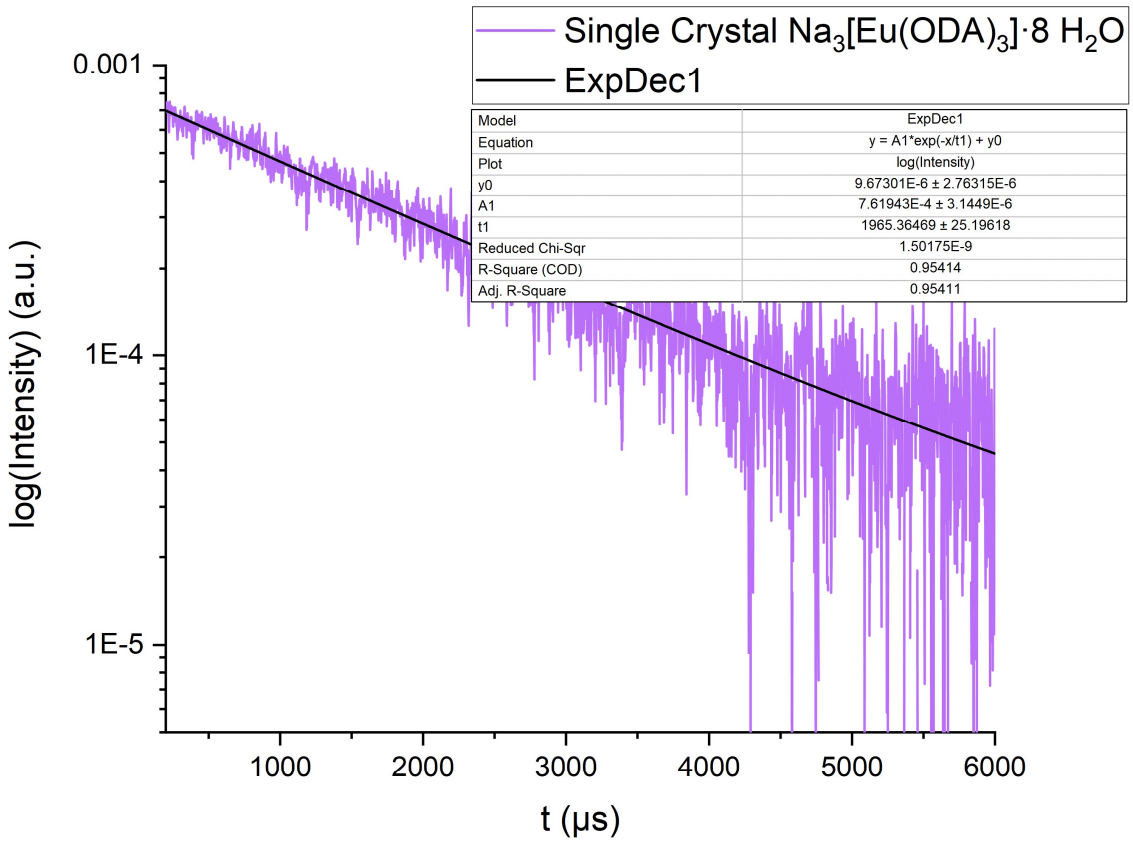


Figure S 29: $Na_3[Eu(ODA)_3]\cdot 8H_2O$ single crystal luminescence lifetime at 293 K. Fitted using OriginPro's ExpDec1 function.

4.2.3 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Spectra

4.2.3.1 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Emission Spectra

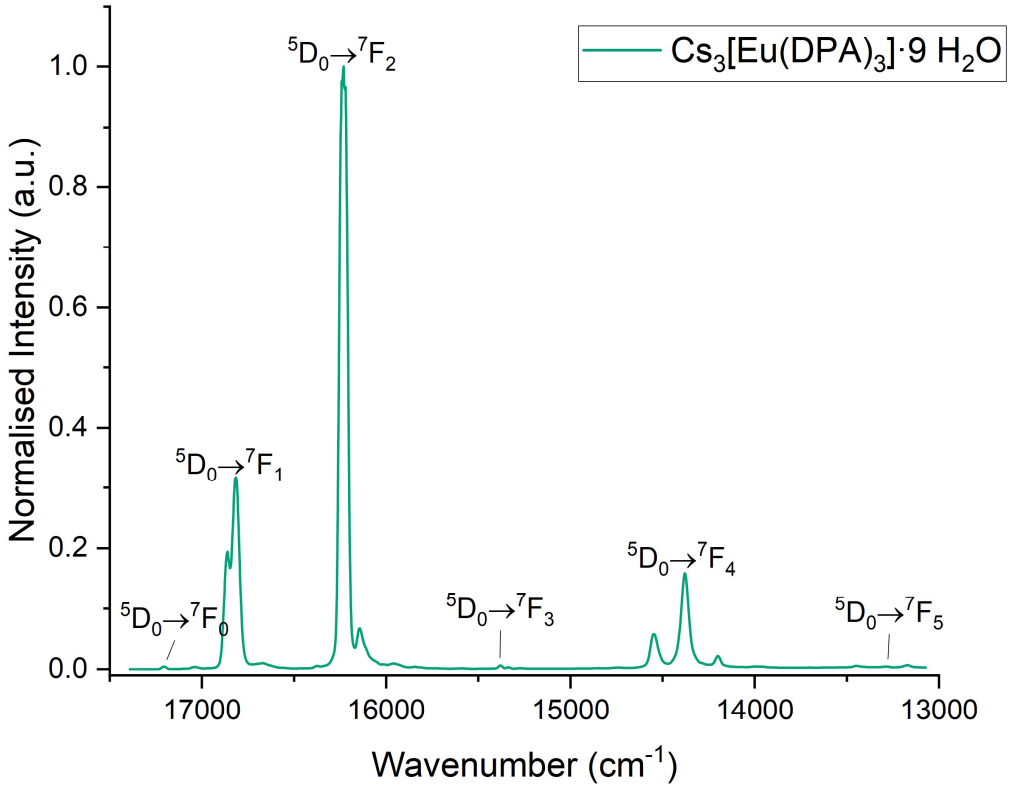


Figure S 30: Normalised emission spectrum (excitation at 394 nm) for $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ in 2-methyltetrahydrofuran glass at 77 K.

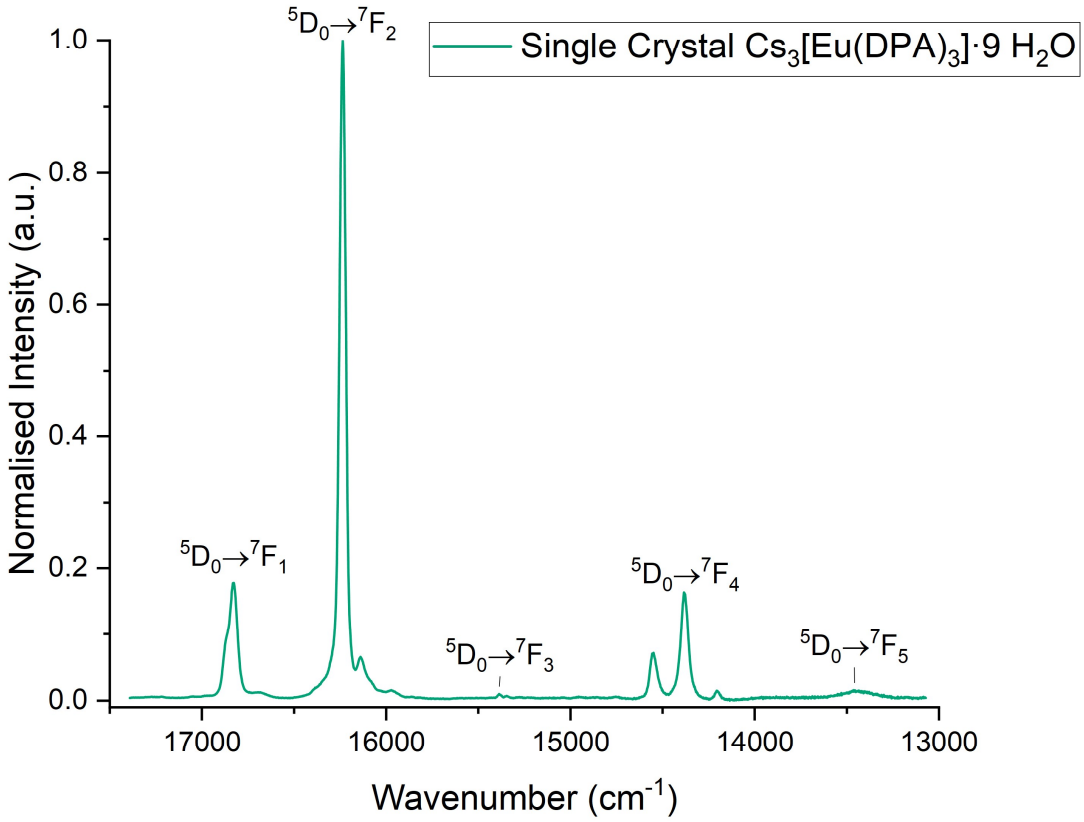


Figure S 31: Normalised emission spectrum (excitation at 394 nm) for single crystal $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ at 293 K.

4.2.3.2 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Excitation Spectra

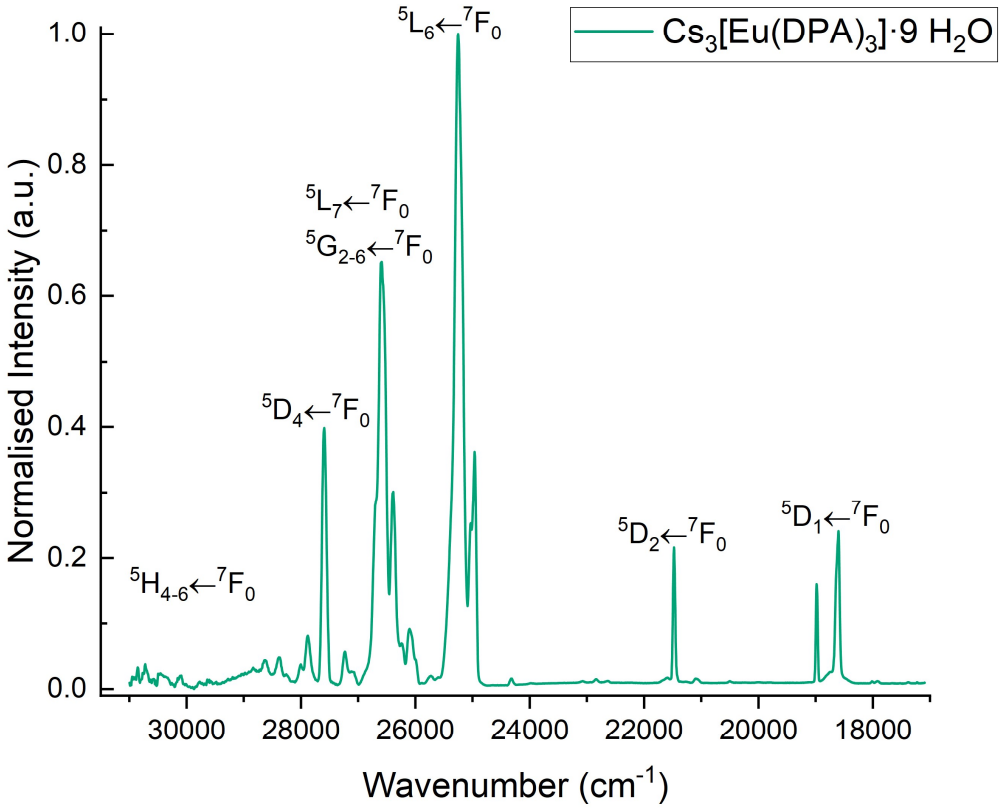


Figure S 32: Normalised excitation spectra (emission at 614 nm) for $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ in 2-methyltetrahydrofuran glass at 77 K.

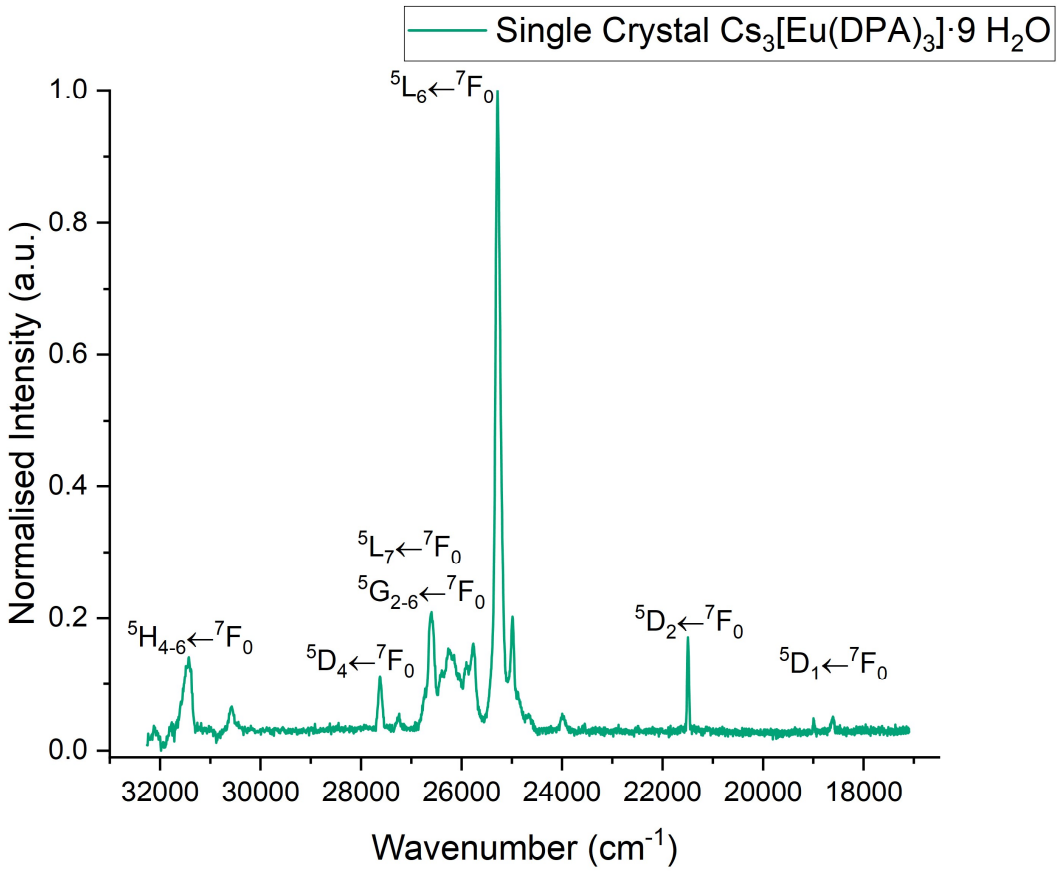


Figure S 33: Normalised excitation spectra (emission at 614 nm) for single crystal $Cs_3[Eu(DPA)_3]$ at 293 K.

4.2.3.3 $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ Luminescence Lifetimes

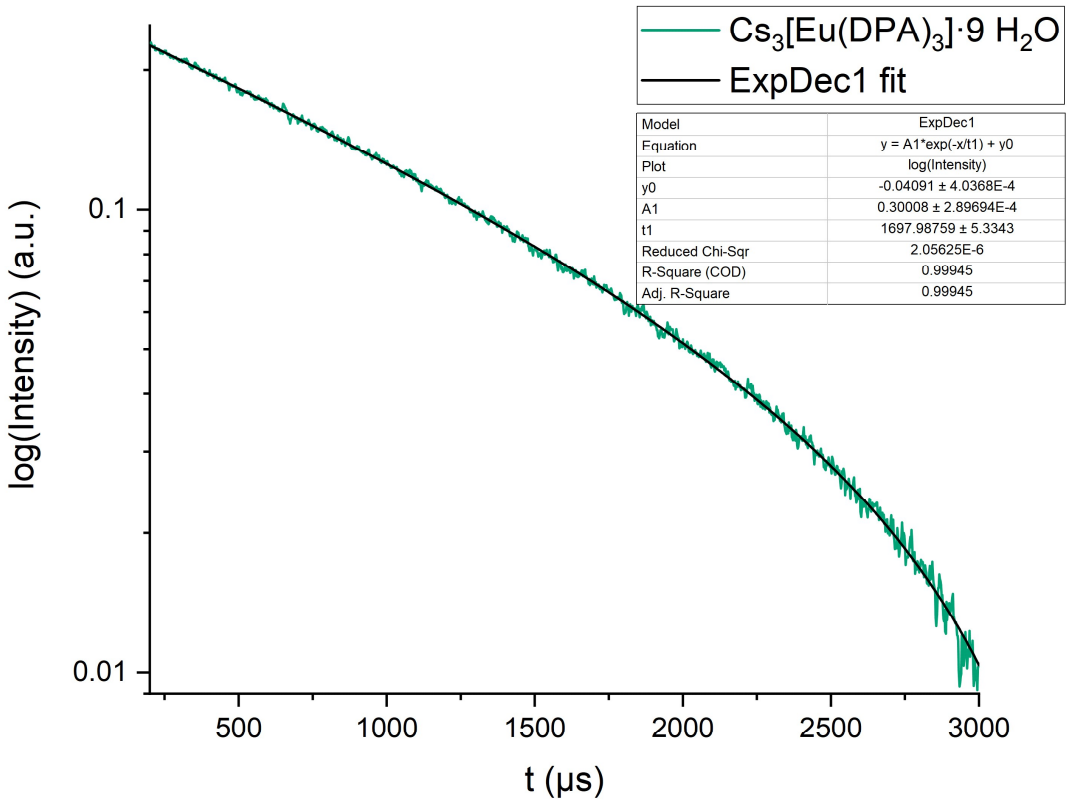


Figure S 34: $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ luminescence lifetime in 2-methyltetrahydrofuran glass at 77 K. Fitted using OriginPro's ExpDec1 function.

