Two beta-phosphorylamide compounds as ligands for Sm^{3+}, Eu^{3+} and Tb^{3+}: X-ray crystallography and luminescence properties

Supplementary Materials

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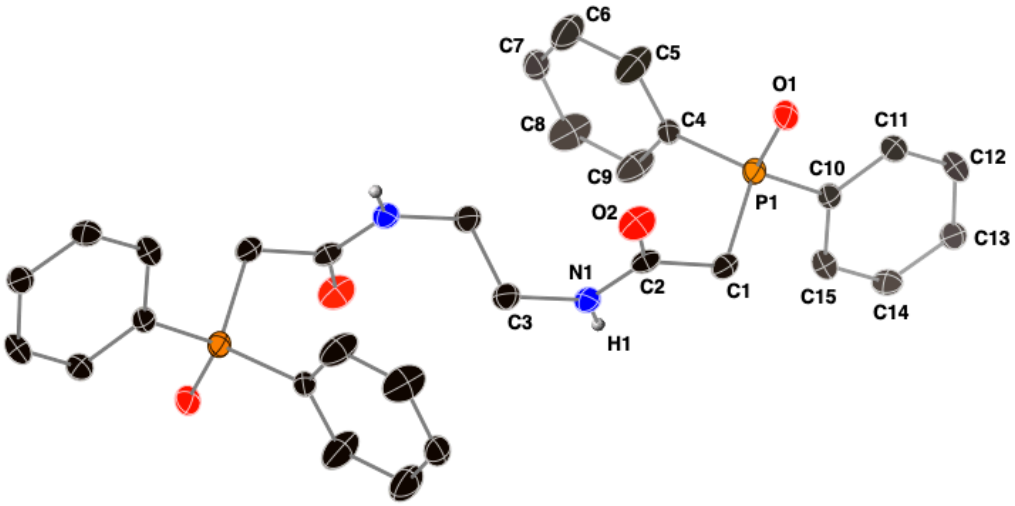
Table of Contents

I. X-Ray crystallography

A. Ligand 2

This figure shows the complete molecular structure of compound **1** using standard CPK colors, with thermal ellipsoids at the 40% probability level. The atom labeling scheme for one unique set of atoms is also depicted here, and only hydrogen atoms bonded to nitrogen atoms have been shown for clarity. Only the major component of ring C10-C15 is shown here.



Refinement notes
(1) Hydrogen atom (O)H1 was located using electron density difference maps and refined.
(2) The electron density corresponding to the aromatic ring C10-C15 was disordered and modeled over two positions with a relative occupancy ratio of 0.499(4) to 0.501(4) by refining against a free variable. No restraints were needed.

Experimental
Single crystals of $C_{30}H_{30}N_2O_4P_2$ compound **2** were grown by vapor diffusion of diethyl ether into a solution of the Eu-ligand complex in methanol and used as received. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table 1 Crystal data and structure refinement for ligand 2.

CCDC number	2003372
Empirical formula	$C_{30}H_{30}N_2O_4P_2$
Formula weight	544.50
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	5.65550(10)
b/Å	28.8994(5)
c/Å	8.4517(2)

α/°	90
β/°	109.4290(10)
γ/°	90
Volume/Å^3	1302.69(5)
Z	2
ρ_{calc}g/cm^3	1.388
μ/mm^{-1}	1.848
F(000)	572.0
Crystal size/mm^3	0.169 × 0.093 × 0.035
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.116 to 136.61
Index ranges	-6 ≤ h ≤ 6, -34 ≤ k ≤ 34, -10 ≤ l ≤ 10
Reflections collected	17978
Independent reflections	2388 [R_{int} = 0.0757, R_{sigma} = 0.0373]
Data/restraints/parameters	2388/0/213
Goodness-of-fit on F^2	1.022
Final R indexes [I>=2σ (I)]	R_1 = 0.0468, wR_2 = 0.1144
Final R indexes [all data]	R_1 = 0.0610, wR_2 = 0.1234
Largest diff. peak/hole / e Å^{-3}	0.67/-0.34

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for LIGAND 2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
P1	4503.2(11)	6439.5(2)	5051.3(8)	24.3(2)
O1	7249(3)	6365.2(6)	5448(2)	32.5(4)
O2	4800(4)	5450.7(7)	6928(3)	41.7(5)
N1	619(4)	5567.5(7)	6115(3)	26.4(5)
C1	3307(4)	6231.8(9)	6661(3)	26.1(5)
C2	2991(5)	5710.4(9)	6597(3)	25.6(5)
C3	-51(5)	5080.5(9)	5849(3)	32.0(6)
C4	2695(4)	6152.1(8)	3136(3)	24.4(5)
C5	3889(6)	5836.0(13)	2447(5)	58.8(11)
C6	2585(6)	5606.1(13)	971(5)	59.5(10)
C7	114(5)	5685.6(10)	182(3)	35.7(6)
C8	-1096(6)	5987.4(13)	890(4)	52.6(9)
C9	170(6)	6216.7(12)	2365(4)	45.0(8)
C10	3754(5)	7052.4(9)	4894(3)	26.7(6)
C11	5619(9)	7331.0(18)	4791(7)	27.8(12)
C12	5256(10)	7800.9(19)	4777(7)	33.1(13)
C13	2937(5)	8001.5(9)	4895(3)	33.4(6)
C14	1235(10)	7689.1(18)	5096(7)	30.4(13)
C15	1597(9)	7211.9(18)	5120(6)	28.9(12)
C11A	5352(9)	7355.8(17)	5997(7)	28.2(12)
C12A	4878(10)	7828.1(18)	6011(7)	31.4(13)
C14A	1152(10)	7740.7(18)	3655(7)	30.4(13)
C15A	1596(9)	7270.0(18)	3622(6)	27.2(12)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for LIGAND 2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
P1	16.1(3)	25.1(3)	30.6(4)	-7.1(3)	6.2(2)	-1.0(2)
O1	19.0(9)	31.7(10)	45.6(11)	-8.4(8)	9.3(8)	-0.7(7)
O2	34.7(11)	43.0(12)	42.5(12)	2.3(9)	6.4(9)	17.9(9)
N1	30.2(12)	19.6(11)	32.1(12)	-0.5(9)	14.0(10)	3.2(9)
C1	21.6(12)	31.1(13)	23.3(13)	-7.2(10)	4.5(10)	0.0(10)
C2	29.8(13)	30.2(13)	16.4(12)	-0.8(9)	7.3(10)	5.5(11)
C3	45.1(15)	21.8(13)	35.4(15)	0.2(11)	21.8(12)	0.1(11)
C4	25.6(12)	24.5(12)	23.4(13)	-2.2(9)	8.4(10)	-5.1(10)
C5	24.9(15)	78(3)	64(2)	-40.5(19)	2.0(14)	8.0(15)
C6	44.4(19)	66(2)	65(2)	-38.9(19)	14.8(17)	6.4(17)
C7	43.5(16)	40.3(16)	21.9(13)	-4.3(11)	8.8(12)	-13.9(13)
C8	30.4(15)	79(2)	35.6(17)	-10.7(16)	-5.5(13)	12.0(16)
C9	37.0(16)	58(2)	33.3(16)	-12.5(14)	2.4(13)	17.1(14)
C10	23.4(12)	25.7(13)	32.2(14)	-5.5(10)	10.9(10)	-3.0(10)
C11	26(3)	28(3)	29(3)	2(2)	9(2)	1(2)
C12	31(3)	29(3)	41(3)	4(2)	14(2)	-7(2)
C13	46.8(17)	23.1(13)	37.1(16)	0.3(11)	22.9(13)	-2.6(12)
C14	25(3)	32(3)	36(3)	1(2)	13(2)	8(2)
C15	26(3)	28(3)	31(3)	3(2)	7(2)	-4(2)
C11A	24(3)	27(3)	31(3)	-3(2)	6(2)	-1(2)
C12A	35(3)	24(3)	40(3)	-11(2)	18(3)	-9(2)
C14A	30(3)	29(3)	34(3)	5(2)	15(2)	2(2)
C15A	26(3)	29(3)	27(3)	-2(2)	8(2)	-3(2)

Table 4 Bond Lengths for LIGAND 2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
P1	O1	1.4912(18)	C8	C9	1.383(4)
P1	C1	1.811(3)	C10	C11	1.352(6)
P1	C4	1.804(2)	C10	C15	1.376(6)
P1	C10	1.816(3)	C10	C11A	1.376(6)
O2	C2	1.224(3)	C10	C15A	1.473(6)
N1	C2	1.332(3)	C11	C12	1.373(7)
N1	C3	1.455(3)	C12	C13	1.467(6)
C1	C2	1.516(4)	C13	C14	1.371(6)
C3	C3[1]	1.528(5)	C13	C12A	1.287(6)
C4	C5	1.375(4)	C13	C14A	1.408(6)
C4	C9	1.371(4)	C14	C15	1.393(7)
C5	C6	1.389(4)	C11A	C12A	1.392(7)
C6	C7	1.352(4)	C14A	C15A	1.385(7)
C7	C8	1.364(4)			

[1]-X,1-Y,1-Z

Table 5 Bond Angles for LIGAND 2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	P1	C1	113.87(11)	C7	C8	C9	121.2(3)
O1	P1	C4	111.87(11)	C4	C9	C8	120.5(3)
O1	P1	C10	110.91(11)	C11	C10	P1	114.7(3)
C1	P1	C10	103.99(12)	C11	C10	C15	123.8(4)
C4	P1	C1	106.24(11)	C15	C10	P1	120.9(3)
C4	P1	C10	109.56(12)	C11A	C10	P1	119.2(3)
C2	N1	C3	122.1(2)	C11A	C10	C15A	114.9(3)
C2	C1	P1	111.80(17)	C15A	C10	P1	125.9(3)
O2	C2	N1	124.1(3)	C10	C11	C12	118.2(5)
O2	C2	C1	121.4(2)	C11	C12	C13	121.7(4)
N1	C2	C1	114.5(2)	C14	C13	C12	115.4(3)
N1	C3	C3[1]	110.5(3)	C12A	C13	C14A	124.2(4)
C5	C4	P1	118.3(2)	C13	C14	C15	123.2(4)
C9	C4	P1	123.6(2)	C10	C15	C14	117.5(4)
C9	C4	C5	118.1(2)	C10	C11A	C12A	123.1(5)
C4	C5	C6	120.6(3)	C13	C12A	C11A	119.7(5)
C7	C6	C5	120.9(3)	C15A	C14A	C13	116.8(5)
C6	C7	C8	118.6(3)	C14A	C15A	C10	121.1(4)

[1]-X,1-Y,1-Z

Table 6 Hydrogen Bonds for LIGAND 2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O1[1]	0.80(3)	2.13(3)	2.924(3)	169(3)

[1]-1+X,+Y,+Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for LIGAND 2.