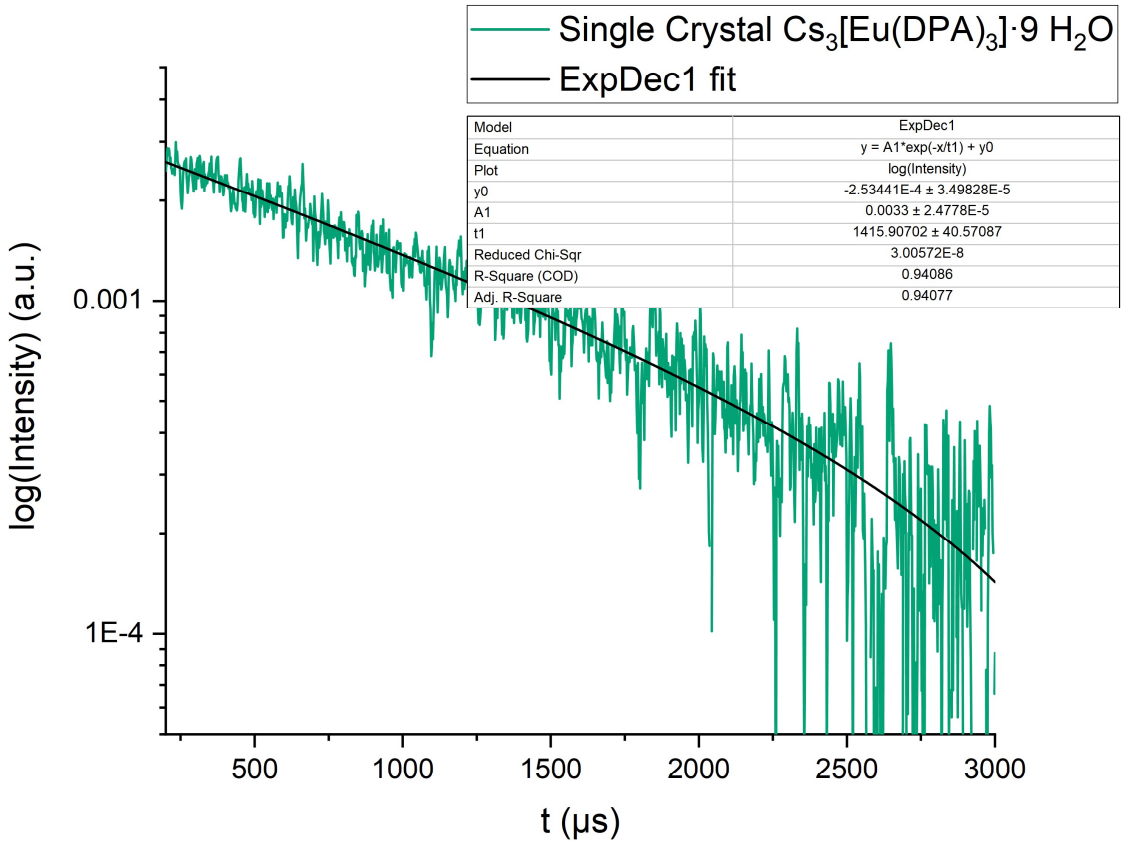


Figure S 35: $Cs_3[Eu(DPA)_3]\cdot 9H_2O$ single crystal luminescence lifetime at 293 K. Fitted using OriginPro's ExpDec1 function.

4.2.4 Na[Eu(DOTA)H$_2$O]·4H$_2$O Spectra

4.2.4.1 Na[Eu(DOTA)H$_2$O]·4H$_2$O Emission Spectra

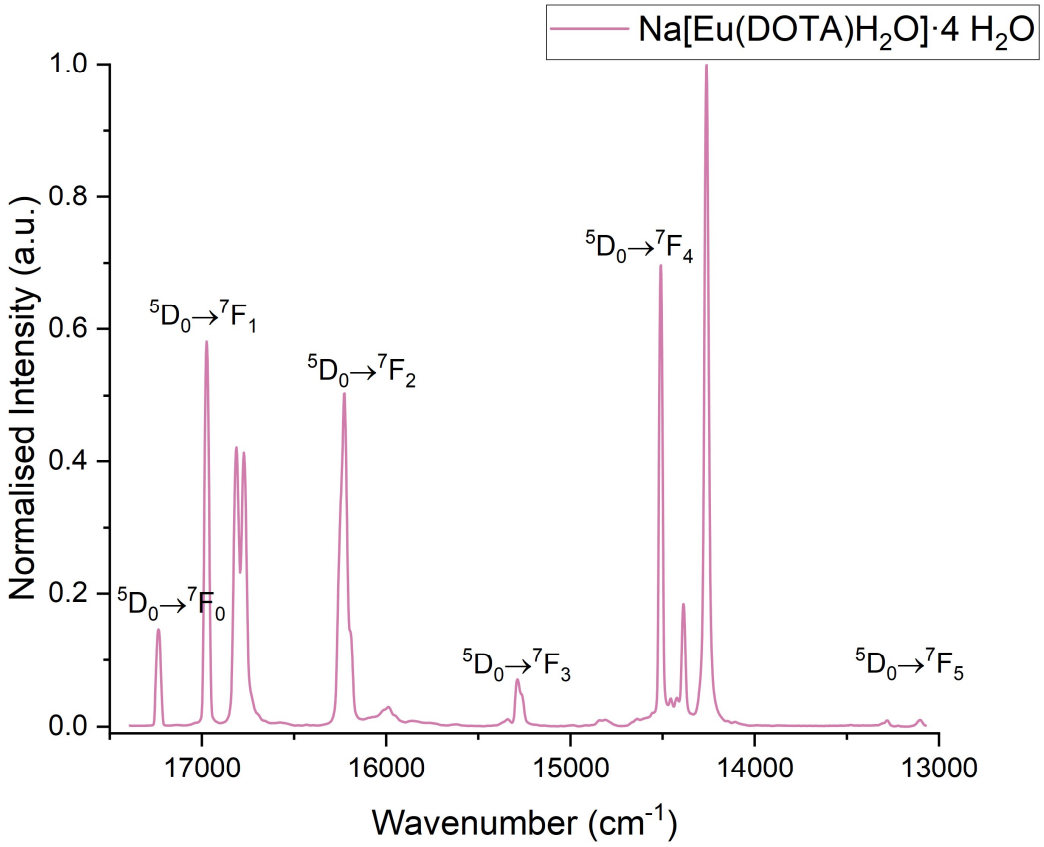


Figure S 36: Normalised emission spectrum (excitation at 394 nm) for Na[Eu(DOTA)H$_2$O]·4H$_2$O in 2-methyltetrahydrofuran glass at 77 K.

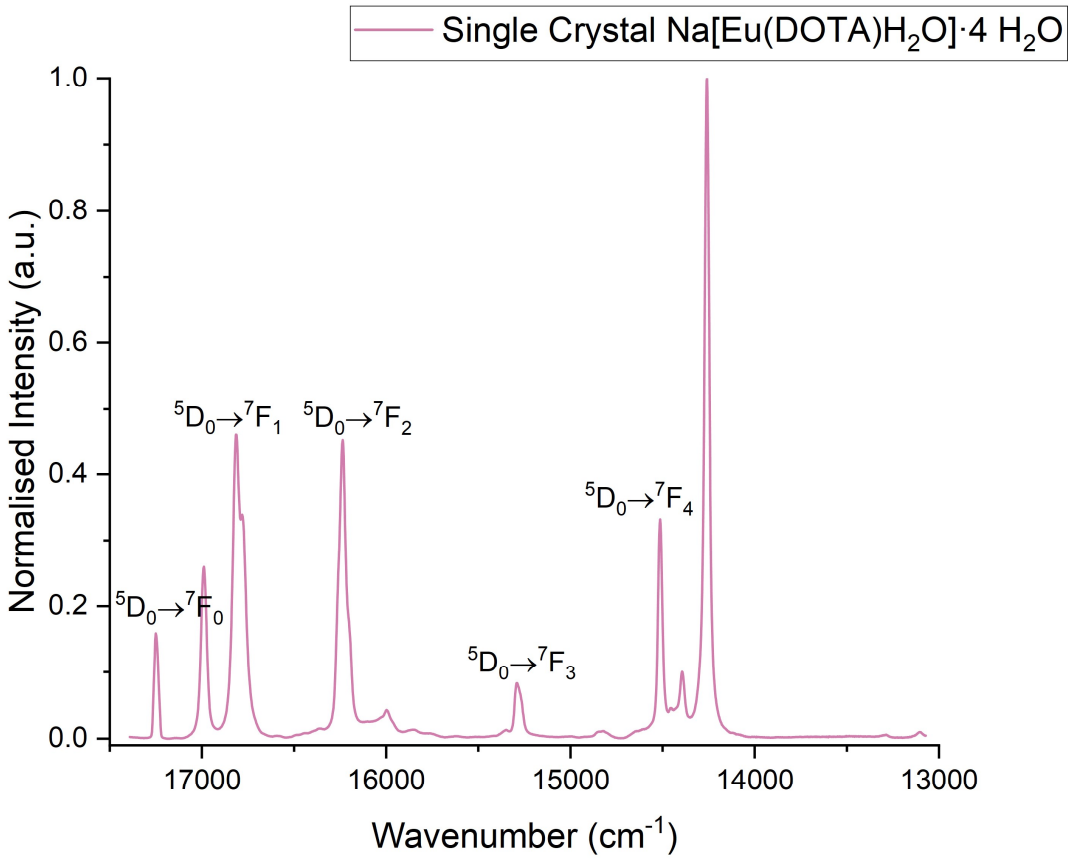


Figure S 37: Normalised emission spectrum (excitation at 394 nm) for single crystal Na[Eu(DOTA)H_2O]·4H_2O at 293 K.

4.2.5 Na[Eu(DOTA)H$_2$O]·4H2O Excitation Spectra

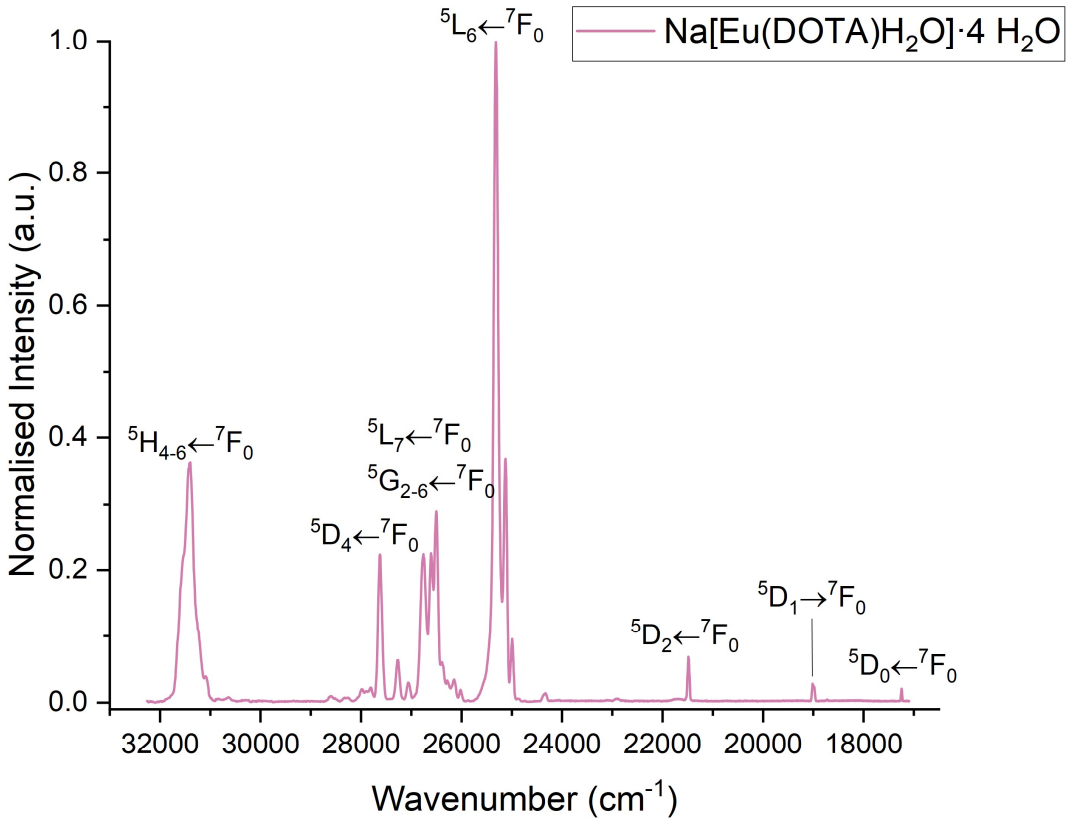


Figure S 38: Normalised excitation spectra (emission at 614 nm) for Na[Eu(DOTA)H$_2$O]·4H$_2$O in 2-methyltetrahydrofuran glass at 77 K.

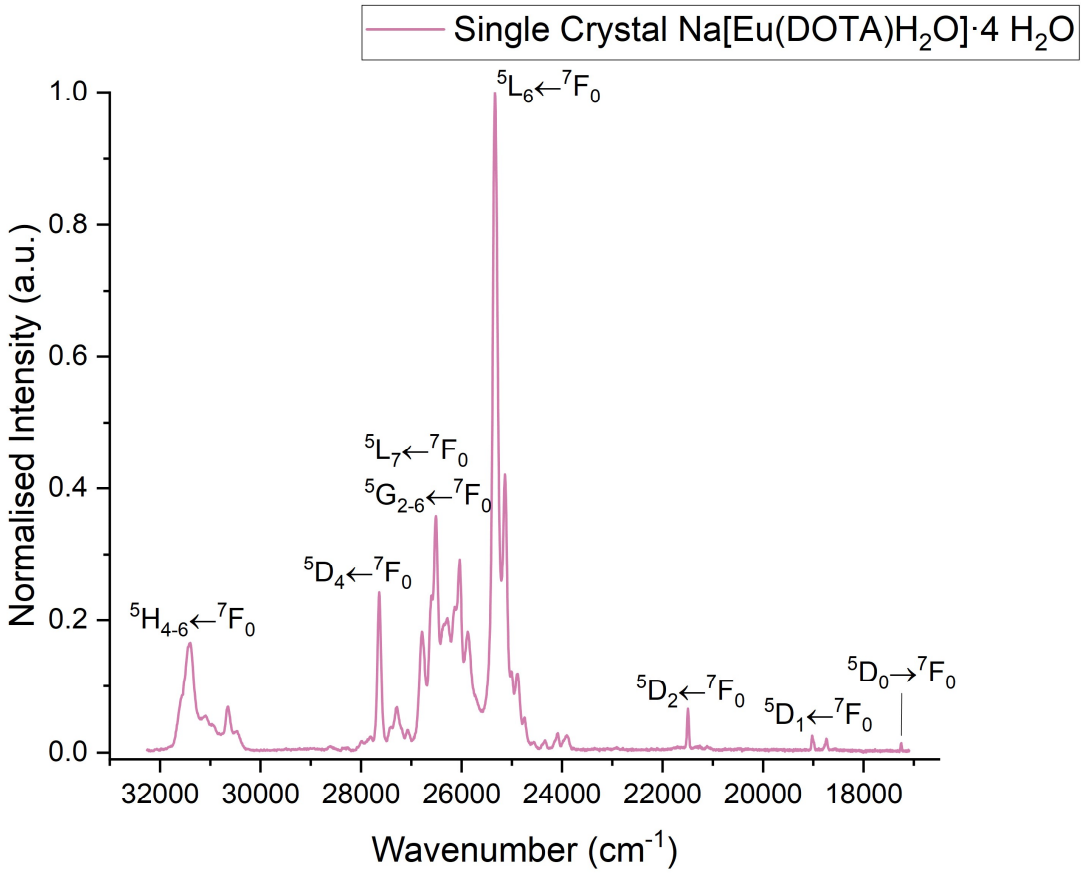


Figure S 39: Normalised excitation spectra (emission at 614 nm) for single crystal $Na[Eu(DOTA)H_2O]\cdot 4H_2O$ at 293 K.

4.2.5.1 Na[Eu(DOTA)H_2O]·4H_2O Luminescence Lifetimes

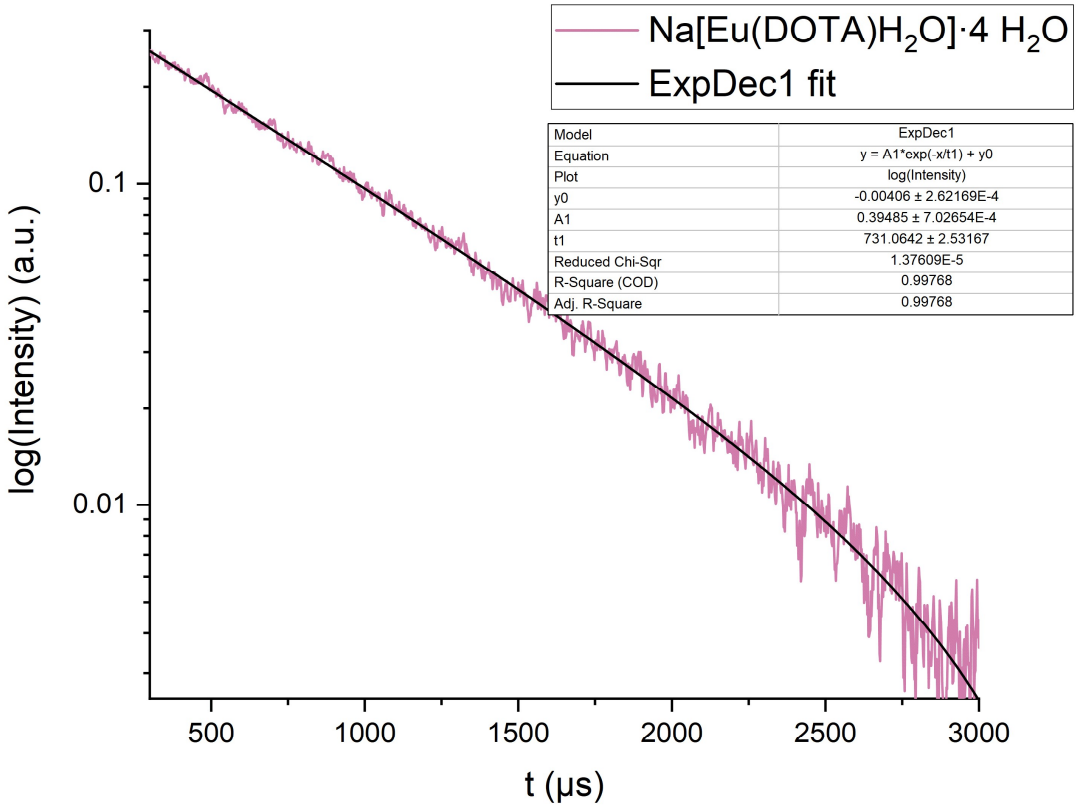


Figure S 40: Na[Eu(DOTA)H_2O]·4H_2O luminescence lifetime in 2-methyltetrahydrofuran glass at 77 K. Fitted using OriginPro's ExpDec1 function.

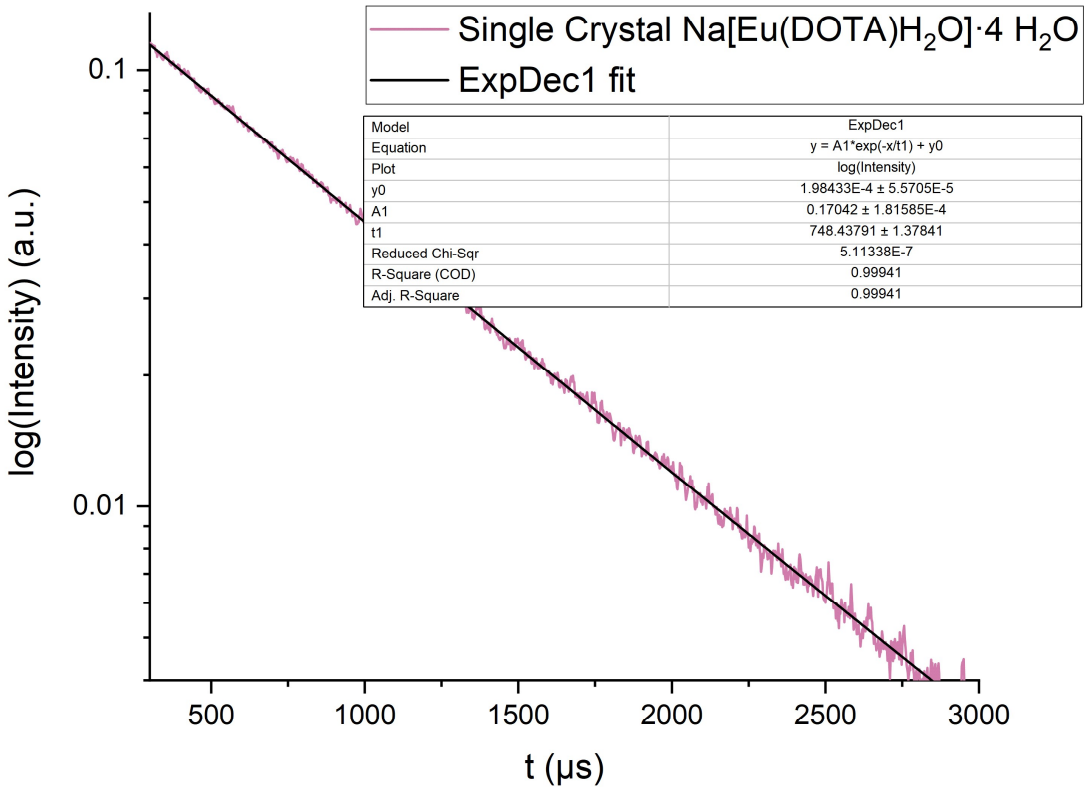


Figure S 41: Na[Eu(DOTA)H_2O]·4H_2O single crystal luminescence lifetime at 293 K. Fitted using OriginPro's ExpDec1 function.

4.2.6 $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ Spectra

4.2.6.1 $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ Emission Spectra

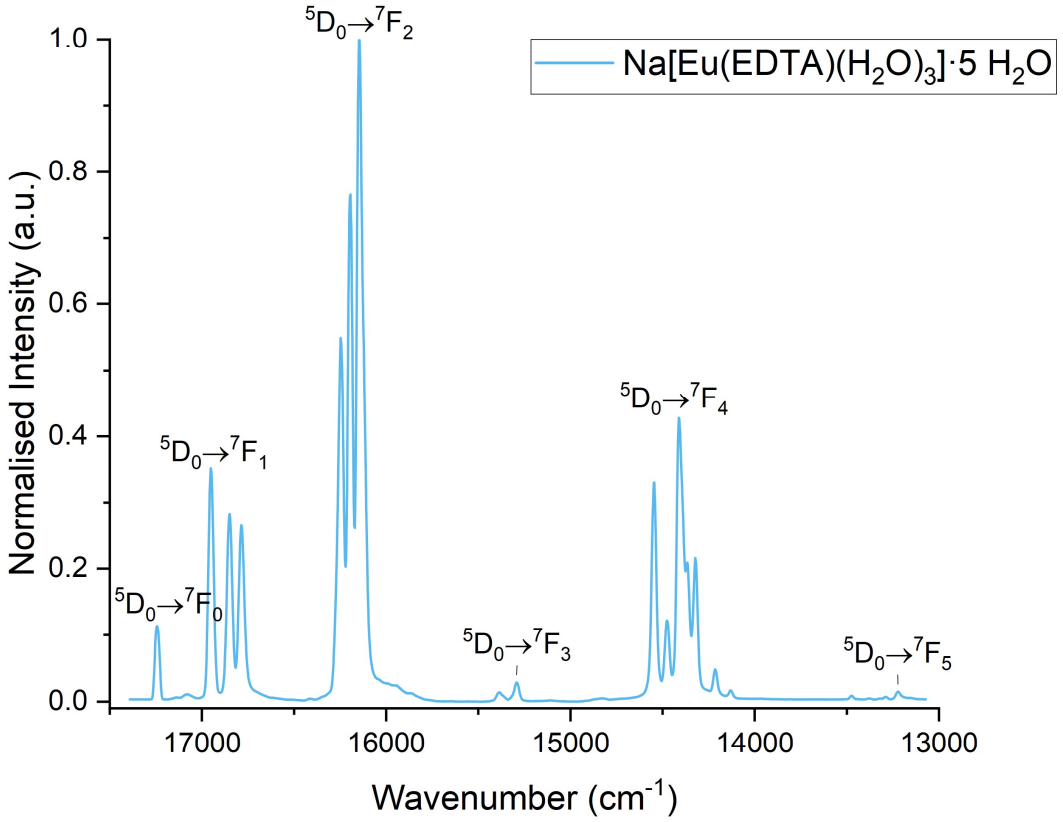


Figure S 42: Normalised emission spectrum (excitation at 394 nm) for $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ in 2-methyltetrahydrofuran glass at 77 K.

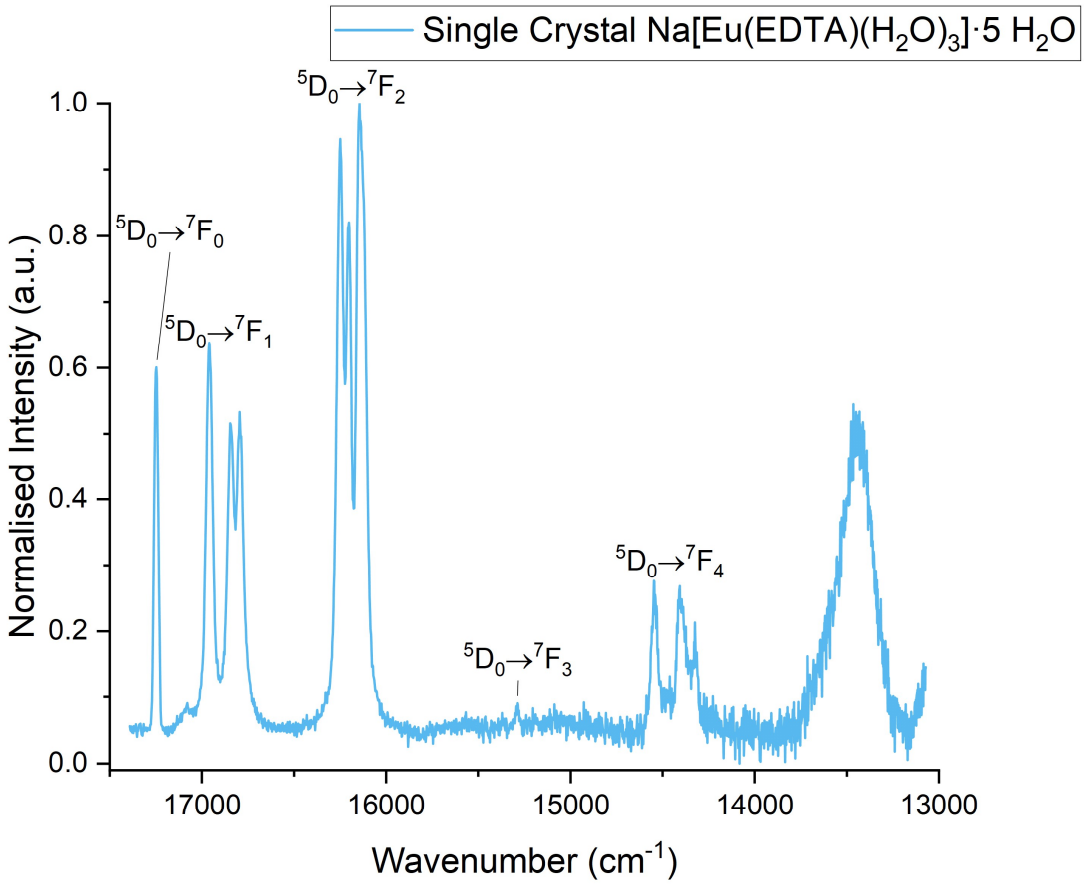


Figure S 43: Normalised emission spectrum (excitation at 394 nm) for single crystal $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ at 293 K.

4.2.6.2 Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O Excitation Spectra

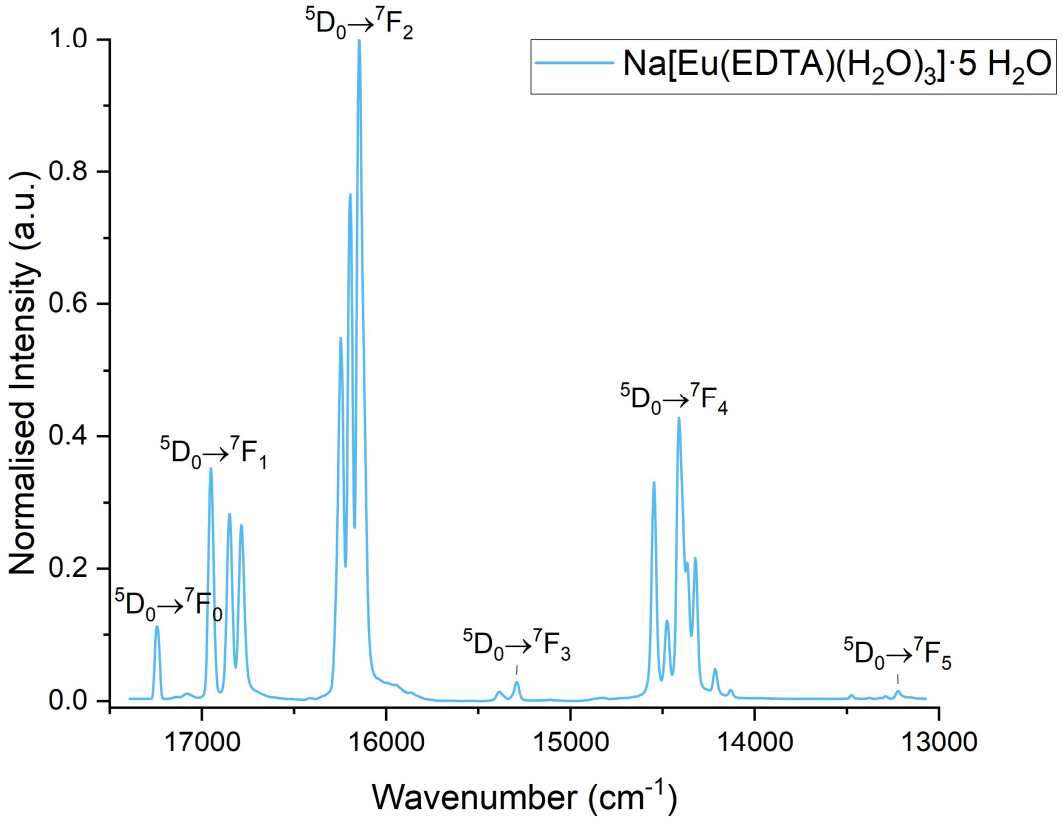


Figure S 44: Normalised excitation spectra (emission at 614 nm) for Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O in 2-methyl tetrahydrofuran glass at 77 K.

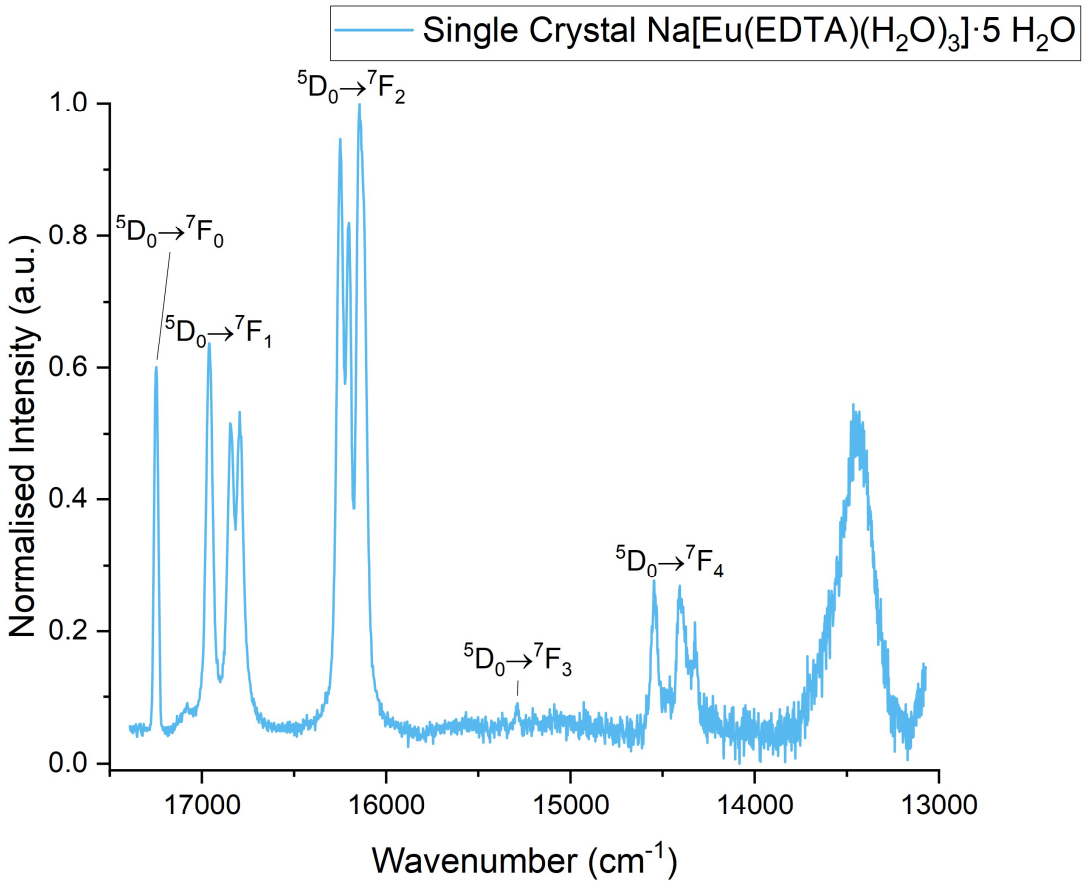


Figure S 45: Normalised excitation spectra (emission at 614 nm) for single crystal $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ at 293 K.