Atom	*x*	*y*	*z*	U(eq)
H1A	4477.27	6322.24	7776.81	31
H1B	1668.15	6379.56	6512.67	31
H3A	-1763.82	5033.57	5890.17	38
H3B	1123.04	4893.66	6754.32	38
H5	5621.6	5774.32	2985.3	71
H6	3439.84	5390.02	508.23	71
H7	-760.13	5534.23	-843.61	43
H8	-2838.79	6041.13	360.67	63
H9	-717.5	6420.62	2849.07	54
H11	7137.16	7205.05	4729.46	33
H12	6538.22	8001.17	4689.6	40
H13	2635.45	8325.46	4836.69	40
H13A	2692.19	8326.46	4910.22	40
H14	-265.05	7803.52	5224.8	36
H15	398.37	7004.38	5286.98	35
H11A	6849.23	7237.34	6785.02	34

H12A	5981.89	8021.67	6839.42	38
H14A	-287.66	7880.84	2877.99	36
H15A	490.43	7084.5	2764.27	33
H1	-460(60)	5760(10)	5940(40)	30(8)

Table 8 Atomic Occupancy for LIGAND 2.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C11	0.499(4)	H11	0.499(4)	C12	0.499(4)
H12	0.499(4)	H13	0.499(4)	H13A	0.501(4)
C14	0.499(4)	H14	0.499(4)	C15	0.499(4)
H15	0.499(4)	C11A	0.501(4)	H11A	0.501(4)
C12A	0.501(4)	H12A	0.501(4)	C14A	0.501(4)
H14A	0.501(4)	C15A	0.501(4)	H15A	0.501(4)

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups

2. Others

Sof(H13A)=Sof(C11A)=Sof(H11A)=Sof(C12A)=Sof(H12A)=Sof(C14A)=Sof(H14A)=
Sof(C15A)=Sof(H15A)=1-FVAR(1)
Sof(C11)=Sof(H11)=Sof(C12)=Sof(H12)=Sof(H13)=Sof(C14)=Sof(H14)=Sof(C15)=
Sof(H15)=FVAR(1)

3.a Secondary CH2 refined with riding coordinates:

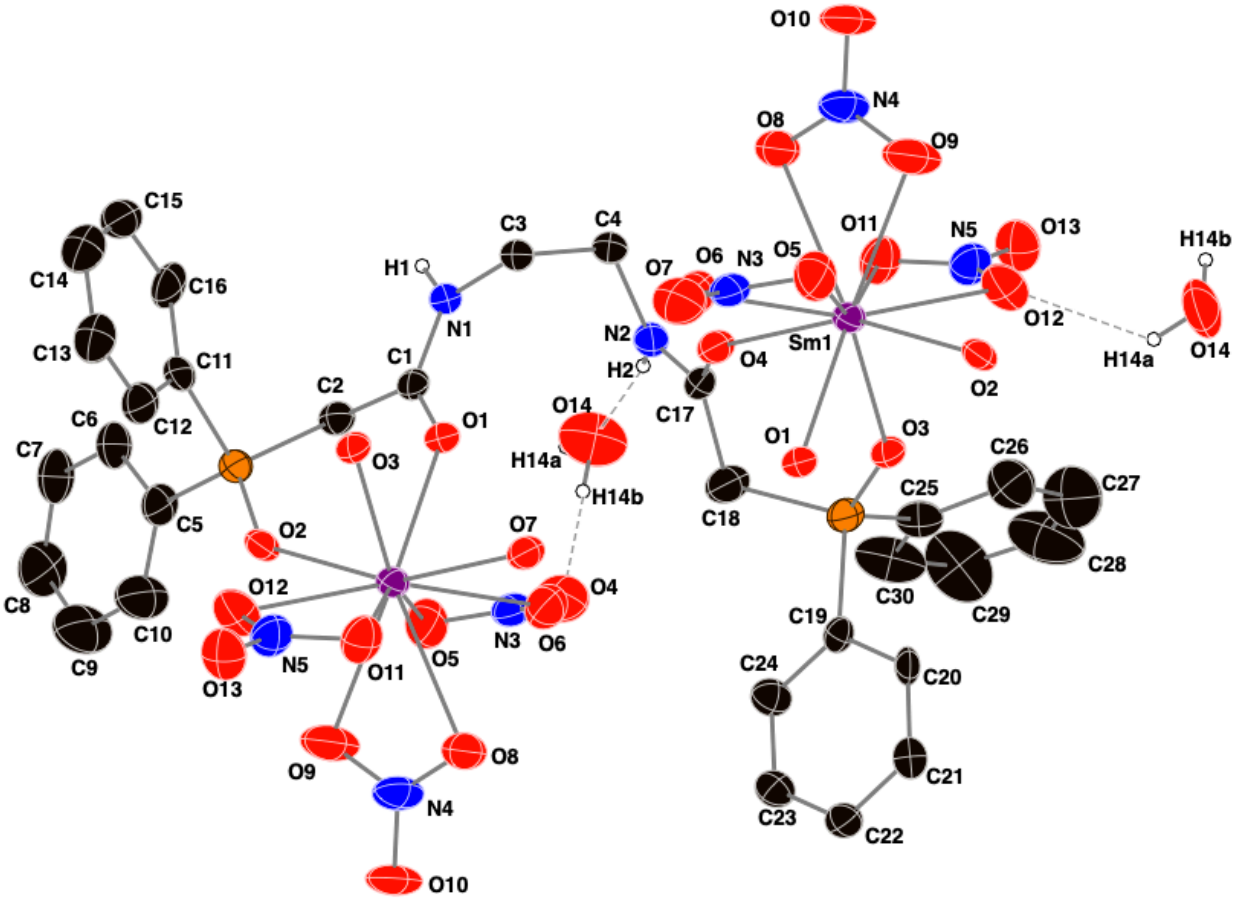
C1(H1A,H1B), C3(H3A,H3B)

3.b Aromatic/amide H refined with riding coordinates:

C5(H5), C6(H6), C7(H7), C8(H8), C9(H9), C11(H11), C12(H12), C13(H13),
C13(H13A), C14(H14), C15(H15), C11A(H11A), C12A(H12A), C14A(H14A), C15A(H15A)

B. $Sm(NO_3)_3$-2

This figure depicts the 2:2 **$Sm(NO_3)_3$-2** complex, where only one ligand is shown for clarity. Both Sm(III) metal centers are shown, along with all of the atoms of the inner coordination sphere. The water of hydration is also shown in two locations, with hydrogen bonds depicted with dashed lines. The structure is shown with thermal ellipsoids at the 30% probability level using standard CPK colors, as well as the atom labeling scheme.



Refinement notes

(1) SIMU and DELU commands were applied to the atoms of ring C5-C10 to ensure more uniform thermal values.

Experimental

Single crystals of $C_{60}H_{64}N_{10}O_{28}P_4Sm_2$ (**$Sm(NO_3)_3$-2)**were grown by slow evaporation of a chloroform solution in a NMR tube. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Table 1 Crystal data and structure refinement for $Sm(NO_3)_3$-2

CCDC Code	2003369
Empirical formula	$C_{60}H_{64}N_{10}O_{28}P_4Sm_2$
Formula weight	1797.79
Temperature/K	173(2)

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	10.5235(15)
b/Å	18.133(3)
c/Å	19.488(3)
α/°	90
β/°	96.944(12)
γ/°	90
Volume/Å^3	3691.6(9)
Z	2
ρ_{calc}g/cm^3	1.617
μ/mm^{-1}	13.393
F(000)	1804.0
Crystal size/mm^3	0.262 × 0.126 × 0.063
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.68 to 143.44
Index ranges	$-12 \le h \le 12$, $-22 \le k \le 22$, $-23 \le l \le 21$
Reflections collected	24709
Independent reflections	6996 [R_{int} = 0.1460, R_{sigma} = 0.1397]
Data/restraints/parameters	6996/48/472
Goodness-of-fit on F^2	1.020
Final R indexes [I>=2σ (I)]	R_1 = 0.0722, wR_2 = 0.1524
Final R indexes [all data]	R_1 = 0.1453, wR_2 = 0.1815
Largest diff. peak/hole / e Å^{-3}	0.91/-0.91

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for Sm(NO3)3-2. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Sm1	6438.6(5)	8266.0(3)	5882.5(4)	43.10(18)
P1	4050(2)	6923.0(14)	6186.2(16)	43.9(7)
P2	5101(2)	9666.9(15)	6947.8(17)	46.7(7)
O1	4121(6)	8465(4)	5437(4)	46.8(19)
O2	5417(6)	7189(4)	6218(4)	44.8(18)
O3	5402(6)	8892(4)	6738(4)	45.2(18)
O4	6678(7)	9554(4)	5656(4)	54(2)
O5	5827(10)	7440(5)	4825(6)	91(3)
O6	6150(8)	8565(6)	4601(5)	77(3)
O7	5082(9)	7892(6)	3823(5)	89(3)
O8	8630(7)	8323(5)	5341(5)	71(2)
O9	8168(8)	7316(5)	5801(7)	112(4)
O10	9915(7)	7371(5)	5307(6)	86(3)
O11	8210(8)	8815(5)	6743(5)	70(3)
O12	7404(7)	7816(5)	7098(5)	74(3)
O13	8851(8)	8399(5)	7789(5)	77(3)
N1	1956(7)	8464(5)	5288(4)	45(2)
N2	2320(8)	9373(5)	4036(5)	48(2)
N3	5681(9)	7961(7)	4411(6)	59(3)
N4	8923(8)	7672(6)	5466(7)	71(3)
N5	8175(9)	8342(6)	7236(6)	68(3)
C1	3078(9)	8128(6)	5386(6)	42(3)

C2	3068(9)	7277(6)	5430(5)	45(3)
C3	1784(9)	9259(6)	5237(6)	47(3)
C4	1346(9)	9504(6)	4500(6)	51(3)
C5	3934(11)	5933(6)	6104(7)	57(3)
C6	2851(12)	5549(7)	6176(7)	65(3)
C7	2778(14)	4786(7)	6110(7)	74(3)
C8	3842(16)	4418(8)	5992(9)	97(4)
C9	4939(17)	4770(8)	5951(11)	119(5)
C10	5002(14)	5543(8)	6014(9)	98(4)
C11	3364(10)	7214(6)	6948(7)	54(3)
C12	4294(13)	7387(6)	7529(8)	68(4)
C13	3867(14)	7602(7)	8132(7)	72(4)
C14	2595(14)	7625(7)	8198(8)	73(4)
C15	1668(13)	7454(7)	7634(8)	75(4)
C16	2099(12)	7235(6)	7004(7)	65(4)
C17	6742(9)	10143(6)	5995(6)	50(3)
C18	5658(12)	10377(6)	6404(8)	76(4)
C19	3409(9)	9827(6)	6923(5)	40(2)
C20	2642(10)	9221(6)	7056(5)	46(3)
C21	1359(10)	9318(6)	7095(6)	52(3)
C22	807(9)	10010(6)	6990(6)	50(3)
C23	1550(10)	10595(6)	6837(6)	51(3)
C24	2832(10)	10510(6)	6796(6)	56(3)
C25	5727(10)	9820(7)	7840(7)	56(3)
C26	6115(13)	9195(9)	8244(8)	83(4)
C27	6452(18)	9297(13)	8953(9)	123(8)
C28	6477(19)	9962(15)	9253(12)	144(10)
C29	6190(20)	10568(12)	8876(12)	131(9)
C30	5763(14)	10511(10)	8132(10)	110(7)
O14	2474(11)	7938(6)	3419(8)	109(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for Sm(NO3)3-2. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm1	38.1(3)	36.0(3)	57.0(4)	4.8(4)	13.2(2)	3.8(3)
P1	44.6(13)	35.9(15)	52.8(19)	5.1(13)	12.9(12)	2.3(10)
P2	45.6(14)	40.2(15)	57(2)	-1.2(14)	16.8(13)	-2.4(11)
O1	46(4)	45(4)	53(5)	3(4)	18(3)	5(3)
O2	38(3)	37(4)	59(5)	5(4)	3(3)	8(3)
O3	52(4)	43(4)	43(5)	-2(4)	19(3)	4(3)
O4	56(4)	39(4)	73(6)	4(4)	30(4)	1(3)
O5	130(9)	55(6)	94(9)	9(6)	43(7)	19(6)
O6	72(6)	90(7)	67(7)	19(6)	7(5)	-12(5)
O7	90(7)	112(9)	63(7)	-20(6)	6(6)	14(6)
O8	54(5)	65(6)	96(7)	7(6)	21(4)	7(4)
O9	55(5)	69(7)	222(14)	21(8)	55(7)	7(5)
O10	43(5)	62(6)	159(10)	-4(6)	38(5)	7(4)
O11	68(5)	69(6)	72(7)	6(5)	7(5)	-22(4)
O12	44(4)	66(6)	106(8)	9(5)	-19(4)	-10(4)