4.2.6.3 Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O Luminescence Lifetimes

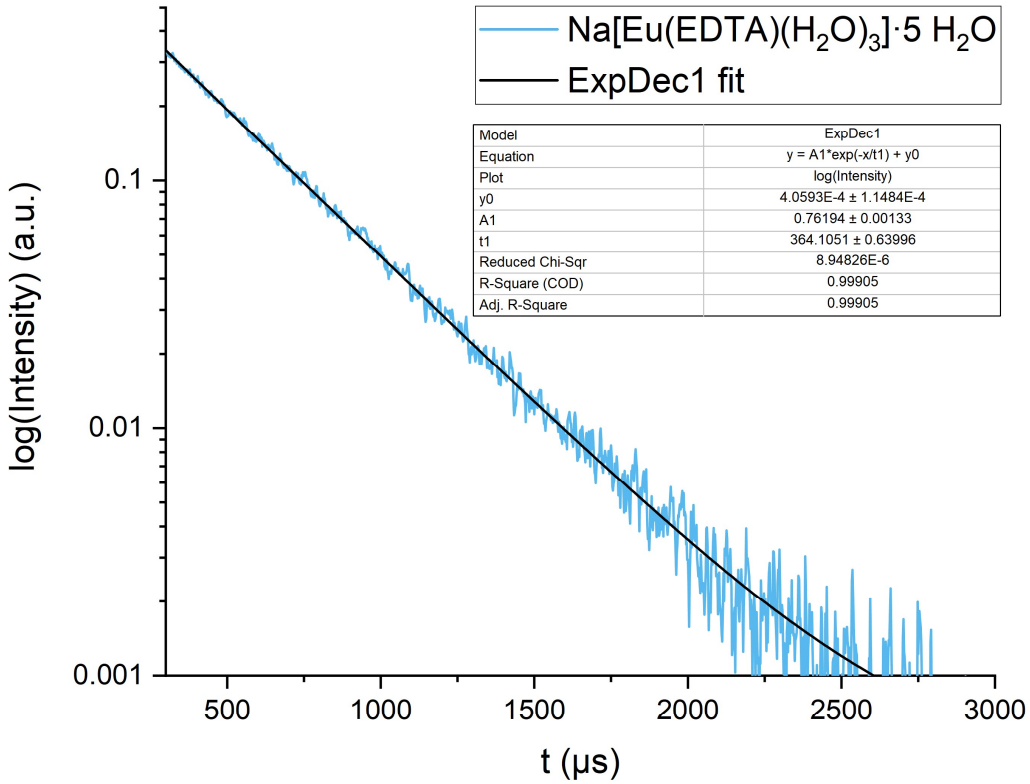


Figure S 46: Na[Eu(EDTA)(H$_2$O)$_3$]·5H$_2$O luminescence lifetime in 2-methyltetrahydrofuran glass at 77 K. Fitted using OriginPro's ExpDec1 function.

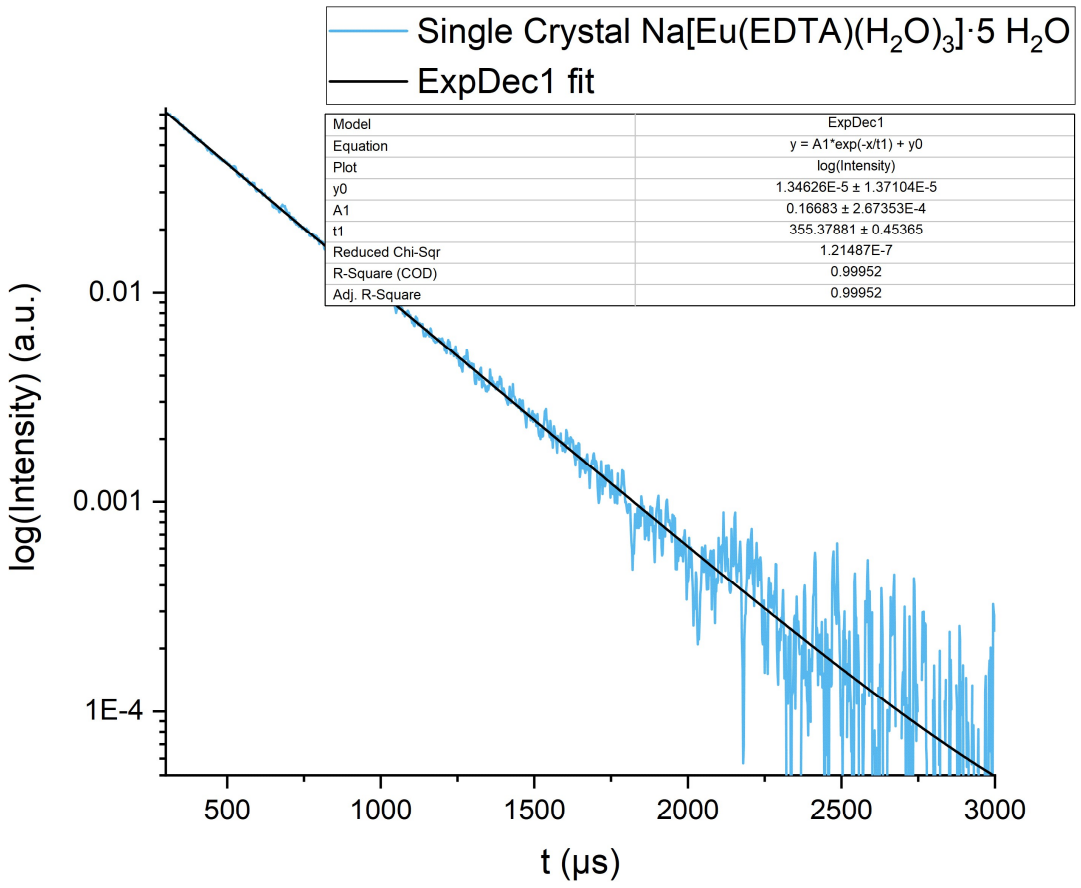


Figure S 47: $Na[Eu(EDTA)(H_2O)_3]\cdot 5H_2O$ single crystal luminescence lifetime at 293 K. Fitted using OriginPro's ExpDec1 function.

4.3 Spectroscopy Data for Sm^{3+} Compounds

4.3.1 Luminescence Lifetimes for Sm^{3+} Compounds

Table S 16: Luminescence lifetimes of the Sm^{3+} complexes for crystals ground to a powder in 2-methyl tetrahydrofuran at 77 K.

Complex	τ_{obs} (µs)
$Na_3[Sm(ODA)_3]\cdot 7H_2O$	35.14
$Cs_3[Sm(DPA)_3]\cdot 9H_2O$	42.24
$Na[Sm(DOTA)(H_2O)]\cdot 4H_2O$	10.88
$Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$	7.63

4.3.2 $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Spectra

4.3.2.1 $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Emission Spectra

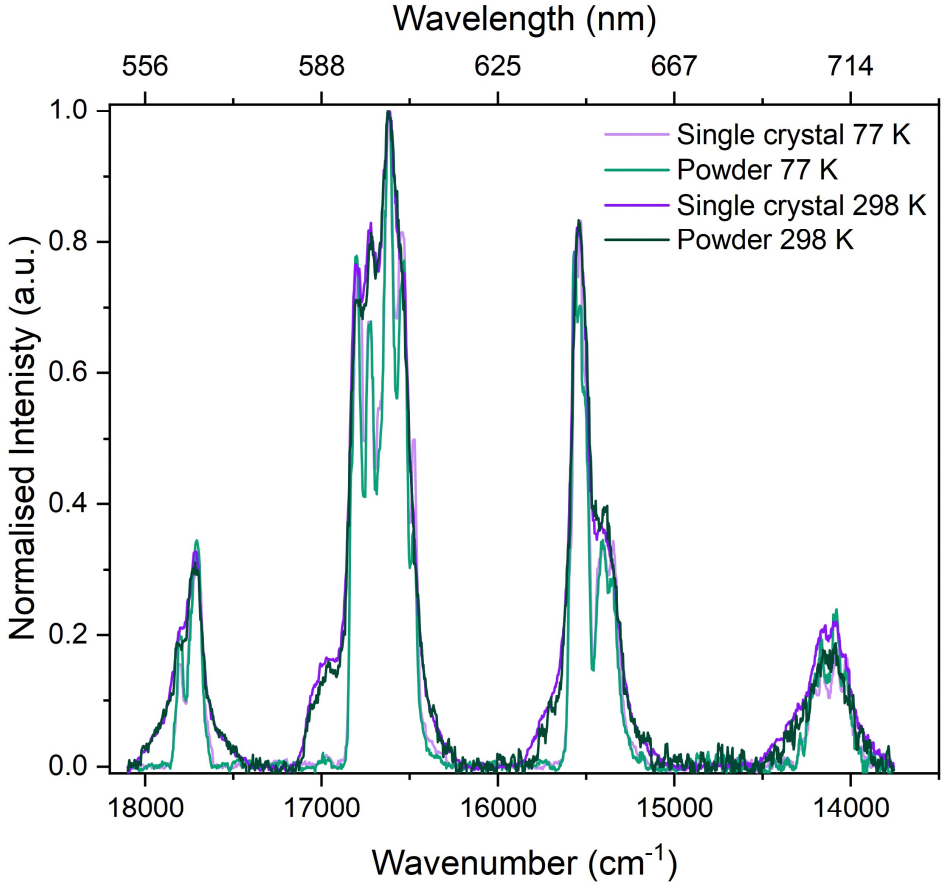
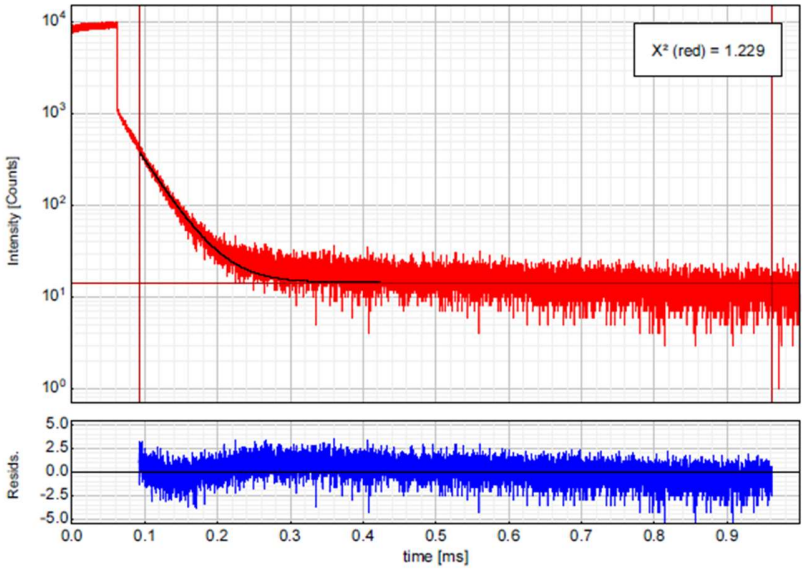


Figure S 48: Normalised emission (excitation at 463 nm) for single crystal and powder $Na_3[Sm(ODA)_3]\cdot 7H_2O$, at 77 K and 298 K.

4.3.2.2 $Na_3[Sm(ODA)_3]\cdot 7H_2O$ Luminescence Lifetime



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	377.0	-18.2	+18.2	Fitting
τ_1 [ms]	0.03514	-0.00150	+0.00150	Fitting
Bkgr. Dec [Cnts]	14.420	-0.760	+0.760	Fitting

Average Lifetime:

$\tau_{Av.1}$=0.03514 ms (intensity weighted)

$\tau_{Av.2}$=0.03514 ms (amplitude weighted)

Figure S 49: $Na_3[Sm(ODA)_3]\cdot 7H_2O$ luminescence lifetime in 2-methyltetrahydrofuran at 77 K. Fitted using the PicoQuant FluoFit software.

4.3.3 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Spectra

4.3.3.1 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Emission Spectrum

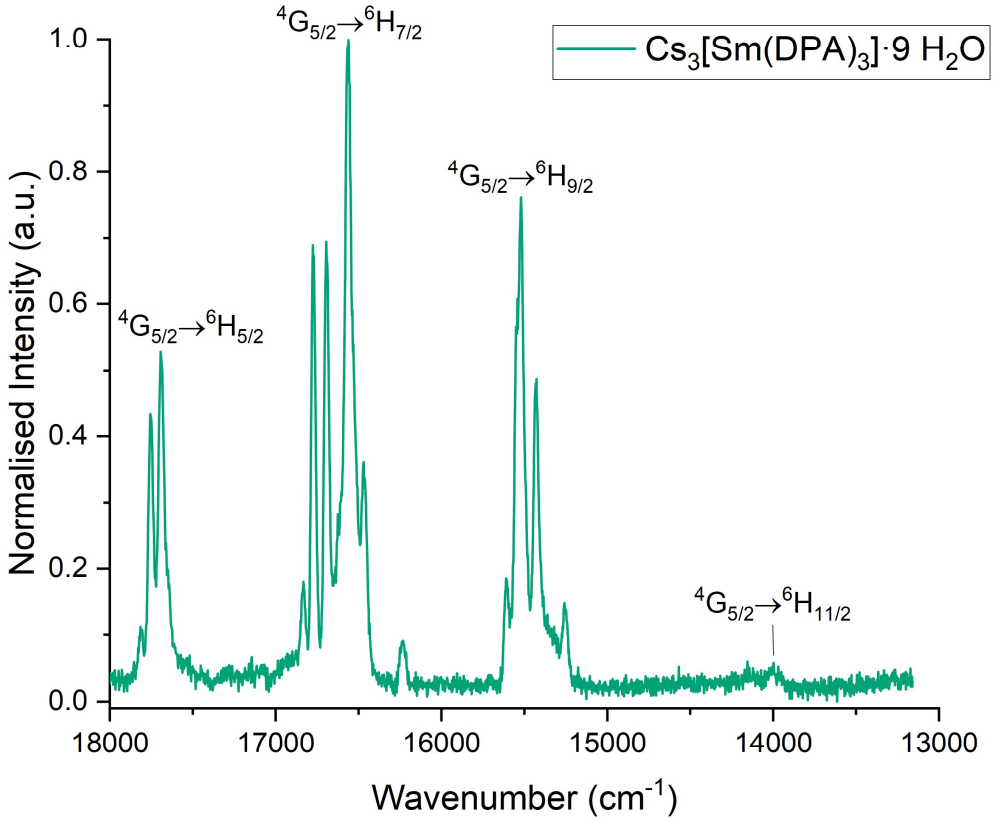


Figure S 50: Normalised emission spectrum (excitation at 401 nm) for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ in 2-methyltetrahydrofuran at 77 K.

4.3.3.2 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Excitation Spectrum

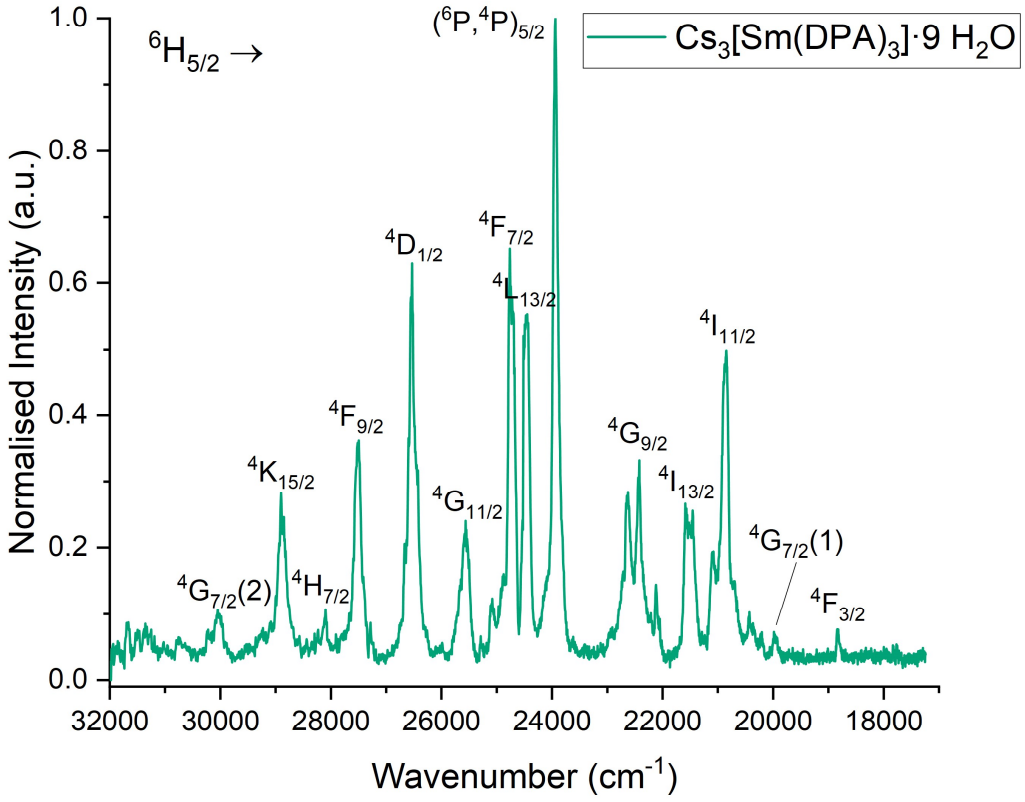
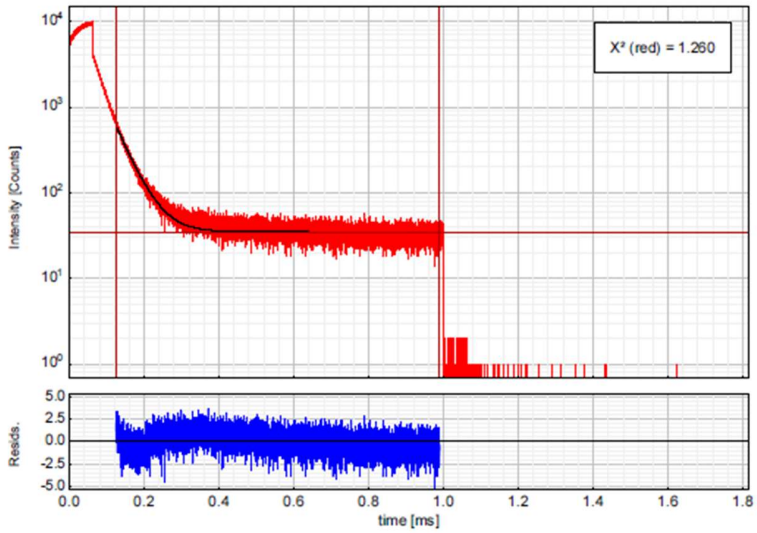


Figure S 51: Normalised excitation spectra (emission at 598 nm) for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ in 2-methyltetrahydrofuran at 77 K.