O13	68(5)	89(8)	69(7)	9(5)	-17(5)	-5(5)
N1	39(4)	53(6)	44(6)	10(4)	13(4)	4(4)
N2	57(5)	44(5)	43(6)	0(4)	13(4)	10(4)
N3	51(6)	78(8)	51(8)	2(6)	18(5)	11(5)
N4	37(5)	64(7)	113(11)	-6(7)	18(6)	-2(5)
N5	52(6)	81(8)	70(8)	10(7)	6(5)	-11(6)
C1	43(5)	45(6)	43(7)	4(5)	22(5)	6(4)
C2	41(5)	56(7)	37(7)	-3(5)	4(4)	2(5)
C3	38(5)	48(6)	56(8)	10(6)	14(5)	4(4)
C4	35(5)	59(7)	58(8)	13(6)	8(5)	6(5)
C5	72(6)	31(5)	72(8)	4(6)	21(6)	-3(4)
C6	76(6)	48(6)	72(8)	13(6)	11(6)	-10(5)
C7	95(7)	52(6)	75(9)	12(7)	7(7)	-24(6)
C8	128(10)	42(6)	126(11)	-2(8)	34(10)	-11(6)
C9	114(9)	51(7)	199(13)	1(10)	51(10)	14(6)
C10	87(7)	48(6)	165(12)	3(8)	45(9)	0(6)
C11	52(6)	36(6)	77(10)	22(6)	18(6)	1(5)
C12	80(9)	43(7)	85(11)	15(7)	33(8)	10(6)
C13	97(11)	61(9)	61(10)	-5(7)	17(8)	-8(7)
C14	99(11)	59(9)	65(11)	-13(8)	25(9)	-10(7)
C15	83(9)	43(7)	106(13)	12(8)	46(9)	5(6)
C16	83(9)	42(7)	73(10)	16(7)	29(8)	-5(6)
C17	53(7)	47(7)	55(8)	14(6)	25(6)	9(5)
C18	82(9)	40(7)	115(13)	5(8)	55(9)	2(6)
C19	46(5)	47(6)	28(6)	2(5)	4(4)	-3(5)
C20	63(7)	45(6)	32(7)	15(5)	11(5)	11(5)
C21	60(7)	48(7)	47(8)	5(6)	3(6)	-3(5)
C22	36(5)	71(8)	41(7)	4(6)	-3(5)	4(5)
C23	52(6)	46(7)	56(8)	-11(6)	9(5)	8(5)
C24	54(7)	49(7)	63(9)	-4(6)	7(6)	2(5)
C25	44(6)	61(8)	62(9)	-19(7)	0(5)	-10(5)
C26	82(10)	91(12)	73(12)	-2(9)	-5(8)	-3(8)
C27	130(16)	170(20)	58(13)	-13(13)	-28(11)	17(15)
C28	109(15)	190(30)	120(20)	-70(20)	-25(13)	31(17)
C29	145(18)	100(16)	130(20)	-62(15)	-45(15)	12(14)
C30	79(10)	104(14)	141(18)	-54(13)	-9(10)	14(9)
O14	108(8)	80(8)	136(11)	-57(8)	0(8)	-6(6)

Table 4 Bond Lengths for Sm(NO3)3-2.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Sm1	O1	2.514(7)	N1	C3	1.456(12)
Sm1	O2	2.360(7)	N2	C4	1.466(13)
Sm1	O3	2.387(7)	N2	C17[1]	1.329(13)
Sm1	O4	2.396(7)	C1	C2	1.545(13)
Sm1	O5	2.567(11)	C3	C4	1.521(14)
Sm1	O6	2.537(9)	C5	C6	1.356(15)
Sm1	O8	2.651(8)	C5	C10	1.357(17)
Sm1	O9	2.525(9)	C6	C7	1.391(16)
Sm1	O11	2.554(8)	C7	C8	1.347(19)

Sm1	O12	2.594(9)	C8	C9	1.33(2)
Sm1	N3	2.935(12)	C9	C10	1.407(18)
P1	O2	1.511(7)	C11	C12	1.438(17)
P1	C2	1.813(10)	C11	C16	1.349(15)
P1	C5	1.806(11)	C12	C13	1.365(17)
P1	C11	1.807(13)	C13	C14	1.361(17)
P2	O3	1.508(7)	C14	C15	1.413(18)
P2	C18	1.809(12)	C15	C16	1.415(17)
P2	C19	1.800(10)	C17	C18	1.528(14)
P2	C25	1.805(13)	C19	C20	1.406(14)
O1	C1	1.251(11)	C19	C24	1.388(14)
O4	C17	1.253(13)	C20	C21	1.373(14)
O5	N3	1.239(13)	C21	C22	1.389(14)
O6	N3	1.240(13)	C22	C23	1.372(15)
O7	N3	1.246(13)	C23	C24	1.370(14)
O8	N4	1.236(12)	C25	C26	1.411(17)
O9	N4	1.265(13)	C25	C30	1.374(18)
O10	N4	1.249(11)	C26	C27	1.40(2)
O11	N5	1.292(12)	C27	C28	1.34(2)
O12	N5	1.260(12)	C28	C29	1.34(3)
O13	N5	1.223(12)	C29	C30	1.47(2)
N1	C1	1.322(12)			

[1]1-X,2-Y,1-Z

Table 5 Bond Angles for Sm(NO3)3-2.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Sm1	O5	70.6(3)	C1	O1	Sm1	139.7(7)
O1	Sm1	O6	68.5(3)	P1	O2	Sm1	135.7(4)
O1	Sm1	O8	135.3(3)	P2	O3	Sm1	139.6(4)
O1	Sm1	O9	138.8(3)	C17	O4	Sm1	137.1(8)
O1	Sm1	O11	140.5(3)	N3	O5	Sm1	94.4(8)
O1	Sm1	O12	128.1(2)	N3	O6	Sm1	95.8(8)
O1	Sm1	N3	63.4(2)	N4	O8	Sm1	95.3(6)
O2	Sm1	O1	76.1(2)	N4	O9	Sm1	100.8(7)
O2	Sm1	O3	86.4(2)	N5	O11	Sm1	98.3(6)
O2	Sm1	O4	156.8(2)	N5	O12	Sm1	97.3(7)
O2	Sm1	O5	70.2(3)	C1	N1	C3	124.6(9)
O2	Sm1	O6	116.4(3)	C17[1]	N2	C4	120.0(9)
O2	Sm1	O8	126.1(2)	O5	N3	Sm1	60.7(7)
O2	Sm1	O9	79.0(3)	O5	N3	O6	117.7(12)
O2	Sm1	O11	117.5(3)	O5	N3	O7	122.1(14)
O2	Sm1	O12	68.1(2)	O6	N3	Sm1	59.3(7)
O2	Sm1	N3	92.0(3)	O6	N3	O7	120.1(12)
O3	Sm1	O1	70.5(2)	O7	N3	Sm1	164.9(8)
O3	Sm1	O4	74.5(2)	O8	N4	O9	115.5(9)
O3	Sm1	O5	138.3(3)	O8	N4	O10	124.3(10)
O3	Sm1	O6	125.1(3)	O10	N4	O9	120.1(11)
O3	Sm1	O8	138.8(3)	O12	N5	O11	114.8(10)
O3	Sm1	O9	139.7(3)	O13	N5	O11	122.3(11)
O3	Sm1	O11	73.5(3)	O13	N5	O12	122.9(12)

O3	Sm1	O12	71.0(3)	O1	C1	N1	123.1(10)
O3	Sm1	N3	132.8(3)	O1	C1	C2	119.7(8)
O4	Sm1	O1	85.1(2)	N1	C1	C2	117.2(9)
O4	Sm1	O5	116.3(3)	C1	C2	P1	113.0(7)
O4	Sm1	O6	67.2(3)	N1	C3	C4	112.0(10)
O4	Sm1	O8	76.9(3)	N2	C4	C3	112.4(8)
O4	Sm1	O9	124.1(3)	C6	C5	P1	123.4(10)
O4	Sm1	O11	69.9(3)	C6	C5	C10	117.7(12)
O4	Sm1	O12	115.9(3)	C10	C5	P1	118.7(10)
O4	Sm1	N3	91.5(3)	C5	C6	C7	122.6(13)
O5	Sm1	O8	81.3(3)	C8	C7	C6	118.1(13)
O5	Sm1	O12	125.6(3)	C9	C8	C7	121.2(14)
O5	Sm1	N3	24.9(3)	C8	C9	C10	120.3(15)
O6	Sm1	O5	49.1(3)	C5	C10	C9	119.9(14)
O6	Sm1	O8	66.8(3)	C12	C11	P1	114.1(9)
O6	Sm1	O11	123.6(3)	C16	C11	P1	124.8(11)
O6	Sm1	O12	162.4(3)	C16	C11	C12	120.9(13)
O6	Sm1	N3	24.9(3)	C13	C12	C11	118.4(13)
O8	Sm1	N3	76.4(3)	C14	C13	C12	121.3(14)
O9	Sm1	O5	70.4(4)	C13	C14	C15	120.9(14)
O9	Sm1	O6	94.9(4)	C14	C15	C16	118.2(13)
O9	Sm1	O8	48.2(3)	C11	C16	C15	120.1(14)
O9	Sm1	O11	80.4(3)	O4	C17	N2[1]	122.1(10)
O9	Sm1	O12	68.7(4)	O4	C17	C18	121.1(10)
O9	Sm1	N3	85.6(4)	N2[1]	C17	C18	116.5(11)
O11	Sm1	O5	147.9(3)	C17	C18	P2	115.0(8)
O11	Sm1	O8	69.2(3)	C20	C19	P2	117.2(8)
O11	Sm1	O12	49.4(3)	C24	C19	P2	124.0(8)
O11	Sm1	N3	143.7(3)	C24	C19	C20	118.8(10)
O12	Sm1	O8	96.4(3)	C21	C20	C19	120.0(10)
O12	Sm1	N3	149.7(3)	C20	C21	C22	120.3(11)
O2	P1	C2	111.5(5)	C23	C22	C21	119.4(10)
O2	P1	C5	112.0(5)	C24	C23	C22	121.1(11)
O2	P1	C11	110.2(5)	C23	C24	C19	120.2(11)
C5	P1	C2	104.7(5)	C26	C25	P2	117.4(10)
C5	P1	C11	109.5(5)	C30	C25	P2	121.8(13)
C11	P1	C2	108.6(5)	C30	C25	C26	120.6(15)
O3	P2	C18	114.3(5)	C27	C26	C25	117.8(17)
O3	P2	C19	112.5(5)	C28	C27	C26	123(2)
O3	P2	C25	109.9(5)	C29	C28	C27	121(2)
C19	P2	C18	105.0(5)	C28	C29	C30	120.5(19)
C19	P2	C25	104.2(5)	C25	C30	C29	117.6(18)
C25	P2	C18	110.4(7)				

[1]1-X,2-Y,1-Z

Table 6 Hydrogen Bonds for Sm(NO3)3-2.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O10[1]	0.88	2.06	2.926(12)	166.6
N2	H2	O14	0.88	2.02	2.878(13)	164.3
O14	H14B	O7	0.87	1.90	2.764(15)	175.0