4.3.3.3 $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ Luminescence Lifetime



$$I(t) = \sum_{i=1}^{n} A_i \, e^{-\frac{t}{\tau_i}}$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	581.4	-21.4	+21.4	Fitting
τ_1 [ms]	0.04224	-0.00143	+0.00143	Fitting
Bkgr. Dec [Cnts]	35.11	-1.16	+1.16	Fitting

Average Lifetime:

$\tau_{Av.1}$=0.04224 ms (intensity weighted)

$\tau_{Av.2}$=0.04224 ms (amplitude weighted)

Figure S 52: $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ luminescence lifetime in 2-methyltetrahydrofuran at 77 K. Fitted using the PicoQuant FluoFit software.

4.3.4 Na[Sm(DOTA)H_2O]·4H_2O Spectra

4.3.4.1 Na[Sm(DOTA)H_2O]·4H_2O Emission Spectrum

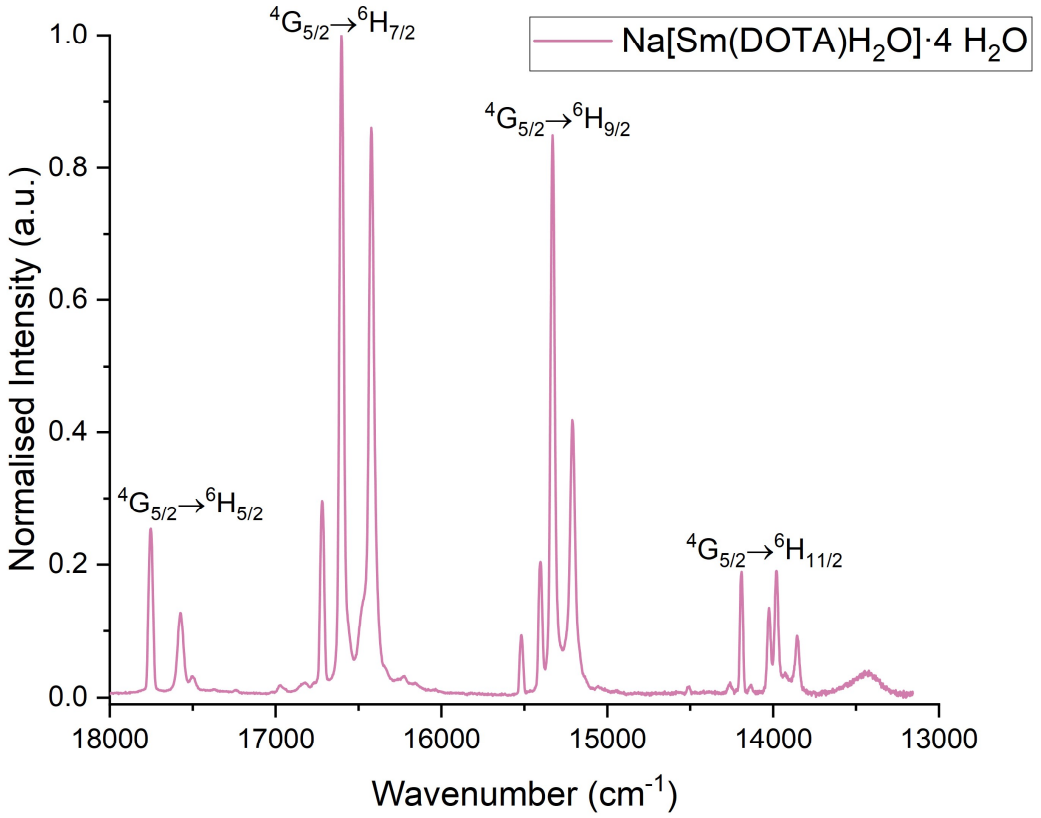


Figure S 53: Normalised emission spectrum (excitation at 401 nm) for Na[Sm(DOTA)H_2O]·4H_2O in 2-methyltetrahydrofuran at 77 K.

4.3.4.2 Na[Sm(DOTA)H_2O]·4H_2O Excitation Spectrum

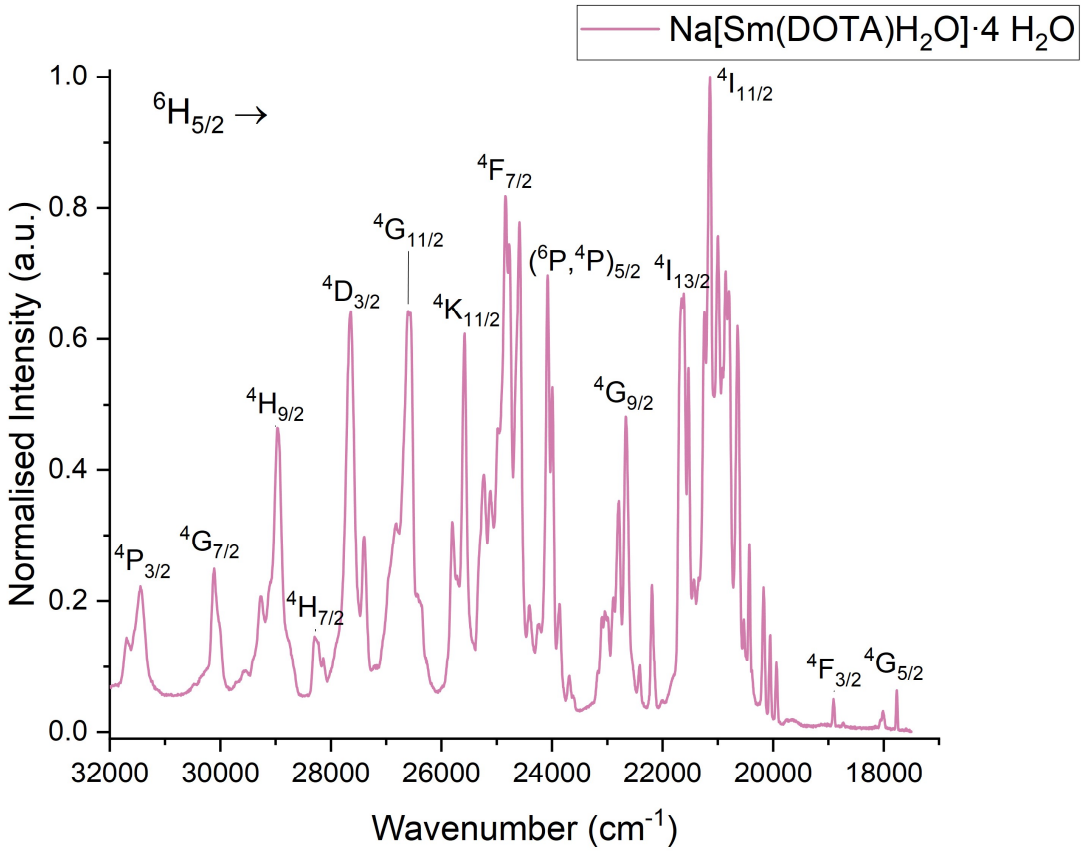
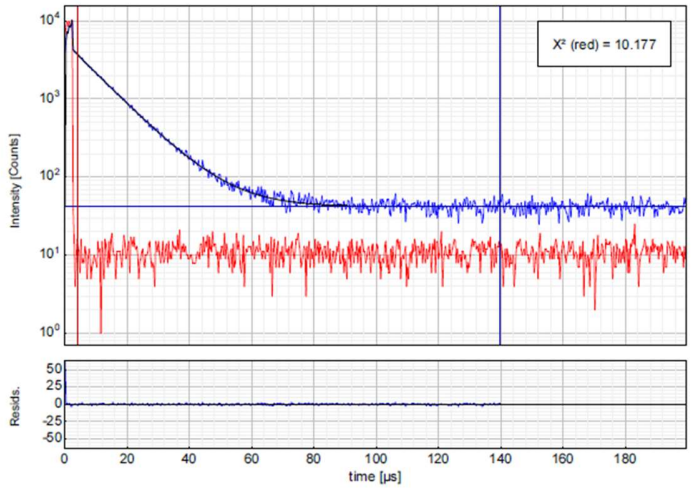


Figure S 54: Normalised excitation spectra (emission at 598 nm) for Na[Sm(DOTA)H_2O]·4H_2O in 2-methyltetrahydrofuran at 77 K.

4.3.4.3 Na[Sm(DOTA)H_2O]·4H_2O Luminescence Lifetime



$$I(t) = \int_{-\infty}^{t} IRF(t') \sum_{i=1}^{n} A_i \, e^{-\frac{t-t'}{\tau_i}} \, dt'$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	5636	-157	+157	Fitting
τ_1 [µs]	10.876	-0.228	+0.228	Fitting
Bkgr. Dec [Cnts]	41.78	-4.18	+4.18	Fitting
Bkgr. IRF [Cnts]	-102	-114	+114	Fitting
Shift IRF [µs]	0.00183	-0.0302	+0.0302	Fitting
A Scat [Cnts]	46040	-2940	+2940	Fitting

Average Lifetime:

$\tau_{Av.1}$=10.876 µs (intensity weighted)

$\tau_{Av.2}$=10.876 µs (amplitude weighted)

Figure S 55: Na[Sm(DOTA)H_2O]·4H_2O luminescence lifetime in 2-methyltetrahydrofuran at 77 K. Fitted using the PicoQuant FluoFit software.

4.3.5 $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ Spectra

4.3.5.1 $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ Emission Spectrum

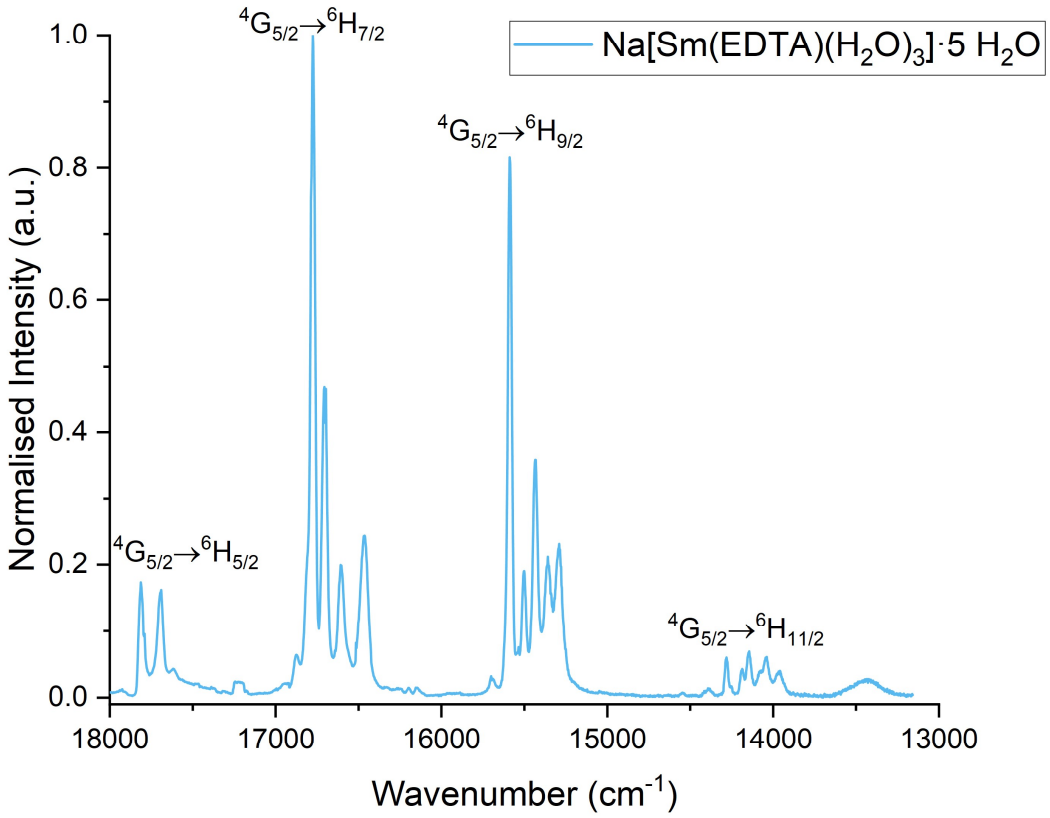


Figure S 56: Normalised emission spectrum (excitation at 401 nm) for $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ in 2-methyltetrahydrofuran at 77 K.

4.3.5.2 Na[Sm(EDTA)(H$_2$O)$_3$]·5H$_2$O Excitation Spectrum

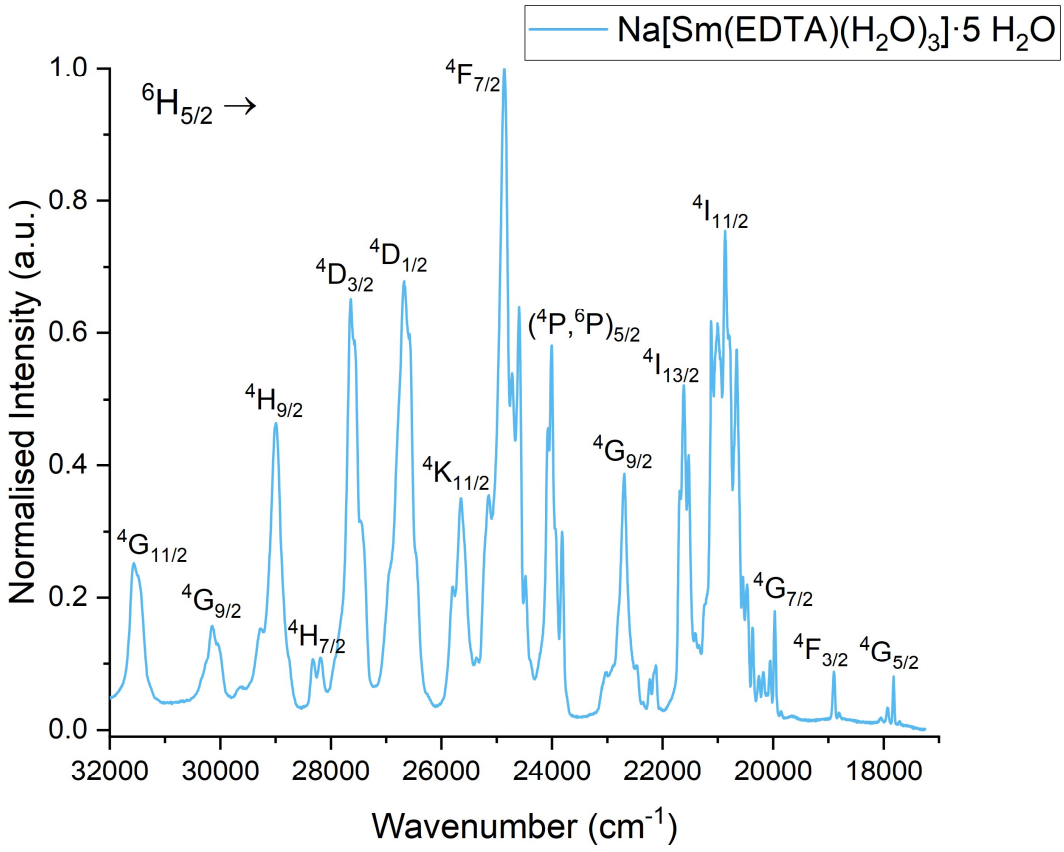
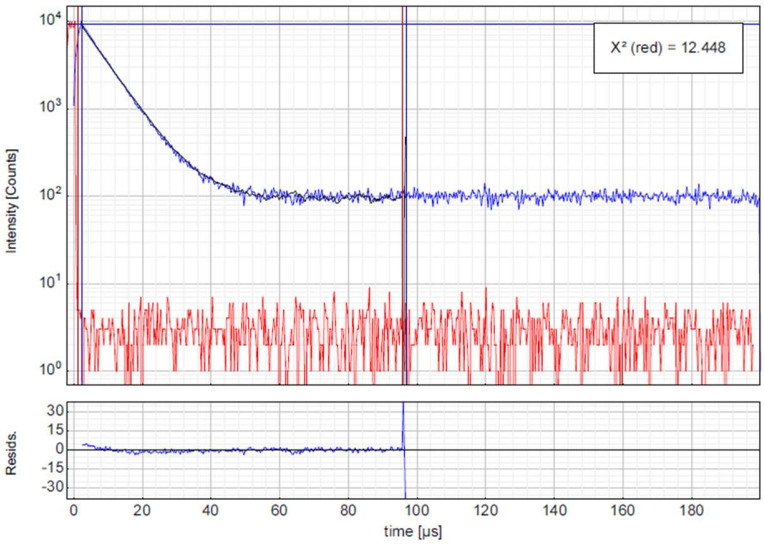


Figure S 57: Normalised excitation spectra (emission at 598 nm) for Na[Sm(EDTA)(H$_2$O)$_3$]·5H$_2$O in 2-methyltetrahydrofuran at 77 K.

4.3.5.3 Na[Sm(EDTA)(H_2O)$_3$]·5H_2O Luminescence Lifetime



$$I(t) = \int_{-\infty}^{t} IRF(t') \sum_{i=1}^{n} A_i \, e^{-\frac{t-t'}{\tau_i}} \, dt'$$

Parameter	Value	Conf. Lower	Conf. Upper	Conf. Estimation
A_1 [Cnts]	-107035.5	-73.8	+73.8	Fitting
τ_1 [µs]	7.62527	-0.00521	+0.00521	Fitting
Bkgr. $_{Dec}$ [Cnts]	9294.89	-6.84	+6.84	Fitting
Bkgr. $_{IRF}$ [Cnts]	-280.064	-0.211	+0.211	Fitting
Shift $_{IRF}$ [µs]	-1.861	-0.420	+0.420	Fitting
A $_{Scat}$ [Cnts]	199640	-1720	+1720	Fitting

Average Lifetime:

$\tau_{Av.1}$=7.62527 µs (intensity weighted)

$\tau_{Av.2}$=7.62527 µs (amplitude weighted)

Figure S 58: Na**[**Sm(EDTA)(H_2O)$_3$]·5H_2O luminescence lifetime in 2-methyltetrahydrofuran at 77 K. Fitted using the PicoQuant FluoFit software.