[1]-1+X,+Y,+Z

Table 7 Torsion Angles for Sm(NO3)3-2.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
Sm1	O1	C1	N1	160.8(7)	C5	P1	O2	Sm1	149.6(6)
Sm1	O1	C1	C2	-19.9(16)	C5	P1	C2	C1	-177.9(7)
Sm1	O4	C17	N2[1]	128.5(10)	C5	P1	C11	C12	102.2(9)
Sm1	O4	C17	C18	-58.4(16)	C5	P1	C11	C16	-74.0(11)
Sm1	O5	N3	O6	17.0(11)	C5	C6	C7	C8	2(2)
Sm1	O5	N3	O7	-162.8(10)	C6	C5	C10	C9	4(3)
Sm1	O6	N3	O5	-17.3(11)	C6	C7	C8	C9	1(3)
Sm1	O6	N3	O7	162.5(9)	C7	C8	C9	C10	-1(3)
Sm1	O8	N4	O9	-3.9(13)	C8	C9	C10	C5	-1(3)
Sm1	O8	N4	O10	179.0(12)	C10	C5	C6	C7	-5(2)
Sm1	O9	N4	O8	4.2(14)	C11	P1	O2	Sm1	-88.2(7)
Sm1	O9	N4	O10	-178.6(10)	C11	P1	C2	C1	65.2(8)
Sm1	O11	N5	O12	3.8(11)	C11	P1	C5	C6	46.5(14)
Sm1	O11	N5	O13	-177.1(11)	C11	P1	C5	C10	-128.8(13)
Sm1	O12	N5	O11	-3.7(11)	C11	C12	C13	C14	2.7(19)
Sm1	O12	N5	O13	177.2(11)	C12	C11	C16	C15	2.2(17)
P1	C5	C6	C7	179.9(11)	C12	C13	C14	C15	-2(2)
P1	C5	C10	C9	179.8(14)	C13	C14	C15	C16	2(2)
P1	C11	C12	C13	-179.0(9)	C14	C15	C16	C11	-1.8(18)
P1	C11	C16	C15	178.2(9)	C16	C11	C12	C13	-2.6(17)
P2	C19	C20	C21	175.2(9)	C17[1]	N2	C4	C3	-83.1(13)
P2	C19	C24	C23	-175.1(9)	C18	P2	O3	Sm1	0.6(9)
P2	C25	C26	C27	-172.3(13)	C18	P2	C19	C20	155.1(9)
P2	C25	C30	C29	174.7(13)	C18	P2	C19	C24	-26.3(12)
O1	C1	C2	P1	51.9(12)	C18	P2	C25	C26	-140.8(10)
O2	P1	C2	C1	-56.5(8)	C18	P2	C25	C30	42.7(13)
O2	P1	C5	C6	169.1(11)	C19	P2	O3	Sm1	120.2(6)
O2	P1	C5	C10	-6.2(15)	C19	P2	C18	C17	-145.3(10)
O2	P1	C11	C12	-21.5(9)	C19	P2	C25	C26	106.9(10)
O2	P1	C11	C16	162.3(9)	C19	P2	C25	C30	-69.6(12)
O3	P2	C18	C17	-21.6(13)	C19	C20	C21	C22	1.3(17)
O3	P2	C19	C20	30.2(10)	C20	C19	C24	C23	3.5(18)
O3	P2	C19	C24	-151.1(9)	C20	C21	C22	C23	0.9(18)
O3	P2	C25	C26	-13.9(11)	C21	C22	C23	C24	-1.0(19)
O3	P2	C25	C30	169.7(11)	C22	C23	C24	C19	-1.3(19)
O4	C17	C18	P2	48.4(16)	C24	C19	C20	C21	-3.5(17)
N1	C1	C2	P1	-128.9(9)	C25	P2	O3	Sm1	-124.1(7)
N1	C3	C4	N2	-65.8(11)	C25	P2	C18	C17	102.9(11)
N2[1]	C17	C18	P2	-138.1(10)	C25	P2	C19	C20	-88.8(9)
C1	N1	C3	C4	106.9(11)	C25	P2	C19	C24	89.8(11)
C2	P1	O2	Sm1	32.6(8)	C25	C26	C27	C28	-3(3)
C2	P1	C5	C6	-69.9(13)	C26	C25	C30	C29	-2(2)
C2	P1	C5	C10	114.9(13)	C26	C27	C28	C29	-1(4)
C2	P1	C11	C12	-144.0(8)	C27	C28	C29	C30	3(4)
C2	P1	C11	C16	39.8(11)	C28	C29	C30	C25	-2(3)
C3	N1	C1	O1	-1.0(17)	C30	C25	C26	C27	4(2)
C3	N1	C1	C2	179.8(10)					

[1]1-X,2-Y,1-Z

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Sm(NO3)3-2.

Atom	*x*	*y*	*z*	U(eq)
H1	1264	8186.86	5251.34	54
H2	2282.25	8973.16	3777.93	57
H2A	3380.18	7071.55	5010.08	53
H2B	2176.3	7106.36	5437.63	53
H3A	2603.61	9505.44	5403.13	56
H3B	1142.22	9414.25	5540.01	56
H4A	555.65	9233.84	4325.06	61
H4B	1139.49	10036.5	4499.67	61
H6	2113.7	5811.83	6274.41	78
H7	1999.58	4531.38	6147.34	89
H8	3808.87	3897.14	5938.16	116
H9	5683.62	4499.2	5878.03	142
H10	5790.81	5791.4	5993.81	117
H12	5184.06	7352.12	7493.49	81
H13	4469.85	7737.99	8513.7	87
H14	2326.1	7759.19	8629.23	88
H15	779.67	7484.05	7676.5	89
H16	1497.45	7102.73	6621.1	77
H18A	4926.09	10544.67	6074.31	91
H18B	5953.27	10803.07	6698.61	91
H20	3012.09	8743.72	7117.93	55
H21	846.58	8909	7194.27	62
H22	-78.69	10078.62	7024.58	60
H23	1169.33	11067.54	6758.82	61
H24	3327.45	10919.33	6680.55	67
H26	6145.92	8720.74	8039.69	100
H27	6672.47	8877.47	9233.66	148
H28	6703.51	10003.82	9738.64	173
H29	6251	11038.88	9090.85	157
H30	5524.58	10936.03	7861.43	132
H14A	2225.14	7493.67	3301.68	164
H14B	3297.1	7899.97	3530.61	164

Crystal structure determination of [Sm(NO3)3-2]

Crystal Data for $C_{60}H_{64}N_{10}O_{28}P_4Sm_2$ (M =1797.79 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 10.5235(15) Å, b = 18.133(3) Å, c = 19.488(3) Å, β = 96.944(12)°, V = 3691.6(9) Å^3, Z = 2, T = 173(2) K, μ(CuKα) = 13.393 mm^{-1}, *Dcalc* = 1.617 g/cm^3, 24709 reflections measured (6.68° ≤ 2Θ ≤ 143.44°), 6996 unique (R_{int} = 0.1460, R_{sigma} = 0.1397) which were used in all calculations. The final R_1 was 0.0722 (I > 2σ(I)) and wR_2 was 0.1815 (all data).

Refinement model description

Number of restraints - 48, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H) groups, All C(H,H) groups, All N(H) groups
At 1.5 times of:
All O(H,H) groups
2. Rigid bond restraints

C5, C10, C9, C8, C7, C6
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
3. Uiso/Uaniso restraints and constraints
C5 ≈ C10 ≈ C9 ≈ C8 ≈ C7 ≈ C6: within 2A with sigma of 0.02
and sigma for terminal atoms of 0.04
4.a Free rotating group:
O14(H14A,H14B)
4.b Secondary CH2 refined with riding coordinates:
C2(H2A,H2B), C3(H3A,H3B), C4(H4A,H4B), C18(H18A,H18B)
4.c Aromatic/amide H refined with riding coordinates:
N1(H1), N2(H2), C6(H6), C7(H7), C8(H8), C9(H9), C10(H10), C12(H12), C13(H13),
C14(H14), C15(H15), C16(H16), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24),
C26(H26), C27(H27), C28(H28), C29(H29), C30(H30)

C. $Tb(NO_3)_3$-2 (MeOH solvate)

The figure on the left depicts the atom numbering scheme of the 2:2 **$Tb(NO_3)_3$-2** complex using a ball and stick model with standard CPK colors (Tb atoms are colored green). Only one ligand of the major component is shown for clarity, although all atoms of the inner coordination sphere of each metal center are shown. Hydrogen atoms bonded to carbon atoms are not shown for clarity, and hydrogen bonds are depicted with blue, dashed lines.
The figure on the right depicts the thermal ellipsoids, which are shown at the 40% probability level.

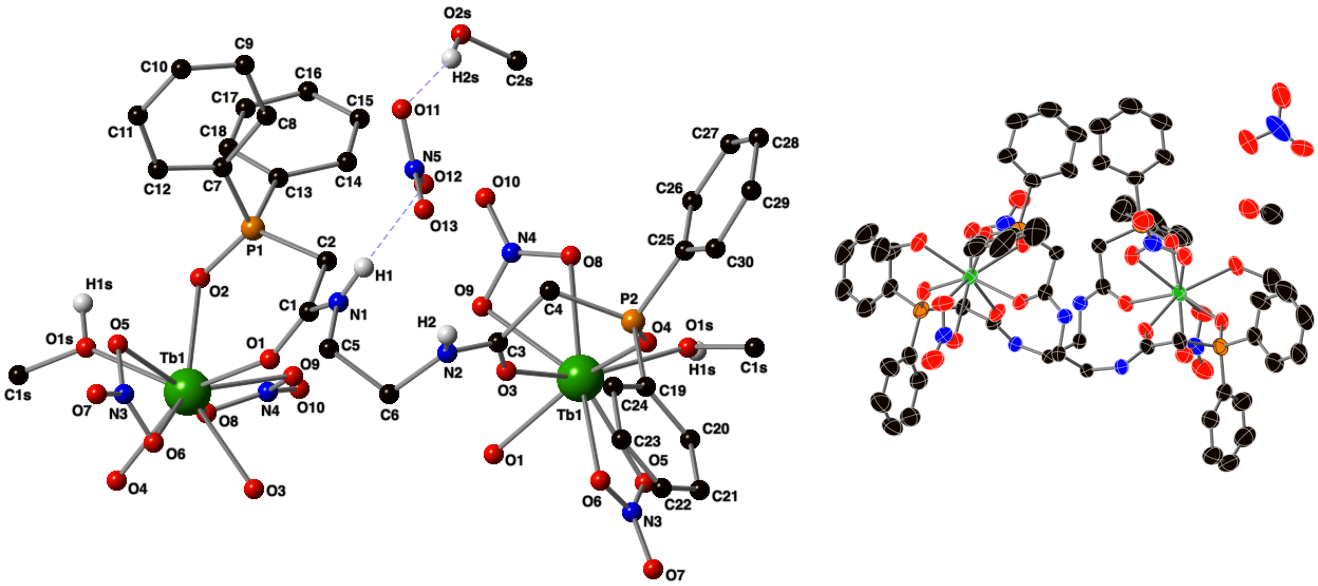
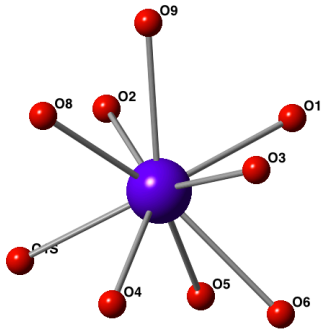


Figure depicting atoms of inner-coordination sphere:



Refinement notes

(1) The electron density corresponding to the atoms of ring C13-C18, along with the ipso P1 atom, was positionally disordered. This electron density was modeled over two positions, and the occupancy of each component was found to be 0.733(17) and 0.267(17) by refining against a free variable. The FLAT command was applied to this ring to ensure a planar benzene ring, and EADP, SIMU and DELU commands were applied to the atoms of the rings to ensure more uniform thermal values.

(2) SIMU and DELU commands were applied to the atoms of ring C19-C24 to ensure more uniform thermal values.