5 Deconvolution of the Electronic Energies using Voigt fitting and Boltzmann Population Analysis

5.1 Fits for $Na[Sm(DOTA)H_2O]\cdot 4H_2O$

In the case of $Na[Sm(DOTA)(H_2O)]\cdot 4H_2O$ three peaks were observed in both the emission and excitation spectra at 77 K. One of the peaks is observed in both emission and excitation. From this we unambiguously resolve the energy levels in both $^6H_{5/2}$ and $^4G_{5/2}$ as is seen in Figure S58. The spectra are fitted in Figure S59 and S60 and the fit values provided in Table S17 and SX18.

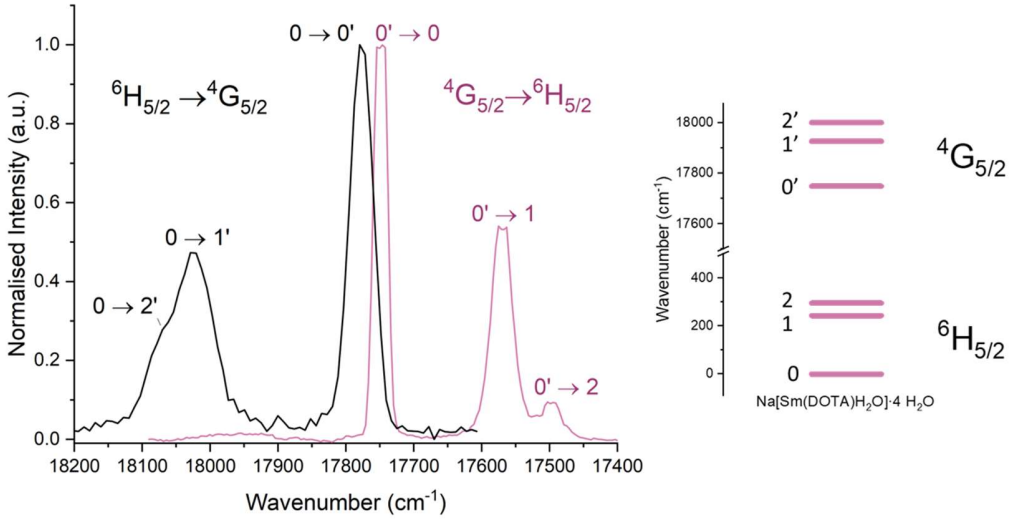


Figure S59: Results for $Na[Sm(DOTA)H_2O]\cdot 4H_2O$. Left: Normalised powdered emission (excitation at 463 nm) recorded at 77 K normalised to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band. Normalised powdered excitation (emission scan from 520 nm to 580 nm) recorded at 77 K normalised to the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band. The spectra were normalised to the transition from the lowest m_J state in the ground state multiplet ($^6H_{5/2}$) to the lowest m_J state in the first emitting state multiplet ($^4G_{5/2}$). The black and pink labels indicate the assumed transitions from the electronic energy levels. Right: Resolved energy levels in $^6H_{5/2}$ and $^4G_{5/2}$.

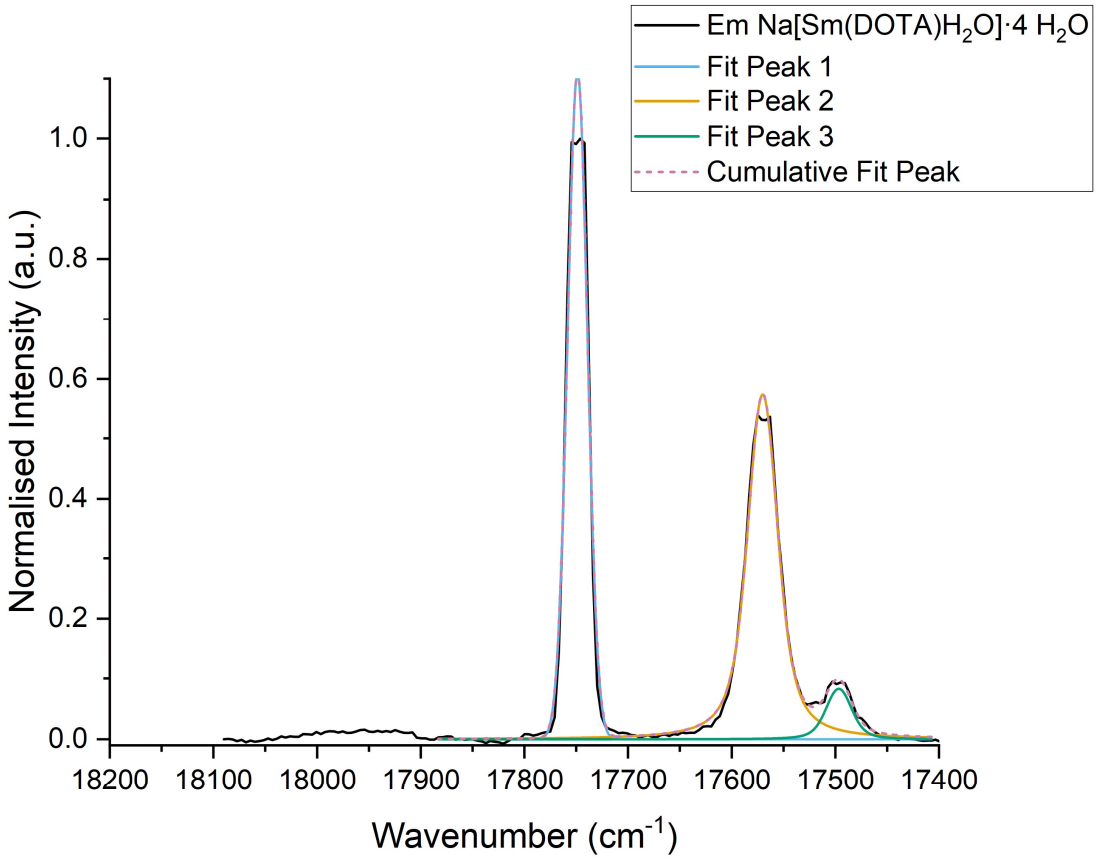


Figure S 60: Voight fitting of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band in the Na[Sm(DOTA)H_2O]·4H_2O emission spectra at 77 K.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(Normalised Intensity)	y0	0	0	--	--	0
	xc	17748.75666	0.15021	118160.80277	0	0.00322
	A	26.6606	0.36211	73.6247	3.90728E-94	0.33884
	wG*	22.5977	0.35479	63.69243	1.72542E-87	0.38306
	wL	5.32291E-16	0.07638	6.969E-15	1	2.02607E-4
	FWHM	22.5977	0.35479			
Peak2(Normalised Intensity)	y0	0	0	--	--	0
	xc	17570.08898	0.38728	45368.48286	0	0.02286
	A	26.59476	0.75356	35.29225	4.04868E-61	0.64695
	wG*	22.5977	0.35479	63.69243	1.72542E-87	0.38306
	wL	19.46843	1.31199	14.83883	7.99864E-28	0.65818
	FWHM	34.75431	0.89838			
Peak3(Normalised Intensity)	y0	0	0	--	--	0
	xc	17496.66776	2.39568	7303.42468	0	0.01704
	A	3.04238	0.66583	4.56933	1.30636E-5	0.66425
	wG*	22.5977	0.35479	63.69243	1.72542E-87	0.38306
	wL	11.59985	8.01491	1.44728	0.15071	0.64768
	FWHM	29.43489	5.15851			

Reduced Chi-sqr = 6.19485291645E-4
COD(R^2) = 0.98874932624925
Iterations Performed = 5
Total Iterations in Session = 25

Table S 17: Voight fit parameters of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band in the $Na[Sm(DOTA)H_2O]\cdot 4H_2O$ emission spectra at 77 K.

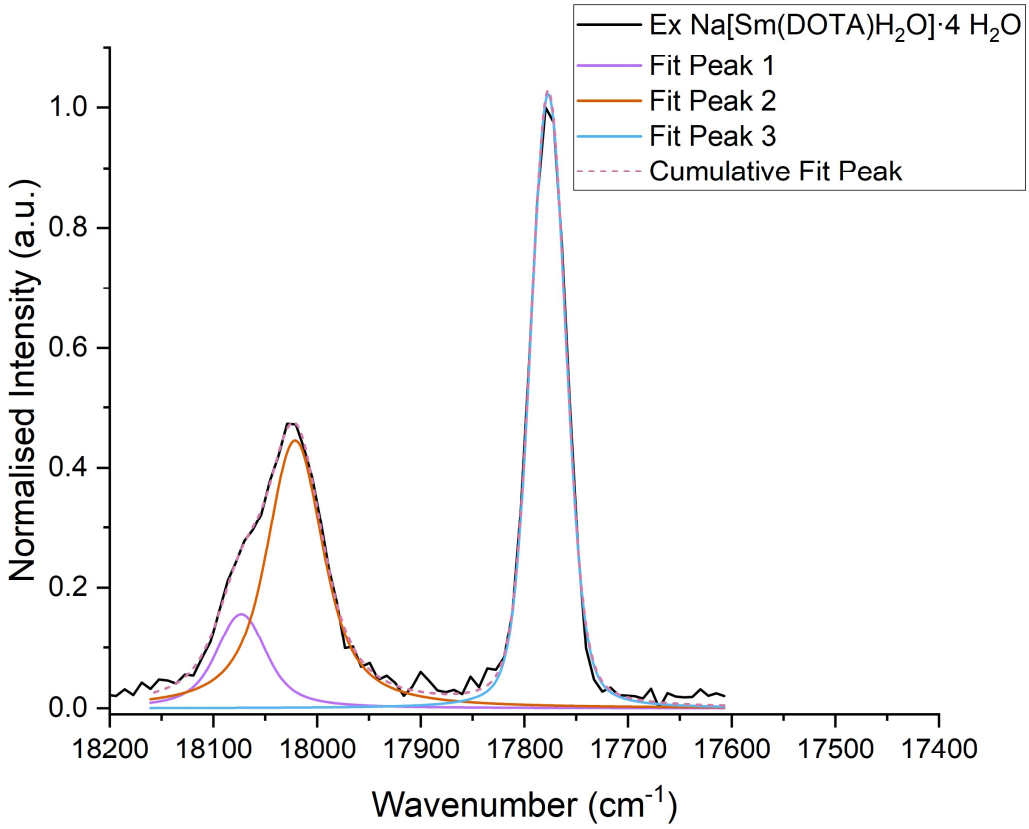


Figure S 61: Voight fitting of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the Na[Sm(DOTA)H_2O]·4H_2O excitation spectra at 77 K.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(Normalised Intensity)	y0	0	0	--	--	0
	xc	18073.18816	3.66763	4927.75277	4.89487E-170	0.83707
	A	12.03993	3.14974	3.82252	3.16424E-4	0.97733
	wG*	34.60451	1.21327	28.52158	1.35806E-36	0.90207
	wL	34.67883	10.20331	3.39878	0.00121	0.91602
	FWHM	56.72255	7.35749			
Peak2(Normalised Intensity)	y0	0	0	--	--	0
	xc	18021.247	1.53554	11736.1328	1.02155E-192	0.86962
	A	40.26348	3.24597	12.40414	3.31395E-18	0.97442
	wG*	34.60451	1.21327	28.52158	1.35806E-36	0.90207
	wL	44.79979	3.38593	13.23115	1.9128E-19	0.89114
	FWHM	64.35038	2.72712			
Peak3(Normalised Intensity)	y0	0	0	--	--	0
	xc	17776.97088	0.17693	100476.07014	6.2181E-249	0.00116
	A	48.21849	0.71166	67.75513	2.14885E-58	0.76874
	wG*	34.60451	1.21327	28.52158	1.35806E-36	0.90207
	wL	9.8168	1.49435	6.56927	1.3515E-8	0.94361
	FWHM	40.15287	0.50983			

Reduced Chi-sqr = 2.02168298544E-4
COD(R^2) = 0.99673235705564
Iterations Performed = 4
Total Iterations in Session = 34

Table S 18: Voight fit parameters of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Na[Sm(DOTA)H_2O]\cdot 4H_2O$ excitation spectra at 77 K.

5.1.1 Boltzmann Population Calculations for $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$

For $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ four peaks were observed in both the emission and excitation spectra at 77 K. Similar as was found for the $Na[Sm(DOTA)H_2O]\cdot 4H_2O$ sample, the three energy levels in levels in both $^6H_{5/2}$ and $^4G_{5/2}$ are unambiguously resolved as is seen in Figure S61. Different to the DOTA complex, the crystal field splitting is found to be slightly lower and thermally populated transitions are observed from 1 and 1'. Only 1'→ 0 and 1 → 0 can be seen as the other three lines convoluted with the primary transitions from 0 and 0'. The spectra are fitted in Figure S62 and S63 and the fit values provided in Table S19 and Table S20.

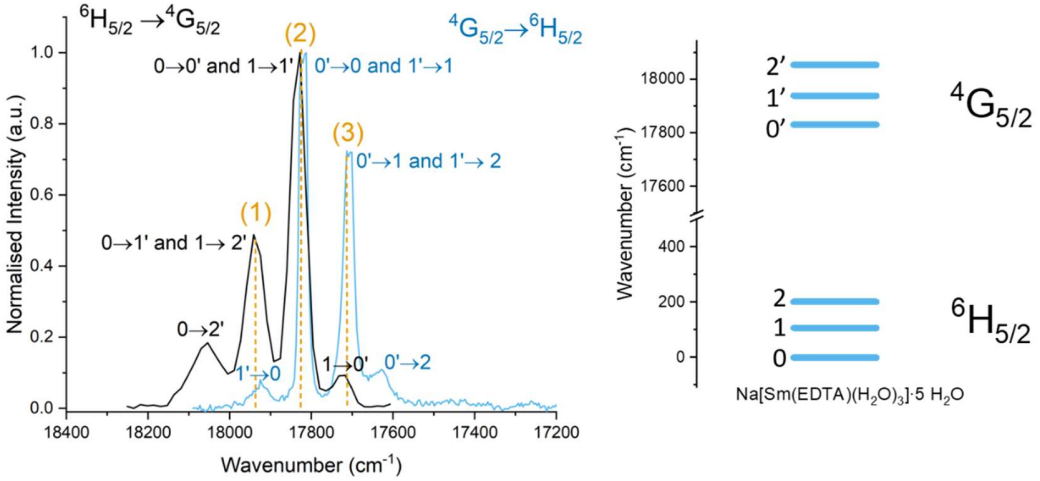


Figure S 62: Results for for $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$. Left: Normalised powdered emission (excitation at 463 nm) recorded at 77 K normalised to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band. Normalised powdered excitation (emission scan from 520 nm to 580 nm) recorded at 77 K normalised to the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band. The spectra were normalised to the transition from the lowest m_J state in the ground state multiplet ($^6H_{5/2}$) to the lowest m_J state in the first emitting state multiplet ($^4G_{5/2}$). Orange labels indicate the numbering of the shared peaks. Right: Resolved energy levels in $^6H_{5/2}$ and $^4G_{5/2}$.

5.2 Boltzmann Population Analysis for $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$

5.2.1 Voight Fitting for $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$

The spectra are fitted such that the spacing between the shared peaks are the same for emission and excitation, but only shifted by a Stokes shift, which in this case was found to be 12.6 cm^{-1}. The excitation spectrum was fitted first, and the emission spectrum fitted afterwards with the peak position fixed. The spectra were fitted with Voight functions with shared Gaussian width but separate Lorentzian widths for each peak.