Experimental

Single crystals of $C_{64}H_{76}N_{10}O_{30}P_4Tb_2$]**$Tb(NO_3)_3$-2 (MeOH solvate)]** were grown by slow diffusion of diethyl ether into a solution of the complex in methanol. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2

[1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

$Tb(NO_3)_3$-2 (MeOH solvate)

Table 1 Crystal data and structure refinement for $Tb(NO_3)_3$-2 (MeOH solvate).

CCDC number	2003371
Empirical formula	$C_{64}H_{76}N_{10}O_{30}P_4Tb_2$
Formula weight	1907.06
Temperature/K	173(2)
Crystal system	tetragonal
Space group	$P\text{-}42_1c$
a/Å	18.2898(4)
b/Å	18.2898(4)
c/Å	27.4073(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	9168.2(4)
Z	4
ρ_{calc}g/cm^3	1.382
μ/mm^{-1}	8.794
F(000)	3840.0
Crystal size/mm^3	0.284 × 0.2 × 0.183
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	5.81 to 136.676
Index ranges	$-22 \le h \le 22$, $-21 \le k \le 22$, $-33 \le l \le 33$
Reflections collected	111590
Independent reflections	8408 [R_{int} = 0.1335, R_{sigma} = 0.0634]
Data/restraints/parameters	8408/165/536
Goodness-of-fit on F^2	1.094
Final R indexes [I>=2σ (I)]	R_1 = 0.0638, wR_2 = 0.1895
Final R indexes [all data]	R_1 = 0.0827, wR_2 = 0.2052
Largest diff. peak/hole / e Å^{-3}	1.10/-0.77
Flack parameter	0.023(4)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TB(NO3)3-2 (MEOH SOLVATE). U_{eq} is defined as 1/3 of of the trace of the 17rthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Tb1	3528.6(4)	6587.3(4)	6374.4(3)	48.5(2)
P1	5005(13)	6906(12)	7168(4)	45(2)
P1A	4990(40)	6890(40)	7270(15)	45(2)

P2	8132.5(17)	3889(2)	5773.8(13)	50.5(8)
O1	4745(4)	6346(5)	6130(3)	51(2)
O2	4239(5)	7023(5)	7007(4)	54(2)
O3	6562(5)	4459(5)	5867(3)	54(2)
O4	7666(4)	3387(5)	6077(3)	54(2)
O5	3922(7)	7805(6)	6051(4)	76(3)
O6	3637(5)	7033(6)	5507(3)	58(2)
O7	4024(8)	8089(7)	5277(5)	89(4)
O8	2819(5)	5841(6)	6946(4)	61(3)
O9	3937(5)	5490(5)	6869(4)	58(2)
O10	3254(7)	4946(8)	7411(4)	82(3)
N1	5978(6)	6344(6)	6033(4)	46(2)
N2	6847(5)	5437(5)	5400(4)	43(2)
N3	3866(7)	7637(8)	5605(5)	66(3)
N4	3341(7)	5413(7)	7083(4)	62(3)
C1	5367(7)	6313(6)	6312(5)	46(3)
C2	5487(7)	6210(8)	6866(4)	50(3)
C3	7019(6)	4897(7)	5690(4)	45(3)
C4	7820(6)	4818(7)	5837(5)	48(3)
C5	5939(7)	6382(7)	5513(4)	44(3)
C6	6088(6)	5635(7)	5290(4)	41(2)
C7	5523(9)	7710(8)	7133(5)	60(4)
C8	6275(9)	7700(10)	7271(7)	82(5)
C9	6700(14)	8331(13)	7268(9)	114(8)
C10	6393(13)	8950(13)	7087(10)	116(10)
C11	5688(15)	8986(10)	6973(7)	96(7)
C12	5213(10)	8346(8)	6982(6)	67(4)
C13	5060(13)	6667(11)	7835(6)	61(5)
C14	5532(15)	6101(13)	8011(7)	69(5)
C15	5586(18)	6031(16)	8514(8)	90(6)
C16	5197(19)	6477(17)	8820(8)	101(6)
C17	4772(19)	6984(17)	8635(9)	104(6)
C18	4704(17)	7109(14)	8151(8)	87(7)
C13A	4770(30)	6520(30)	7773(13)	61(5)
C14A	5160(30)	5900(30)	7958(15)	73(9)
C15A	5000(40)	5710(30)	8437(17)	90(6)
C16A	4520(40)	6100(40)	8713(16)	101(6)
C17A	4170(40)	6650(30)	8520(17)	104(6)
C18A	4290(30)	6880(30)	8057(17)	80(9)
C19	8141(8)	3660(10)	5144(6)	66(3)
C20	8015(10)	2932(12)	5000(7)	83(4)
C21	8022(11)	2760(13)	4514(7)	96(5)
C22	8144(11)	3327(16)	4167(7)	101(5)
C23	8281(9)	4007(14)	4285(7)	91(5)
C24	8286(8)	4179(12)	4788(6)	75(4)
C25	9058(7)	3923(9)	5997(6)	59(4)
C26	9152(8)	3940(11)	6496(6)	77(5)
C27	9874(10)	3990(13)	6682(8)	97(7)
C28	10460(8)	4019(11)	6378(9)	97(6)
C29	10356(8)	3982(12)	5864(8)	88(6)
C30	9645(8)	3903(11)	5682(7)	76(5)

O1S	2864(5)	7515(6)	6801(4)	63(3)
C1S	2235(10)	7958(12)	6647(10)	95(6)
O11	1887(9)	2846(9)	6515(6)	122(6)
O12	2612(6)	3709(7)	6547(4)	71(3)
O13	2163(9)	3437(9)	5853(6)	114(5)
N5	2249(8)	3325(8)	6301(6)	101(6)
O2S	1622(9)	3353(6)	7462(5)	86(4)
C2S	1605(14)	4105(12)	7541(8)	101(6)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for TB(NO3)3-2 (MEOH SOLVATE). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb1	38.3(4)	53.5(4)	53.7(4)	-13.3(4)	2.0(4)	-1.6(3)
P1	53(2)	52(2)	30(6)	-6(5)	0(5)	1.1(17)
P1A	53(2)	52(2)	30(6)	-6(5)	0(5)	1.1(17)
P2	35.4(15)	62(2)	53.8(18)	12.1(16)	-1.0(14)	4.7(14)
O1	31(4)	67(6)	54(5)	-14(4)	2(4)	0(4)
O2	46(5)	52(5)	64(6)	-17(4)	-10(4)	-1(4)
O3	40(4)	61(5)	61(5)	27(4)	-2(4)	-4(4)
O4	33(4)	59(5)	71(6)	17(5)	10(4)	2(4)
O5	107(9)	69(7)	51(6)	-8(5)	15(6)	-10(6)
O6	53(5)	67(6)	55(5)	-4(5)	2(4)	-3(5)
O7	117(10)	67(7)	81(8)	-3(6)	25(7)	-5(7)
O8	45(5)	76(6)	62(6)	4(5)	15(4)	6(5)
O9	38(5)	58(6)	78(7)	0(5)	3(4)	2(4)
O10	74(7)	102(9)	71(7)	7(7)	5(6)	-3(7)
N1	37(5)	56(6)	45(6)	-3(5)	-2(4)	-2(4)
N2	37(5)	44(5)	48(5)	1(4)	-3(4)	1(4)
N3	66(8)	74(9)	57(7)	-10(7)	7(6)	10(7)
N4	54(7)	77(8)	55(7)	-8(6)	4(6)	-6(6)
C1	44(6)	39(6)	56(7)	-5(5)	2(6)	-3(5)
C2	49(7)	58(7)	43(7)	-2(6)	3(5)	7(6)
C3	30(5)	57(7)	48(6)	7(6)	-4(5)	-4(5)
C4	33(6)	47(7)	63(8)	12(6)	-2(5)	-5(5)
C5	39(6)	42(6)	51(7)	-2(5)	-3(5)	3(5)
C6	38(6)	44(6)	40(6)	0(5)	-2(5)	2(5)
C7	82(10)	56(8)	42(7)	-18(6)	-3(7)	1(7)
C8	65(10)	73(11)	106(14)	-3(10)	-25(10)	-15(8)
C9	107(17)	91(15)	150(20)	-55(15)	-30(15)	-9(13)
C10	88(15)	96(16)	160(20)	-65(16)	46(16)	-37(13)
C11	150(20)	59(10)	79(13)	-5(9)	33(13)	6(12)
C12	90(11)	52(8)	59(8)	-10(7)	15(8)	-1(8)
C13	80(13)	61(10)	41(7)	-5(7)	-10(8)	8(9)
C14	90(14)	69(12)	49(8)	2(8)	-10(10)	16(10)
C15	120(15)	96(13)	55(8)	17(8)	0(10)	15(10)
C16	144(16)	106(13)	53(8)	7(9)	10(10)	14(11)
C17	146(16)	112(13)	55(8)	-9(10)	14(11)	28(11)
C18	125(17)	86(14)	50(9)	-5(9)	16(11)	32(12)
C13A	80(13)	61(10)	41(7)	-5(7)	-10(8)	8(9)

C14A	100(20)	78(19)	45(13)	4(15)	-10(15)	15(15)
C15A	120(15)	96(13)	55(8)	17(8)	0(10)	15(10)
C16A	144(16)	106(13)	53(8)	7(9)	10(10)	14(11)
C17A	146(16)	112(13)	55(8)	-9(10)	14(11)	28(11)
C18A	110(20)	83(19)	48(14)	-12(13)	0(16)	17(16)
C19	46(7)	89(9)	64(7)	1(6)	7(6)	14(7)
C20	77(10)	99(9)	72(8)	-14(8)	2(8)	13(9)
C21	86(11)	119(12)	83(9)	-33(8)	-3(9)	21(10)
C22	73(10)	168(14)	61(8)	-19(8)	7(8)	19(12)
C23	52(8)	154(13)	67(8)	8(9)	11(7)	12(10)
C24	47(7)	111(10)	67(8)	11(7)	4(7)	9(8)
C25	28(6)	76(10)	72(10)	17(8)	0(6)	-1(6)
C26	49(8)	112(14)	68(10)	27(10)	-7(7)	-14(8)
C27	59(10)	141(19)	91(13)	29(13)	-24(9)	6(11)
C28	37(7)	123(16)	130(17)	48(15)	1(10)	6(8)
C29	39(8)	129(17)	96(14)	33(12)	15(8)	14(9)
C30	46(8)	104(13)	78(11)	15(10)	-3(7)	1(8)
O1S	54(5)	61(6)	75(7)	-30(5)	3(5)	10(4)
C1S	68(11)	91(13)	126(18)	-20(12)	4(11)	8(10)
O11	126(12)	128(13)	113(11)	32(10)	27(10)	-46(11)
O12	58(6)	100(9)	54(6)	5(6)	13(5)	27(6)
O13	120(12)	96(10)	125(12)	19(10)	30(10)	-20(9)
N5	82(11)	103(13)	118(15)	43(12)	57(11)	27(9)
O2S	114(10)	64(7)	80(8)	14(6)	3(8)	-7(7)
C2S	120(18)	96(14)	87(13)	13(11)	0(13)	-8(13)

Table 4 Bond Lengths for TB(NO3)3-2 (MEOH SOLVATE).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tb1	O1	2.365(8)	C5	C6	1.519(17)
Tb1	O2	2.308(9)	C7	C8	1.43(2)
Tb1	O3[1]	2.372(8)	C7	C12	1.36(2)
Tb1	O4[1]	2.332(8)	C8	C9	1.39(3)
Tb1	O5	2.503(11)	C9	C10	1.36(4)
Tb1	O6	2.521(9)	C10	C11	1.33(3)
Tb1	O8	2.450(10)	C11	C12	1.46(3)
Tb1	O9	2.534(10)	C13	C14	1.43(3)
Tb1	N3	2.919(14)	C13	C18	1.35(3)
Tb1	N4	2.916(14)	C14	C15	1.39(3)
Tb1	O1S	2.392(9)	C15	C16	1.37(3)
P1	O2	1.48(2)	C16	C17	1.31(4)
P1	C2	1.76(2)	C17	C18	1.35(3)
P1	C7	1.75(3)	C13A	C14A	1.43(3)
P1	C13	1.88(2)	C13A	C18A	1.35(3)
P1A	O2	1.57(7)	C14A	C15A	1.39(3)
P1A	C2	1.89(6)	C15A	C16A	1.37(4)
P1A	C7	1.83(7)	C16A	C17A	1.31(4)
P1A	C13A	1.59(6)	C17A	C18A	1.35(3)
P2	O4	1.505(9)	C19	C20	1.41(3)
P2	C4	1.800(13)	C19	C24	1.39(2)