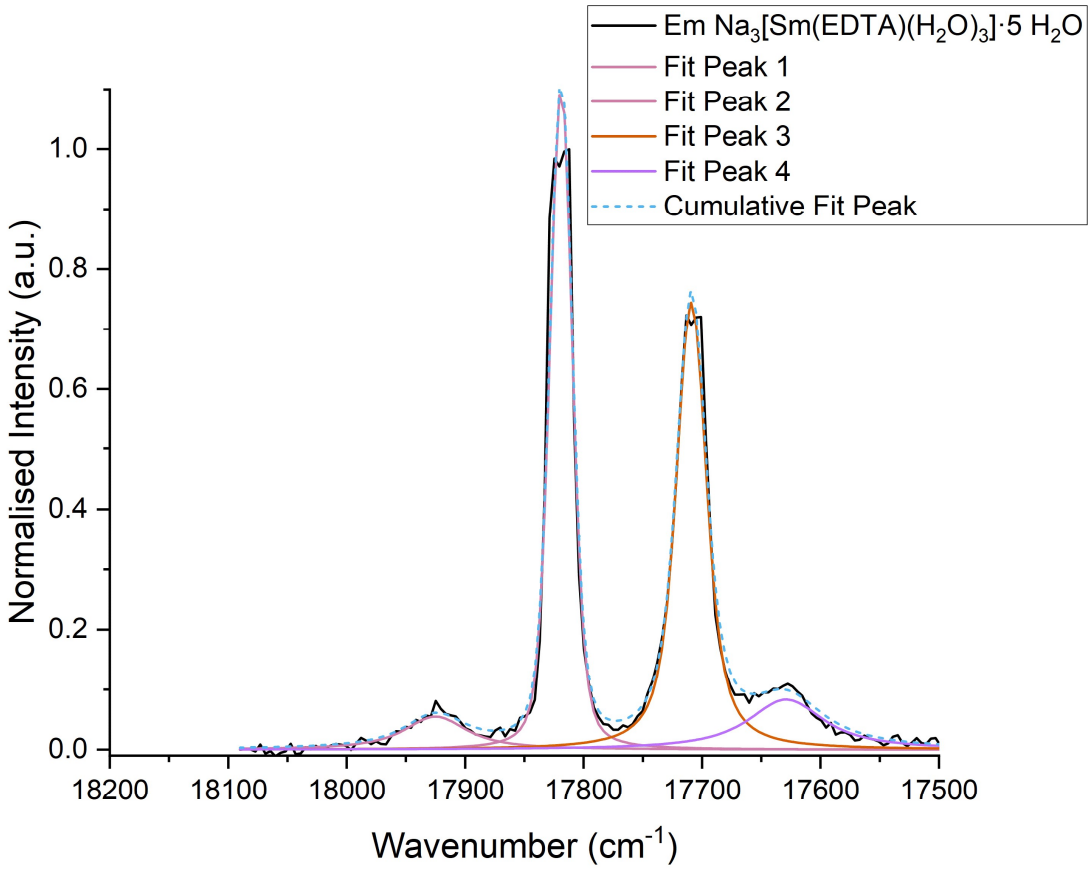


Figure S 63: Voight fitting of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band in the $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ emission spectra at 77 K.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(Normalised Intensity)	y0	0	0	--	--	0
	xc	17925	0	--	--	0
	A	5.28904	36.3944	0.14533	0.88448	0.62034
	wG*	18.58295	34.24125	0.54271	0.58742	0.90558
	wL	57.58969	592.17534	0.09725	0.92254	0.59734
	FWHM	63.4018	547.65505			
Peak2(Normalised Intensity)	y0	0	0	--	--	0
	xc	17819	0	--	--	0
	A	30.10155	23.31782	1.29092	0.19695	0.78901
	wG*	18.58295	34.24125	0.54271	0.58742	0.90558
	wL	6.98775	41.68065	0.16765	0.86688	0.94122
	FWHM	22.60102	14.54687			
Peak3(Normalised Intensity)	y0	0	0	--	--	0
	xc	17709	0	--	--	0
	A	31.03679	31.80021	0.97599	0.32925	0.80944
	wG*	18.58295	34.24125	0.54271	0.58742	0.90558
	wL	18.83968	45.17743	0.41702	0.67673	0.83898
	FWHM	30.61931	26.3484			
Peak4(Normalised Intensity)	y0	0	0	--	--	0
	xc	17629.06173	151.42211	116.4233	0	0.21725
	A	9.82237	49.31771	0.19917	0.84216	0.75336
	wG*	18.58295	34.24125	0.54271	0.58742	0.90558
	wL	71.96948	484.11748	0.14866	0.88184	0.69156
	FWHM	76.77931	458.29441			

Reduced Chi-sqr = 0.63908162107
COD(R^2) = -0.13332200411659
Iterations Performed = 1
Total Iterations in Session = 4

Table S 19: Voight fit parameters of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band in the $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ emission spectra at 77 K.

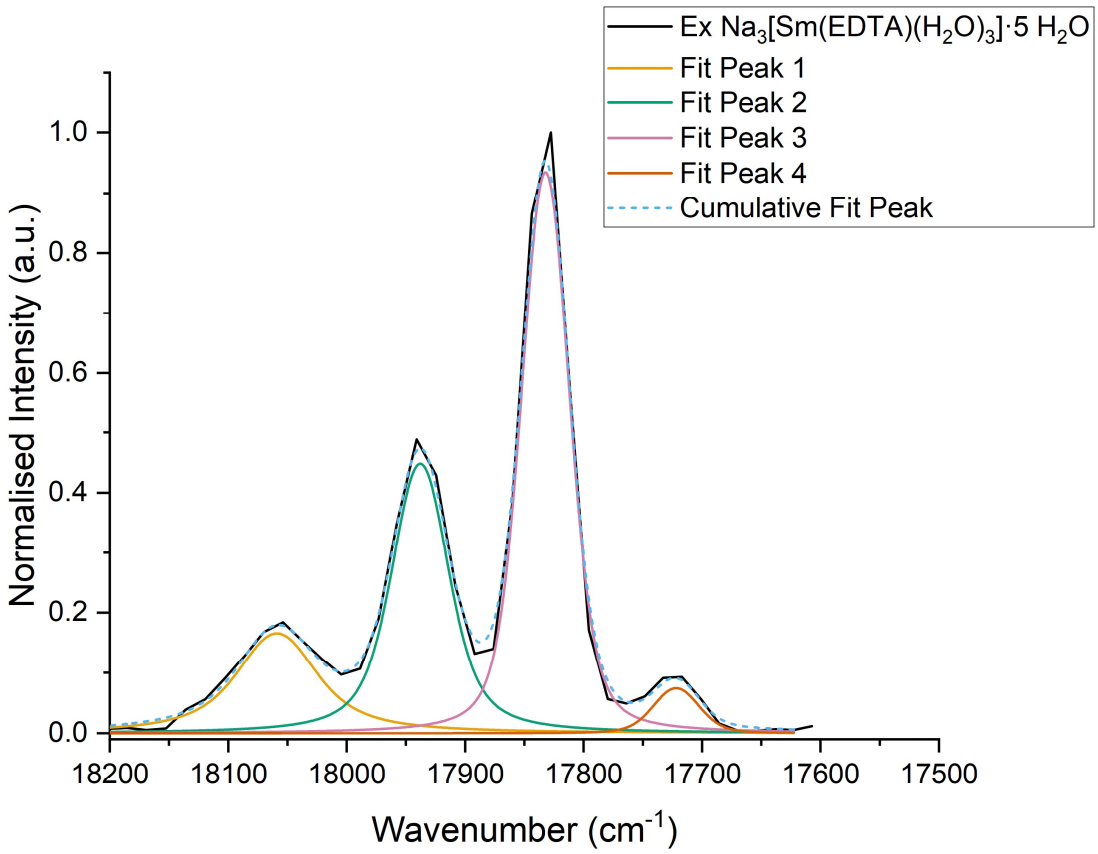


Figure S 64: Voight fitting of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ excitation spectra at 77 K.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(Normalised Intensity)	y0	0	0	--	--	0
	xc	18058.95619	4.51514	3999.64561	1.35355E-79	0.13301
	A	19.29867	2.87632	6.70949	3.33958E-7	0.7363
	wG*	39.15061	5.16585	7.57874	3.75247E-8	0.95289
	wL	61.11802	15.30037	3.99454	4.49001E-4	0.69697
	FWHM	81.06646	12.49706			
Peak2(Normalised Intensity)	y0	0	0	--	--	0
	xc	17937.89357	1.38214	12978.34559	1.67986E-93	0.18403
	A	33.59118	2.59455	12.94681	4.28225E-13	0.808
	wG*	39.15061	5.16585	7.57874	3.75247E-8	0.95289
	wL	29.47274	6.50108	4.53352	1.06657E-4	0.84906
	FWHM	57.24007	4.19472			
Peak3(Normalised Intensity)	y0	0	0	--	--	0
	xc	17832.20906	0.54785	32549.41276	2.15669E-104	0.05237
	A	54.24611	2.85607	18.99328	3.75688E-17	0.88678
	wG*	39.15061	5.16585	7.57874	3.75247E-8	0.95289
	wL	15.2651	6.54289	2.33308	0.02734	0.97332
	FWHM	47.9507	1.76383			
Peak4(Normalised Intensity)	y0	0	0	--	--	0
	xc	17721.88204	6.58753	2690.21792	6.42895E-75	0.06125
	A	3.98461	1.78785	2.22872	0.03435	0.74671
	wG*	39.15061	5.16585	7.57874	3.75247E-8	0.95289
	wL	11.37161	22.34855	0.50883	0.615	0.66943
	FWHM	45.58596	15.22849			

Reduced Chi-sqr = 6.1883115501E-4
COD(R^2) = 0.99173988409474
Iterations Performed = 1
Total Iterations in Session = 34

Table S 20: Voight fit parameters of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ excitation spectra at 77 K.

5.3 Boltzmann Population Analysis for $Na_3[Sm(ODA)_3]\cdot 7H_2O$

For $Na_3[Sm(ODA)_3]\cdot 7H_2O$ the spectra recorded at 77 K are not as easily interpreted as for the $Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ and $Na[Sm(DOTA)H_2O]\cdot 4H_2O$ samples. The crystal field splitting is smaller and therefore a larger contribution of thermally populations are found in the spectra. To arrive at the results seen in Figure S 64 we use a Boltzmann population approach.

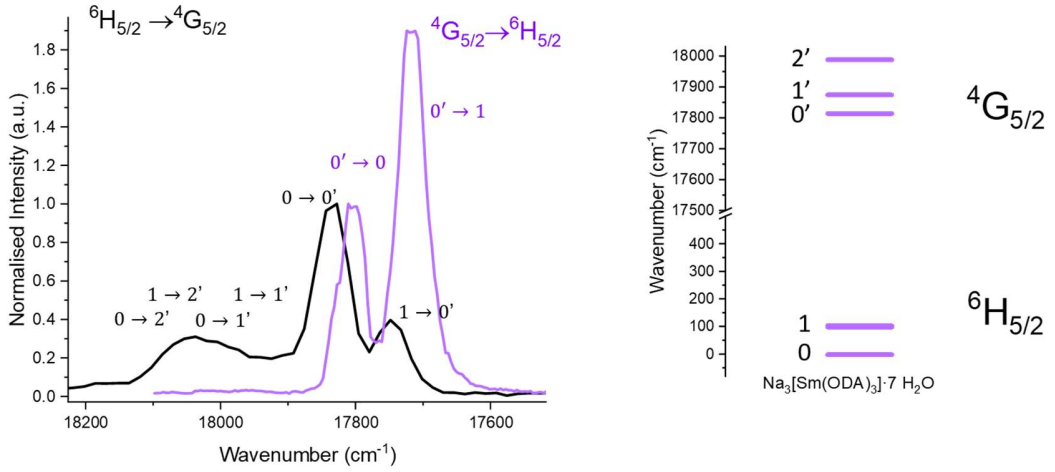


Figure S 65: Result for for Na3[Sm(ODA)3]·7H2O. Left: Normalised powdered emission (excitation at 463 nm) recorded at 77 K normalised to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band. Normalised powdered excitation (emission scan from 520 nm to 580 nm) recorded at 77 K normalised to the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band. The spectra were normalised to the transition from the lowest m_J state in the ground state multiplet ($^6H_{5/2}$) to the lowest m_J state in the first emitting state multiplet ($^4G_{5/2}$). Right: Resolved energy levels in $^6H_{5/2}$ and $^4G_{5/2}$.

In the thermal analysis it is exploited only two lines are observed in the emission spectra. These are fitted and the results are used as initial fit parameters for the excitation spectrum. In the emission spectra the splitting between the two observed states in $^6H_{5/2}$ are found to be 90 cm^{-1} therefore the excitation spectrum is fitted with a set of double Voigt functions with a shared splitting parameter initialised at 90 cm^{-1}.The fit of the emission spectrum and the fit of the excitation spectrum is shown in Figure S65 and 66. Based on these results the thermal analysis is performed as shown in the main text.

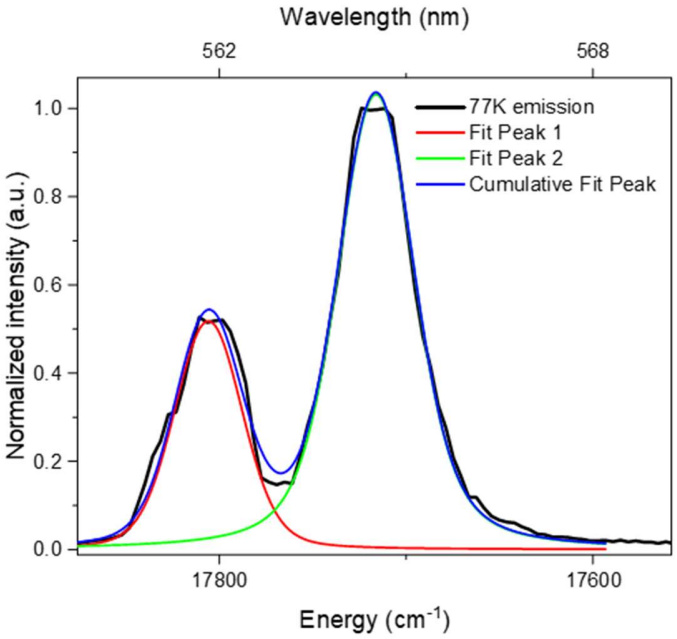


Figure S 66: Voight fitting of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Na_3[Sm(ODA)_3]\cdot 7H_2O$ emission spectra at 77 K.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(77K emission)	y0	0	0	--	--	0
	xc	17805.932716	0.468734	37987.286154	1.360048E-254	0.06774
	A	25.692759	0.835914	30.736111	5.396064E-42	0.725065
	wG*	38.087069	1.95439	19.487961	9.145427E-30	0.936522
	wL	8.695158	2.619667	3.319184	0.001444	0.880229
	FWHM	42.949881	1.241136			
	ymax	0.5178	0.010405			
Peak2(77K emission)	y0	0	0	--	--	0
	xc	17716.139483	0.254799	69529.835501	8.681761E-273	0.053914
	A	63.046158	1.136488	55.474535	5.636831E-59	0.806294
	wG*	38.087069	1.95439	19.487961	9.145427E-30	0.936522
	wL	18.886249	2.277336	8.293133	5.816601E-12	0.952409
	FWHM	49.184745	0.801029			
	ymax	1.031413	0.010485			

Table S 21: Voight fit parameters of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band in the $Na_3[Sm(ODA)3]\cdot 7H_2O$ emission spectra at 77 K.

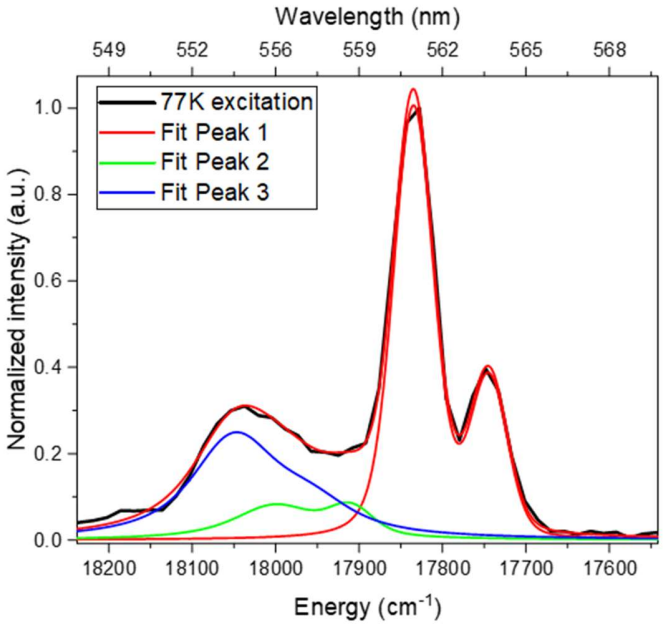


Figure S 67: Voight fitting of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Na_3[Sm(ODA)_3]\cdot 7H_2O$ excitation spectra at 77 K with two sets of two Voigt functions fitted with a shared parameter.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(77K excitation)	y0*	0	0	--	--	0
	Delta*	-90.393957	29.7666	-3.036758	0.004429	0.554872
	wG*	47.957257	167.580491	0.286174	0.776385	0.991204
	xc1	17834.766453	126.825333	140.624637	6.119653E-51	0.983455
	A1	69.360019	244.416172	0.283778	0.778206	0.996205
	wL1	16.990711	285.09868	0.059596	0.952807	0.996967
	A2	21.312751	62.267396	0.342278	0.734132	0.954204
	wL2*	7.891567	220.973561	0.035713	0.971709	0.967088
Peak2(77K excitation)	y0	0	0	--	--	0
	Delta*	-90.393957	29.7666	-3.036758	0.004429	0.554872
	wG*	47.957257	167.580491	0.286174	0.776385	0.991204
	xc1	18000.403651	9733.864246	1.849256	0.072645	0.999701
	A1	14.182178	12113.235881	0.001171	0.999072	0.999995
	wL1	100	40883.112323	0.002446	0.998062	0.999943
	A2	4.963538	1023.225032	0.004851	0.996156	0.999741
	wL2*	25.325132	3067.92647	0.008255	0.993459	0.992476
Peak3(77K excitation)	y0	0	0	--	--	0
	Delta*	-90.393957	29.7666	-3.036758	0.004429	0.554872
	wG*	47.957257	167.580491	0.286174	0.776385	0.991204
	xc1	18050	334.980323	53.883762	5.099572E-36	0.962398
	A1	40.771702	6850.466838	0.005952	0.995284	0.999985
	wL1	100	5883.326629	0.016997	0.986533	0.999659

	A2	12.296676	6554.984144	0.001876	0.998514	0.999984
	wL2*	100	18448.288659	0.005421	0.995705	0.999629

Table S 22: Voight fit parameters of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Na_3[Sm(ODA)3]\cdot 7H_2O$ excitation spectra at 77 K.