P2	C19	1.777(16)	C20	C21	1.37(2)
P2	C25	1.801(13)	C21	C22	1.42(3)
O1	C1	1.245(15)	C22	C23	1.31(3)
O3	C3	1.255(14)	C23	C24	1.42(2)
O5	N3	1.267(15)	C25	C26	1.38(2)
O6	N3	1.212(16)	C25	C30	1.38(2)
O7	N3	1.254(17)	C26	C27	1.42(2)
O8	N4	1.291(15)	C27	C28	1.36(3)
O9	N4	1.245(15)	C28	C29	1.42(3)
O10	N4	1.250(17)	C29	C30	1.40(2)
N1	C1	1.355(15)	O1S	C1S	1.47(2)
N1	C5	1.429(15)	O11	N5	1.246(11)
N2	C3	1.307(15)	O12	N5	1.178(12)
N2	C6	1.464(14)	O13	N5	1.255(12)
C1	C2	1.545(17)	O2S	C2S	1.39(2)
C3	C4	1.527(15)			

[1]1-X,1-Y,+Z

Table 5 Bond Angles for TB(NO3)3-2 (MEOH SOLVATE).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Tb1	O3[1]	75.4(3)	P2	O4	Tb1[1]	135.4(5)
O1	Tb1	O5	78.2(4)	N3	O5	Tb1	95.9(9)
O1	Tb1	O6	73.7(3)	N3	O6	Tb1	96.5(8)
O1	Tb1	O8	125.2(3)	N4	O8	Tb1	97.5(7)
O1	Tb1	O9	74.1(3)	N4	O9	Tb1	94.8(8)
O1	Tb1	N3	73.7(3)	C1	N1	C5	121.7(11)
O1	Tb1	N4	99.3(3)	C3	N2	C6	122.6(10)
O1	Tb1	O1S	138.5(3)	O5	N3	Tb1	58.5(8)
O2	Tb1	O1	75.4(3)	O6	N3	Tb1	59.1(7)
O2	Tb1	O3[1]	139.3(3)	O6	N3	O5	117.6(13)
O2	Tb1	O4[1]	141.5(3)	O6	N3	O7	121.4(13)
O2	Tb1	O5	78.3(4)	O7	N3	Tb1	178.9(12)
O2	Tb1	O6	123.5(4)	O7	N3	O5	121.0(14)
O2	Tb1	O8	90.6(4)	O8	N4	Tb1	56.4(7)
O2	Tb1	O9	72.9(3)	O9	N4	Tb1	60.0(7)
O2	Tb1	N3	101.4(4)	O9	N4	O8	116.2(12)
O2	Tb1	N4	79.6(4)	O9	N4	O10	121.9(13)
O2	Tb1	O1S	71.0(3)	O10	N4	Tb1	175.7(10)
O3[1]	Tb1	O5	122.1(3)	O10	N4	O8	121.9(12)
O3[1]	Tb1	O6	73.3(3)	O1	C1	N1	121.6(12)
O3[1]	Tb1	O8	83.6(3)	O1	C1	C2	122.0(11)
O3[1]	Tb1	O9	72.3(3)	N1	C1	C2	116.3(11)
O3[1]	Tb1	N3	97.0(4)	C1	C2	P1	107.7(10)
O3[1]	Tb1	N4	77.8(3)	C1	C2	P1A	115.2(19)
O3[1]	Tb1	O1S	145.4(3)	O3	C3	N2	123.9(10)
O4[1]	Tb1	O1	141.8(3)	O3	C3	C4	118.5(10)
O4[1]	Tb1	O3[1]	75.3(3)	N2	C3	C4	117.6(11)
O4[1]	Tb1	O5	97.3(4)	C3	C4	P2	111.7(9)

O4[1]	Tb1	O6	74.8(3)	N1	C5	C6	110.4(10)
O4[1]	Tb1	O8	74.8(3)	N2	C6	C5	108.0(10)
O4[1]	Tb1	O9	118.6(3)	C8	C7	P1	119.7(14)
O4[1]	Tb1	N3	86.1(4)	C8	C7	P1A	117(2)
O4[1]	Tb1	N4	97.9(4)	C12	C7	P1	120.6(15)
O4[1]	Tb1	O1S	71.4(3)	C12	C7	P1A	123(3)
O5	Tb1	O6	49.9(3)	C12	C7	C8	119.7(16)
O5	Tb1	O9	144.0(4)	C9	C8	C7	121.7(19)
O5	Tb1	N3	25.6(3)	C10	C9	C8	118(2)
O5	Tb1	N4	157.7(4)	C11	C10	C9	122(2)
O6	Tb1	O9	137.5(3)	C10	C11	C12	122(2)
O6	Tb1	N3	24.4(3)	C7	C12	C11	116.3(18)
O6	Tb1	N4	151.1(3)	C14	C13	P1	121.9(16)
O8	Tb1	O5	151.0(3)	C18	C13	P1	117.3(16)
O8	Tb1	O6	145.6(3)	C18	C13	C14	120.4(17)
O8	Tb1	O9	51.2(3)	C15	C14	C13	116(2)
O8	Tb1	N3	160.2(3)	C16	C15	C14	121(2)
O8	Tb1	N4	26.0(3)	C17	C16	C15	120(2)
O9	Tb1	N3	147.7(3)	C16	C17	C18	123(2)
O9	Tb1	N4	25.2(3)	C17	C18	C13	119(2)
N4	Tb1	N3	172.3(3)	C14A	C13A	P1A	121(4)
O1S	Tb1	O5	71.8(4)	C18A	C13A	P1A	117(4)
O1S	Tb1	O6	105.8(4)	C18A	C13A	C14A	121(2)
O1S	Tb1	O8	79.2(4)	C15A	C14A	C13A	116(2)
O1S	Tb1	O9	116.7(4)	C16A	C15A	C14A	122(3)
O1S	Tb1	N3	89.7(4)	C17A	C16A	C15A	120(3)
O1S	Tb1	N4	97.9(4)	C16A	C17A	C18A	123(3)
O2	P1	C2	116.0(13)	C17A	C18A	C13A	119(3)
O2	P1	C7	112.0(14)	C20	C19	P2	119.6(13)
O2	P1	C13	111.8(13)	C24	C19	P2	121.5(14)
C2	P1	C13	105.2(13)	C24	C19	C20	118.9(16)
C7	P1	C2	108.1(13)	C21	C20	C19	119(2)
C7	P1	C13	102.6(13)	C20	C21	C22	119(2)
O2	P1A	C2	105(3)	C23	C22	C21	123.8(19)
O2	P1A	C7	104(3)	C22	C23	C24	117(2)
O2	P1A	C13A	104(4)	C19	C24	C23	122(2)
C7	P1A	C2	99(3)	C26	C25	P2	117.0(11)
C13A	P1A	C2	111(4)	C30	C25	P2	121.3(12)
C13A	P1A	C7	131(4)	C30	C25	C26	121.7(14)
O4	P2	C4	110.1(6)	C25	C26	C27	118.3(16)
O4	P2	C19	113.4(7)	C28	C27	C26	121.0(18)
O4	P2	C25	111.5(6)	C27	C28	C29	120.0(16)
C19	P2	C4	108.5(7)	C30	C29	C28	118.8(15)
C19	P2	C25	109.3(7)	C25	C30	C29	119.9(17)
C25	P2	C4	103.6(7)	C1S	O1S	Tb1	130.4(11)
C1	O1	Tb1	139.0(8)	O11	N5	O13	120.6(17)
P1	O2	Tb1	134.8(8)	O12	N5	O11	116.6(17)
P1A	O2	Tb1	142(2)	O12	N5	O13	122.3(14)
C3	O3	Tb1[1]	142.0(8)				

[1]1-X,1-Y,+Z

Table 6 Hydrogen Bonds for TB(NO3)3-2 (MEOH SOLVATE).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O12[1]	0.88	2.06	2.941(14)	176.1
N2	H2	O6[2]	0.88	2.46	3.025(14)	122.2
N2	H2	O7[2]	0.88	2.26	3.093(16)	157.9
N2	H2	O13[1]	0.88	2.55	3.010(18)	113.7
C6	H6B	O6[2]	0.99	2.57	3.087(15)	112.2
C17A	H17A	O11[3]	0.95	2.24	2.92(5)	127.3
C18A	H18A	O11[3]	0.95	2.47	3.02(5)	116.1
O1S	H1S	O2S[3]	0.875(14)	1.84(2)	2.704(16)	169(6)
O2S	H2S	O11	0.84	1.98	2.80(2)	163.5

[1]1-X,1-Y,+Z; [2]+Y,1-X,1-Z; [3]1/2-X,1/2+Y,3/2-Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for TB(NO3)3-2 (MEOH SOLVATE).

Atom	*x*	*y*	*z*	U(eq)
H1	6409.03	6340.5	6175.34	55
H2	7200.79	5692.69	5264.66	52
H2AA	6014.52	6241.58	6944.39	60
H2AB	5305.06	5724.98	6970.01	60
H2BC	6017.43	6246.09	6934.13	60
H2BD	5328.7	5710.68	6956.19	60
H4A	7880.41	4975.97	6179.63	57
H4B	8123.23	5141.16	5629.21	57
H5A	6303.71	6737.73	5390.9	53
H5B	5447.79	6552.01	5413.16	53
H6A	5750.75	5267.41	5429.83	49
H6B	6012.15	5652.34	4932.82	49
H8	6491.56	7250.81	7368.13	98
H9	7186.85	8328.73	7388.46	137
H10	6691.05	9369.23	7040.08	139
H11	5486.32	9444.45	6881.47	116
H12	4713.96	8371.98	6887.6	81
H14	5793.63	5789.62	7795.57	83
H15	5897.73	5668.03	8648.88	108
H16	5235.25	6420.11	9163.23	122
H17	4496.29	7279.21	8853.65	125
H18	4412.07	7501.81	8035.14	104
H14A	5501.89	5633.73	7765.96	88
H15A	5240.82	5295.6	8577.04	108
H16A	4431.96	5964.32	9043.12	122
H17A	3821.57	6906.11	8713.4	125
H18A	4028.77	7292.16	7932.78	96
H20	7926.46	2564.09	5237.39	99
H21	7946.59	2270	4409.99	115
H22	8125.79	3203.81	3830.39	121

H23	8372.34	4368.95	4043.63	109
H24	8393.19	4666.04	4885.99	90
H26	8743.05	3920.14	6709.44	92
H27	9949.37	4002.55	7024.93	116
H28	10939.47	4063.49	6507.88	116
H29	10761.57	4009.86	5647.83	106
H30	9567.55	3836.88	5342.27	91
H1S	3090(30)	7770(50)	7030(30)	95
H1SA	2350.95	8206.34	6340.22	143
H1SB	2125.58	8322.03	6899.12	143
H1SC	1809.47	7640.1	6600.2	143
H2S	1644.11	3269.4	7161.3	129
H2SA	1207.63	4224.42	7767.46	151
H2SB	1524.82	4357.92	7230.61	151
H2SC	2072.26	4263.24	7681.71	151

Table 8 Atomic Occupancy for TB(NO3)3-2 (MEOH SOLVATE).