The calculations for the thermal analysis on the two levels in $^6H_{5/2}$ are provided here:

Relative transition probabilities

$$A^{rel}_{0\prime\to 0} = \frac{I^{rel}_{0\prime\to 0}}{\sum I^{rel}_{0\prime\to i}} = \frac{38.08}{101.126}$$

$$A^{rel}_{0\prime\to 1} = \frac{I^{rel}_{0\prime\to 1}}{\sum I^{rel}_{0\prime\to i}} = \frac{63.05}{101.126}$$

$$B^{rel}_{0\to 0\prime} = \frac{I^{rel}_{0\to 0\prime}}{\sum I^{rel}_{0\to i\prime}} = \frac{43.08}{113.6}$$

$$B^{rel}_{0\to 1\prime} = \frac{I^{rel}_{0\to 1\prime}}{\sum I^{rel}_{0\to i\prime}} = \frac{63.05}{113.6}$$

Relative thermal populations as observed from relative transition probabilities

Using these values we calculated the observed thermal populations:

$$P^{6H5/2}_{i_{obs}} = \frac{I^{rel}_{i\to j}}{N \cdot B^{rel}_{i\leftarrow j}}, N = \sum_j \frac{I^{rel}_{i\to j}}{B^{rel}_{i\leftarrow j}}$$

$$P^{6H5/2}_{0_{obs}} = 0.730$$

$$P^{6H5/2}_{1_{obs}} = 0.269$$

Relative thermal populations as calculated based on the Boltzmann distrubution

The two energy levels are separated by 90 cm^{-1}, using the Boltzmann distribution we find:

$$P^{system}_{i_{calc}} = \frac{e^{\frac{-E_i}{k_B T}}}{\sum_i^{system} e^{\frac{-E_i}{k_B T}}}$$

$$P^{6H5/2}_{0_{calc}} = 0.843$$

$$P^{6H5/2}_{1_{calc}} = 0.156$$

Evaluating interpretations with the Loss function

Three interpretations can be done with the knowledge that 3 energy levels are present in $^6H_{5/2}$: Only two levels are observed, (0,1), the first level is degenerate, (0,0,1), the second level is degenerate, (0,1,1). These interpretations are evaluated using the loss function:

$$L = \sum_i 100 \cdot \frac{\left(P_{i_{obs}}^{6H5/2} - P_{i_{calc}}^{6H5/2}\right)^2}{N}$$

The results are compiled in Figure S67. The Loss values found are unambiguously in favour of the (0,1,1) splitting.

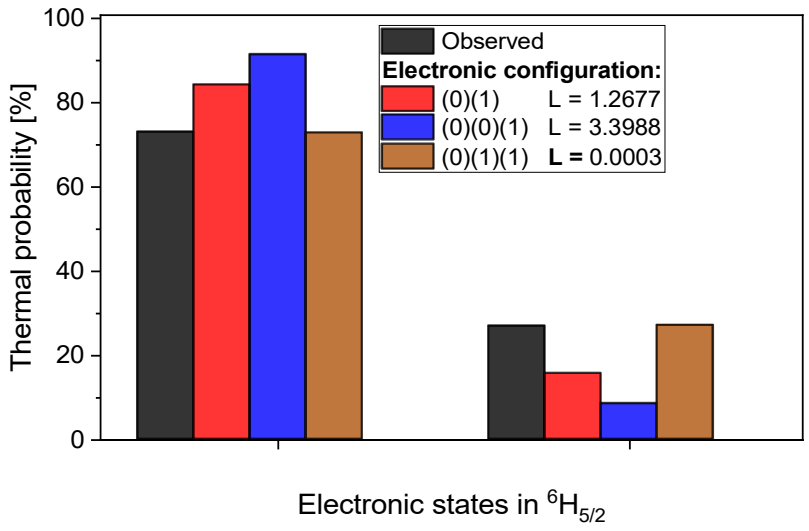


Figure S 68: Thermal populations of the electronic states in $^6H_{5/2}$ for $Na_3[Sm(ODA)_3]\cdot 7H_2O$.

5.4 Boltzmann Population Analysis for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$

For $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ the spectra recorded at 77 K are following the same patterns as for the ODA complex and the spectra are analysed with the same approach. The final results obtained are shown in Figure S68.

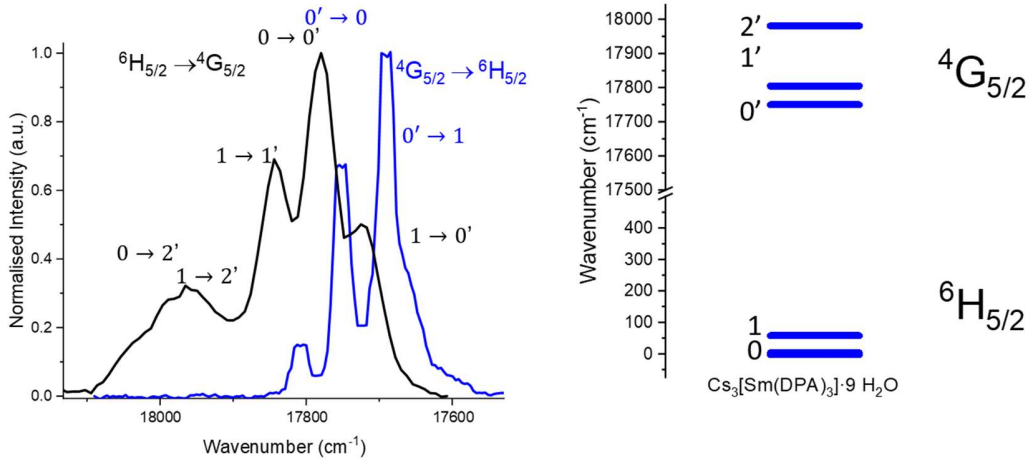


Figure S 69: Left: Normalised powdered emission (excitation at 463 nm) recorded at 77 K normalised to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band. Normalised powdered excitation (emission scan from 520 nm to 580 nm) recorded at 77 K normalised to the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band. The spectra were normalised to the transition from the lowest m_J state in the ground state multiplet ($^6H_{5/2}$) to the lowest m_J state in the first emitting state multiplet ($^4G_{5/2}$). Orange labels indicate the numbering of the shared peaks. Right: Resolved energy levels in $^6H_{5/2}$ and $^4G_{5/2}$.

However, for this sample, the crystal field splitting in the $^4G_{5/2}$ state allows for a larger contribution of thermal populated emission. This further complicates the spectra. In the emission spectrum all states of $^6H_{5/2}$ are resolved, but these cannot be resolved in the excitation spectrum as the spectral resolution is slightly lower. See figure 69 and S70 where the fits are provided and Table S23 and S24 where the fit parameters are provided.

Therefore, the areas from the emission is summed and the centre of emission is chosen to be 75, the average of 60 and 90. Using this interpretation, the splitting of the $^6H_{5/2}$ is evaluated with the loss function similar as was done for the $Na_3[Sm(ODA)_3]\cdot 7H_2O$ sample. The results are visualised in Figure S71. Similarly, the (1) state is found to be degenerate, matching the already expected result obtained for the fitting of the emission spectrum in Figure S69.

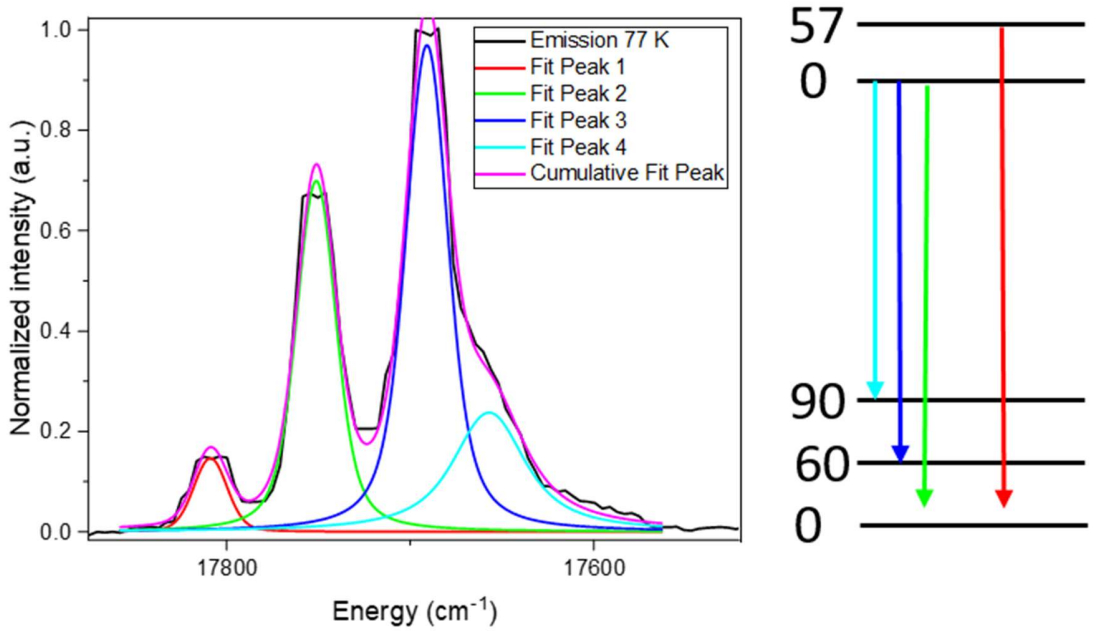


Figure S 70: Voight fitting of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ emission spectra at 77 K.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(B)	y0	0	0	--	--	0
	xc	17808.807523	1.466287	12145.516655	1.296234E-193	0.022352
	A	3.640053	0.697021	5.222301	2.331239E-6	0.677047
	wG*	19.234844	1.951762	9.855116	3.703431E-14	0.929935
	wL	4.206583	5.101737	0.824539	0.412899	0.676362
	FWHM	21.583058	3.158188			
	ymax	0.14643	0.018711			
Peak2(B)	y0	0	0	--	--	0
	xc	17751.160081	0.351635	50481.792535	6.749193E-231	0.063616
	A	22.639247	0.902559	25.083412	1.677888E-33	0.729482
	wG*	19.234844	1.951762	9.855116	3.703431E-14	0.929935
	wL	10.823412	2.127991	5.086212	3.854374E-6	0.897485
	FWHM	25.669684	1.109348			
	ymax	0.699046	0.018144			

Peak3(B)	y0	0	0	--	--	0
	xc	17690.865645	0.432816	40873.83215	2.281773E-225	0.649894
	A	34.753511	3.02374	11.493552	8.469125E-17	0.972811
	wG*	19.234844	1.951762	9.855116	3.703431E-14	0.929935
	wL	13.688745	2.808595	4.873876	8.370152E-6	0.966642
	FWHM	27.580433	1.243806			
	ymax	0.969496	0.03352			
Peak4(B)	y0	0	0	--	--	0
	xc	17657.032468	3.547168	4977.78366	2.665885E-170	0.838483
	A	16.365799	3.486003	4.694718	1.595119E-5	0.956327
	wG*	19.234844	1.951762	9.855116	3.703431E-14	0.929935
	wL	38.370137	7.672364	5.001084	5.267104E-6	0.86049
	FWHM	46.759053	6.578574			
	ymax	0.237487	0.025174			

Table S 23: Voight fit parameters of the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ band in the $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ emission spectra at 77 K.

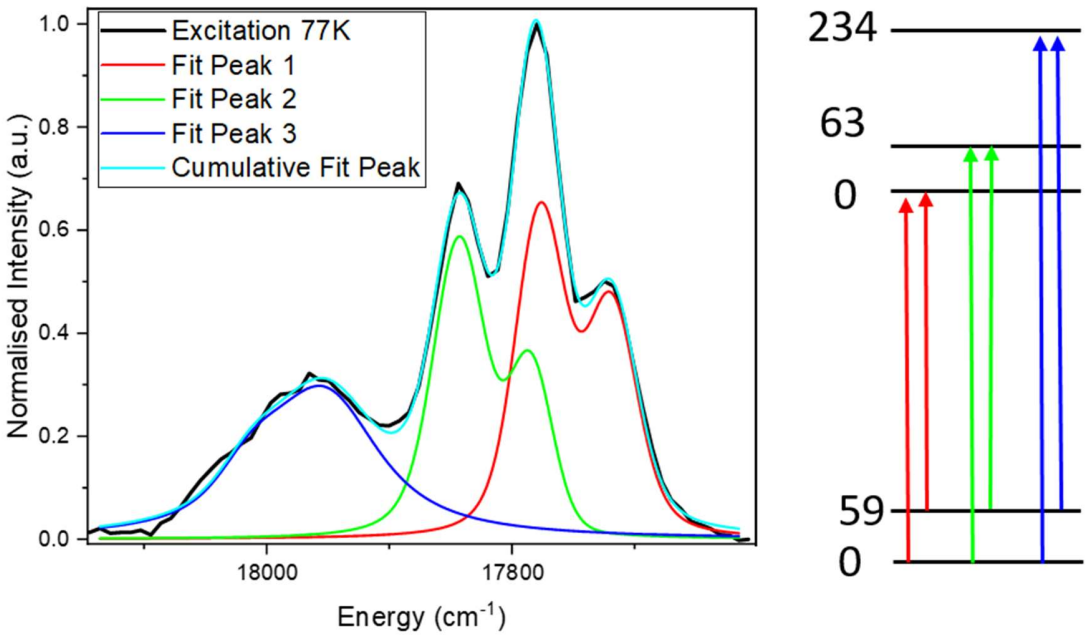


Figure S 71: Voight fitting of the $^4G_{5/2} \leftarrow {}^6H_{5/2}$ band in the $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ excitation spectra at 77 K with two sets of two Voigt functions fitted with a shared parameter.

		Value	Standard Error	t-Value	Prob>|t|	Dependency
Peak1(C)	y0*	0	0	--	--	0
	Delta*	-58.780459	1.326807	-44.302187	3.405765E-41	0.890433
	wG*	44.756484	3.81032	11.746121	7.39535E-16	0.990895
	xc1	17779.373352	19.343302	919.148838	1.682629E-105	0.999074
	A1	29.744507	8.291096	3.587524	7.692259E-4	0.998399
	wL1	8.687704E-16	8.901622E7	9.759686E-24	1	--
	A2	31.313266	5.914108	5.294672	2.795433E-6	0.99516
	wL2*	17.034953	4.13481	4.119888	1.454724E-4	0.952176
Peak2(C)	y0	0	0	--	--	0
	Delta*	-58.780459	1.326807	-44.302187	3.405765E-41	0.890433
	wG*	44.756484	3.81032	11.746121	7.39535E-16	0.990895
	xc1	17842.45976	11.364862	1569.967167	6.525571E-117	0.996458
	A1	35.218887	19.324358	1.822513	0.074482	0.999603

	wL1	10.253762	14.654039	0.699723	0.487409	0.997827
	A2	15.80605	17.565622	0.899829	0.372613	0.999596
	wL2*	4.285784	33.029872	0.129755	0.897292	0.998498
Peak3(C)	y0	0	0	--	--	0
	Delta*	-58.780459	1.326807	-44.302187	3.405765E-41	0.890433
	wG*	44.756484	3.81032	11.746121	7.39535E-16	0.990895
	xc1	17990	7.488532	2402.339879	5.529525E-126	0.966395
	A1	27.930153	6.589692	4.238461	9.911423E-5	0.990098
	wL1	74.65384	20.978402	3.558605	8.395423E-4	0.978381
	A2	27.06199	8.752826	3.0918	0.003279	0.994075
	wL2*	78.490868	51.160237	1.534216	0.131409	0.995551

Table S 24: Voight fit parameters of the $^{4}G_{5/2} \leftarrow {}^{6}H_{5/2}$ band in the $Cs_3[Sm(DPA)_3]\cdot 9H_2O$ excitation spectra at 77 K.

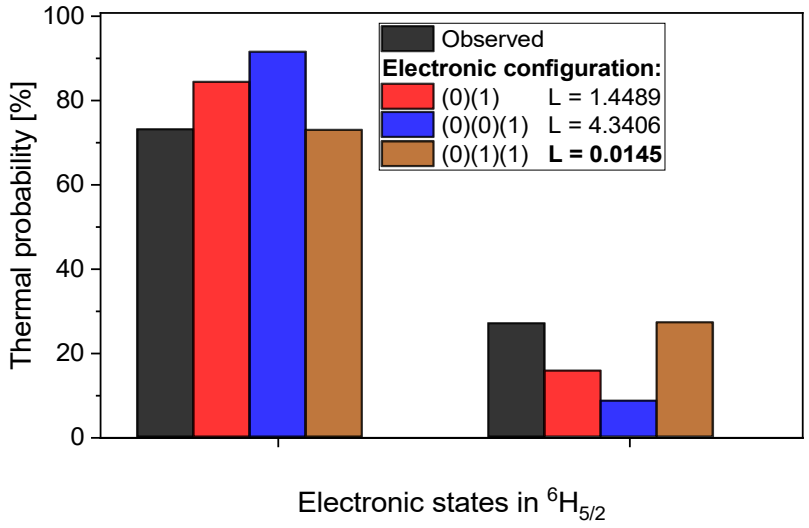


Figure S 72: Thermal populations of the electronic states in $^{6}H_{5/2}$ for $Cs_3[Sm(DPA)_3]\cdot 9H_2O$.

5.5 Electronic Energy Levels for the Sm^{3+} Compounds

The electronic energy levels determined from the Boltzmann population analysis of the excitation and emission spectra.

Table S 25: Electronic energy levels (**cm^{-1}**) for the Sm3+ compounds determined from the spectra.

	$Na_3[Sm(ODA)_3]\cdot 7H_2O$	$Cs_3[Sm(DPA)_3]\cdot 9H_2O$	$Na[Sm(DOTA)(H_2O)]\cdot 4H_2O$	$Na[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$
$^6H_{5/2}$	0	0	0	0
	2x90	2x59	244	110
	-	-	296	202
$^4G_{5/2}$	17834	17779	17749	17832
	18000	17842	17927	17940
	18050	18013	18001	18054

6 References

1 Brayshaw, P. A. *et al.* Synthetic, Structural, and Spectroscopic Studies on Solids Containing Tris(dipicolinato) Rare Earth Anions and Transition or Main Group Metal Cations. *Inorganic Chemistry* **34**, 2068-2076, doi:10.1021/ic00112a019 (1995).

2 Thomsen, M. S., Anker, A. S., Kacenauskaite, L. & Sørensen, T. J. We Are Never Ever Getting (back to) Ideal Symmetry: Structure and Luminescence in a Ten-Coordinated Europium (III) Sulfate Crystal. (2022).