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
P1	0.733(17)	P1A	0.267(17)	H2AA	0.733(17)
H2AB	0.733(17)	H2BC	0.267(17)	H2BD	0.267(17)
C13	0.733(17)	C14	0.733(17)	H14	0.733(17)
C15	0.733(17)	H15	0.733(17)	C16	0.733(17)
H16	0.733(17)	C17	0.733(17)	H17	0.733(17)
C18	0.733(17)	H18	0.733(17)	C13A	0.267(17)
C14A	0.267(17)	H14A	0.267(17)	C15A	0.267(17)
H15A	0.267(17)	C16A	0.267(17)	H16A	0.267(17)
C17A	0.267(17)	H17A	0.267(17)	C18A	0.267(17)
H18A	0.267(17)				

Crystal structure determination of [TB(NO3)3-2 (MEOH SOLVATE)]

Crystal Data for $C_{64}H_{76}N_{10}O_{30}P_4Tb_2$ (M =1907.06 g/mol): tetragonal, space group P-42$_1$c (no. 114), a = 18.2898(4) Å, c = 27.4073(6) Å, V = 9168.2(4) Å^3, Z = 4, T = 172.97 K, μ(CuKα) = 8.794 mm^{-1}, *Dcalc* = 1.382 g/cm^3, 111590 reflections measured (5.81° ≤ 2Θ ≤ 136.676°), 8408 unique (R_{int} = 0.1335, R_{sigma} = 0.0634) which were used in all calculations. The final R_1 was 0.0638 (I > 2σ(I)) and wR_2 was 0.2052 (all data).

Refinement model description

Number of restraints – 165, number of constraints – unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups, All C(H,H) groups, All C(H,H,H,H) groups, All N(H) groups

At 1.5 times of:

All C(H,H,H) groups, All O(H) groups

2. Restrained distances

O12-N5 = O11-N5 = O13-N5

1.25 with sigma of 0.01

O1S-H1S

0.87 with sigma of 0.01

C1S-H1S

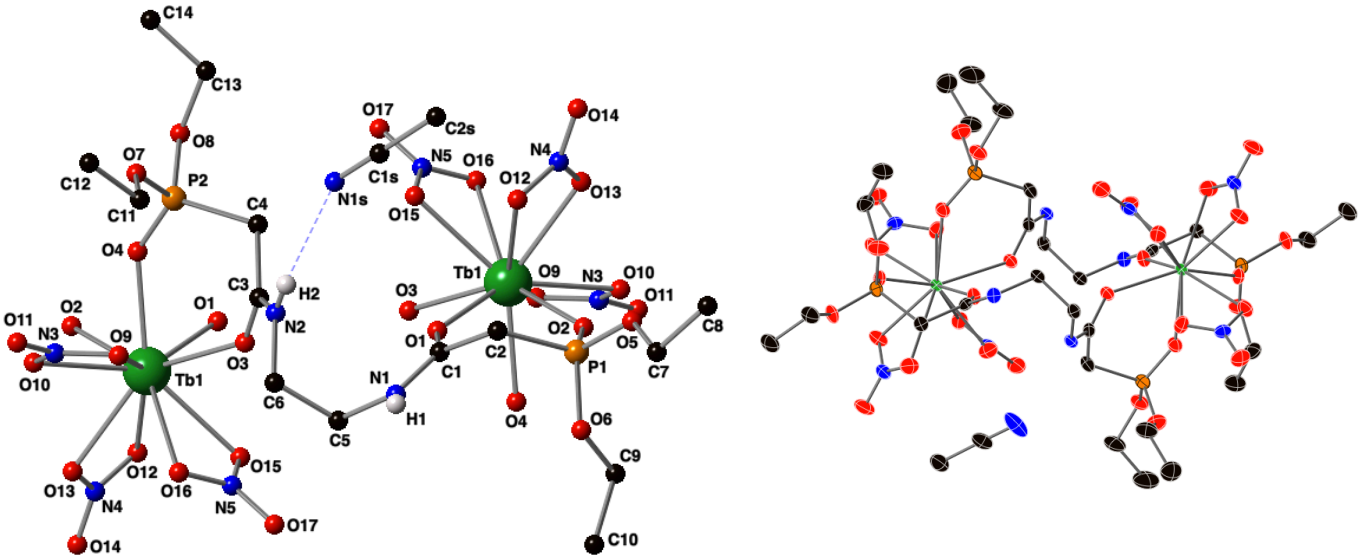
1.931945 with sigma of 0.02

Tb1-H1S

2.938614 with sigma of 0.02
3. Restrained planarity
C13A, C14A, C15A, C16A, C17A, C18A
with sigma of 0.1
4. Rigid bond restraints
C13A, C18A, C17A, C16A, C15A, C14A
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
C13, C18, C17, C16, C15, C14
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
C19, C20, C21, C22, C23, C24
with sigma for 1-2 distances of 0.01 and sigma for 1-3 distances of 0.01
5. Uiso/Uaniso restraints and constraints
C13A ≈ C18A ≈ C17A ≈ C16A ≈ C15A ≈ C14A: within 2A with
sigma of 0.02 and sigma for terminal atoms of 0.04
C13 ≈ C18 ≈ C17 ≈ C16 ≈ C15 ≈ C14: within 2A with sigma of
0.02 and sigma for terminal atoms of 0.04
C19 ≈ C20 ≈ C21 ≈ C22 ≈ C23 ≈ C24: within 2A with sigma of
0.02 and sigma for terminal atoms of 0.04
Uanis(C13) = Uanis(C13A)
Uanis(C17) = Uanis(C17A)
Uanis(C16) = Uanis(C16A)
Uanis(C15) = Uanis(C15A)
Uanis(P1A) = Uanis(P1)
6. Same fragment restrains
{C13, C14, C15, C16, C17, C18} sigma for 1-2: 0.01, 1-3: 0.02
as
{C13A, C14A, C15A, C16A, C17A, C18A}
7. Others
Sof(P1A)=Sof(H2BC)=Sof(H2BD)=Sof(C13A)=Sof(C14A)=Sof(H14A)=Sof(C15A)=
Sof(H15A)=Sof(C16A)=Sof(H16A)=Sof(C17A)=Sof(H17A)=Sof(C18A)=Sof(H18A)=1-FVAR(1)
Sof(P1)=Sof(H2AA)=Sof(H2AB)=Sof(C13)=Sof(C14)=Sof(H14)=Sof(C15)=Sof(H15)=
Sof(C16)=Sof(H16)=Sof(C17)=Sof(H17)=Sof(C18)=Sof(H18)=FVAR(1)
8.a Secondary CH2 refined with riding coordinates:
C2(H2AA,H2AB), C2(H2BC,H2BD), C4(H4A,H4B), C5(H5A,H5B), C6(H6A,H6B)
8.b Aromatic/amide H refined with riding coordinates:
N1(H1), N2(H2), C8(H8), C9(H9), C10(H10), C11(H11), C12(H12), C14(H14),
C15(H15), C16(H16), C17(H17), C18(H18), C14A(H14A), C15A(H15A), C16A(H16A),
C17A(H17A), C18A(H18A), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24),
C26(H26), C27(H27), C28(H28), C29(H29), C30(H30)
8.c Idealised Me refined as rotating group:
C1S(H1SA,H1SB,H1SC), C2S(H2SA,H2SB,H2SC)
8.d Idealised tetrahedral OH refined as rotating group:
O2S(H2S)

D. $Tb(NO_3)_3$-1

The figure on the left depicts the atom numbering scheme of the 2:2 $Tb(NO_3)_3$-1 complex using a ball and stick model with standard CPK colors (Tb atoms are colored green). Only one ligand of the major component is shown for clarity, although all atoms of the inner coordination sphere of each metal center are shown. Hydrogen atoms bonded to carbon atoms are not shown for clarity, and hydrogen bonds are depicted with blue, dashed lines.
The figure on the right depicts the thermal ellipsoids of all atoms of the 2:2 complex, which are shown at the 40% probability level.



Refinement notes

(1) The electron density corresponding to C9 of one ethyl group was positionally disordered. This disordered was modeled over two positions, and the relative occupancy of each component was determined to be 0.610(12) to 0.390(12) by refining against a free variable.

Experimental

Single crystals of $C_{32}H_{66}N_{12}O_{34}P_4Tb_2$ (**$Tb(NO_3)_3$-1)** were grown by vapor diffusion of diethyl ether into a solution of the complex in acetonitrile. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

$Tb(NO_3)_3$-1

Table 1 Crystal data and structure refinement for $Tb(NO_3)_3$-1

CCDC number	2003373
Empirical formula	$C_{32}H_{66}N_{12}O_{34}P_4Tb_2$
Formula weight	1604.68

Temperature/K	173(2)
Crystal system	monoclinic
Space group	C2/c
a/Å	32.3189(5)
b/Å	12.5255(2)
c/Å	16.4158(3)
α/°	90
β/°	116.1620(10)
γ/°	90
Volume/Å^3	5964.48(18)
Z	4
ρ_{calc}g/cm^3	1.787
μ/mm^{-1}	13.430
F(000)	3216.0
Crystal size/mm^3	0.264 × 0.173 × 0.103
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.094 to 140.374
Index ranges	-39 ≤ h ≤ 39, -15 ≤ k ≤ 15, -17 ≤ l ≤ 19
Reflections collected	44653
Independent reflections	5582 [R_{int} = 0.0588, R_{sigma} = 0.0348]
Data/restraints/parameters	5582/0/402
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0287, wR_2 = 0.0636
Final R indexes [all data]	R_1 = 0.0336, wR_2 = 0.0653
Largest diff. peak/hole / e Å^{-3}	0.57/-0.75

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TB(NO3)3-1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Tb1	3494.3(2)	3928.6(2)	6790.8(2)	16.92(6)
P1	4369.2(3)	4582.5(7)	6087.1(6)	22.55(18)
P2	1288.3(3)	3916.2(7)	3394.1(6)	25.04(18)
O1	3354.7(8)	3753.4(19)	5248.3(15)	24.4(5)
O2	4217.2(8)	4340.2(19)	6793.9(16)	24.5(5)
O3	2124.9(8)	2341.3(18)	3770.2(16)	24.9(5)
O4	1154.7(8)	2781.3(19)	3209.2(17)	29.6(6)
O5	4691.2(8)	5574(2)	6365.2(17)	29.2(6)
O6	4628.0(10)	3658(2)	5868(2)	38.4(7)
O7	1098.5(10)	4649(2)	2535.1(19)	38.4(6)
O8	1066.0(9)	4411(2)	3980.4(19)	32.9(6)
O9	3491.2(8)	2762(2)	8087.8(17)	32.9(6)
O10	4086.9(9)	3749(2)	8428.6(17)	31.7(6)
O11	4063.5(10)	2649(2)	9432.3(18)	40.1(7)
O12	3504.6(10)	5948(2)	6201.3(18)	37.7(6)
O13	3690.3(10)	5689.1(19)	7612.7(18)	31.4(6)
O14	3596.9(11)	7315(2)	7084(2)	46.0(8)
O15	2711.2(9)	4819(2)	5922.6(19)	38.2(6)

O16	2883.4(9)	4493(2)	7319.8(18)	33.1(6)
O17	2176.0(9)	4888(2)	6376(2)	43.9(7)
N1	3433.4(10)	3503(2)	3969(2)	23.1(6)
N2	2405.3(10)	3725(2)	3300(2)	23.9(6)
N3	3885.2(10)	3039(2)	8674(2)	26.7(6)
N4	3597.7(10)	6350(2)	6960(2)	28.1(7)
N5	2579.5(11)	4734(2)	6538(2)	29.9(7)
C1	3535.0(11)	3993(3)	4741(2)	21.3(7)
C2	3895.3(12)	4871(3)	5005(2)	24.0(7)
C3	2156.9(11)	3322(3)	3687(2)	23.3(7)
C4	1902.6(12)	4087(3)	4014(3)	28.0(8)
C5	3098.8(12)	2641(3)	3619(2)	23.1(7)
C6	2634.7(12)	3027(3)	2917(2)	23.6(7)
C7	5031.0(14)	5794(3)	6028(3)	37.1(9)
C8	5257.3(15)	6821(3)	6429(4)	48.5(12)
C9	4884(2)	2830(6)	6503(5)	39(2)
C10	4979.3(17)	1941(4)	6010(4)	55.0(13)
C11	1316.7(16)	4895(3)	1956(3)	43.1(10)
C12	979.7(17)	5530(4)	1181(3)	51.5(12)
C13	1088.6(16)	5571(3)	4144(3)	44.9(11)
C14	624(2)	6041(4)	3674(5)	74.7(18)
C9A	4582(4)	2605(8)	5893(8)	37(3)
N1S	2481.1(18)	6111(3)	3770(3)	62.1(12)
C1S	2702.8(16)	6812(3)	4143(3)	37.4(9)
C2S	2983.7(16)	7722(3)	4599(3)	42.8(10)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for TB(NO3)3-1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb1	19.61(10)	16.49(10)	17.27(10)	-1.45(7)	10.53(7)	-1.74(8)
P1	20.6(4)	24.7(4)	24.2(5)	-2.8(3)	11.6(3)	-4.5(3)
P2	25.9(4)	21.5(4)	31.8(5)	-2.9(4)	16.4(4)	-0.4(4)
O1	27.4(12)	29.8(13)	20.1(12)	-2.9(9)	14.1(10)	-7.8(10)
O2	20.3(12)	31.2(13)	22.0(12)	-1.1(9)	9.2(9)	-5.1(10)
O3	24.4(12)	21.8(13)	30.2(13)	-1.7(10)	13.7(10)	-3.4(10)
O4	24.7(13)	26.4(13)	39.5(15)	-6.4(10)	15.7(11)	-1.2(10)
O5	26.6(13)	33.3(14)	33.3(14)	-8.5(11)	18.3(11)	-11.8(11)
O6	48.2(17)	32.2(15)	45.3(17)	3.7(12)	30.2(14)	9.6(12)
O7	37.8(15)	41.2(16)	40.6(16)	9.5(12)	21.2(13)	7.6(13)
O8	36.5(14)	25.6(13)	45.7(17)	-7.7(11)	26.4(13)	-2.5(11)
O9	24.5(13)	40.8(16)	30.4(14)	4.6(11)	9.5(11)	-3.2(11)
O10	38.5(15)	28.4(14)	27.7(14)	0.6(10)	14.0(11)	-8.6(11)
O11	46.6(17)	44.3(17)	24.4(14)	13.5(12)	11.3(12)	3.0(13)
O12	47.1(16)	35.4(15)	29.0(15)	-0.8(12)	15.3(12)	6.3(13)
O13	48.1(16)	23.2(12)	33.4(15)	-2.4(10)	27.5(12)	-4.1(11)
O14	62(2)	21.4(14)	53.3(19)	-3.3(12)	24.7(15)	0.8(13)
O15	34.5(15)	39.1(16)	43.5(17)	11.1(12)	19.4(13)	6.6(12)
O16	33.4(14)	34.2(14)	33.3(15)	-6.0(11)	16.0(12)	2.8(11)
O17	27.9(15)	33.5(15)	75(2)	-1.2(14)	26.8(14)	2.7(12)

N1	25.4(15)	28.2(15)	20.2(16)	-1.2(12)	14.2(12)	-2.8(12)
N2	24.8(15)	17.5(15)	29.5(16)	-1.0(11)	11.8(12)	-2.6(12)
N3	31.4(16)	26.5(16)	24.1(16)	2.7(12)	13.9(13)	6.3(13)
N4	30.2(16)	21.3(15)	36.2(19)	-3.6(12)	17.9(14)	-2.7(12)
N5	29.7(17)	17.3(14)	46(2)	-1.9(13)	19.3(15)	-1.3(12)
C1	20.8(16)	25.1(17)	16.7(16)	2.7(13)	7.1(12)	2.6(14)
C2	27.4(18)	26.2(18)	21.7(18)	0.2(13)	13.8(14)	-2.5(14)
C3	20.1(16)	24.4(18)	23.7(18)	-4.4(13)	7.9(13)	-3.6(14)
C4	27.5(18)	24.2(18)	35(2)	-8.8(15)	16.7(15)	-6.7(15)
C5	27.2(18)	19.8(17)	25.7(18)	-2.3(13)	14.8(14)	-2.4(14)
C6	25.5(17)	24.4(18)	22.6(18)	-1.6(13)	12.0(14)	-4.3(14)
C7	33(2)	35(2)	54(3)	1.4(18)	29.2(19)	-2.6(17)
C8	34(2)	35(2)	84(4)	-1(2)	32(2)	-8.8(19)
C9	26(4)	42(4)	48(5)	4(3)	17(4)	6(3)
C10	51(3)	35(2)	75(4)	-4(2)	24(3)	9(2)
C11	54(3)	35(2)	48(3)	11.0(19)	30(2)	6(2)
C12	55(3)	53(3)	44(3)	10(2)	20(2)	1(2)
C13	54(3)	27(2)	63(3)	-14.2(19)	35(2)	-2.8(19)
C14	71(4)	41(3)	113(5)	-8(3)	41(4)	21(3)
C9A	40(7)	25(5)	50(8)	-6(4)	25(6)	-2(4)
N1S	103(4)	40(2)	58(3)	-14(2)	49(3)	-31(2)
C1S	60(3)	27(2)	36(2)	3.6(17)	31(2)	-1.8(19)
C2S	58(3)	31(2)	38(2)	-0.5(17)	19(2)	-6.4(19)

Table 4 Bond Lengths for TB(NO3)3-1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tb1	O1	2.378(2)	O7	C11	1.445(5)
Tb1	O2	2.390(2)	O8	C13	1.472(5)
Tb1	O3[1]	2.400(2)	O9	N3	1.260(4)
Tb1	O4[1]	2.424(2)	O10	N3	1.268(4)
Tb1	O9	2.586(3)	O11	N3	1.220(4)
Tb1	O10	2.531(3)	O12	N4	1.251(4)
Tb1	O12	2.714(3)	O13	N4	1.281(4)
Tb1	O13	2.516(2)	O14	N4	1.226(4)
Tb1	O15	2.549(3)	O15	N5	1.262(4)
Tb1	O16	2.581(3)	O16	N5	1.261(4)
P1	O2	1.477(2)	O17	N5	1.226(4)
P1	O5	1.554(2)	N1	C1	1.312(4)
P1	O6	1.560(3)	N1	C5	1.455(4)
P1	C2	1.797(3)	N2	C3	1.324(5)
P2	O4	1.478(3)	N2	C6	1.455(4)
P2	O7	1.564(3)	C1	C2	1.519(5)
P2	O8	1.561(3)	C3	C4	1.507(5)
P2	C4	1.800(4)	C5	C6	1.513(5)
O1	C1	1.246(4)	C7	C8	1.483(6)
O3	Tb1[1]	2.400(2)	C9	C10	1.487(8)
O3	C3	1.245(4)	C10	C9A	1.468(11)
O4	Tb1[1]	2.424(2)	C11	C12	1.488(6)
O5	C7	1.458(4)	C13	C14	1.476(7)

O6	C9	1.444(7)	N1S	C1S	1.129(6)
O6	C9A	1.331(10)	C1S	C2S	1.443(6)

[1]1/2-X,1/2-Y,1-Z

Table 5 Bond Angles for TB(NO3)3-1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Tb1	O2	75.44(8)	O6	P1	C2	103.39(16)
O1	Tb1	O3[1]	78.21(8)	O4	P2	O7	114.63(16)
O1	Tb1	O4[1]	77.73(8)	O4	P2	O8	109.67(14)
O1	Tb1	O9	139.17(8)	O4	P2	C4	112.32(16)
O1	Tb1	O10	145.31(9)	O7	P2	C4	109.64(17)
O1	Tb1	O12	74.50(8)	O8	P2	O7	102.62(15)
O1	Tb1	O13	122.45(8)	O8	P2	C4	107.29(16)
O1	Tb1	O15	76.68(9)	C1	O1	Tb1	139.9(2)
O1	Tb1	O16	124.70(8)	P1	O2	Tb1	134.89(14)
O2	Tb1	O3[1]	142.45(8)	C3	O3	Tb1[1]	135.0(2)
O2	Tb1	O4[1]	74.55(8)	P2	O4	Tb1[1]	139.09(14)
O2	Tb1	O9	118.60(8)	C7	O5	P1	124.0(2)
O2	Tb1	O10	74.69(8)	C9	O6	P1	124.2(3)
O2	Tb1	O12	68.53(8)	C9A	O6	P1	130.6(5)
O2	Tb1	O13	78.18(8)	C11	O7	P2	127.4(3)
O2	Tb1	O15	129.45(8)	C13	O8	P2	120.3(3)
O2	Tb1	O16	146.31(8)	N3	O9	Tb1	95.92(19)
O3[1]	Tb1	O4[1]	74.06(8)	N3	O10	Tb1	98.38(19)
O3[1]	Tb1	O9	68.65(8)	N4	O12	Tb1	93.20(19)
O3[1]	Tb1	O10	117.45(8)	N4	O13	Tb1	101.96(19)
O3[1]	Tb1	O12	128.34(8)	N5	O15	Tb1	96.8(2)
O3[1]	Tb1	O13	139.19(8)	N5	O16	Tb1	95.2(2)
O3[1]	Tb1	O15	67.72(9)	C1	N1	C5	123.7(3)
O3[1]	Tb1	O16	71.24(8)	C3	N2	C6	120.7(3)
O4[1]	Tb1	O9	70.87(9)	O9	N3	O10	116.0(3)
O4[1]	Tb1	O10	77.66(8)	O11	N3	O9	122.2(3)
O4[1]	Tb1	O12	138.10(9)	O11	N3	O10	121.8(3)
O4[1]	Tb1	O13	140.11(9)	O12	N4	O13	115.9(3)
O4[1]	Tb1	O15	137.37(9)	O14	N4	O12	123.0(3)
O4[1]	Tb1	O16	132.01(9)	O14	N4	O13	121.0(3)
O9	Tb1	O12	145.63(8)	O16	N5	O15	116.6(3)
O10	Tb1	O9	49.53(8)	O17	N5	O15	121.0(3)
O10	Tb1	O12	109.83(8)	O17	N5	O16	122.4(3)
O10	Tb1	O15	137.10(9)	O1	C1	N1	122.7(3)
O10	Tb1	O16	89.98(9)	O1	C1	C2	120.6(3)
O13	Tb1	O9	98.35(8)	N1	C1	C2	116.7(3)
O13	Tb1	O10	67.34(8)	C1	C2	P1	110.4(2)
O13	Tb1	O12	48.28(8)	O3	C3	N2	121.7(3)
O13	Tb1	O15	82.51(9)	O3	C3	C4	120.2(3)
O13	Tb1	O16	68.20(8)	N2	C3	C4	118.0(3)
O15	Tb1	O9	110.13(8)	C3	C4	P2	111.2(2)
O15	Tb1	O12	63.79(9)	N1	C5	C6	112.2(3)

O15	Tb1	O16	49.48(9)	N2	C6	C5	112.6(3)
O16	Tb1	O9	66.20(8)	O5	C7	C8	107.6(3)
O16	Tb1	O12	89.79(9)	O6	C9	C10	109.6(5)
O2	P1	O5	110.19(14)	O7	C11	C12	106.9(4)
O2	P1	O6	115.22(15)	O8	C13	C14	109.9(4)
O2	P1	C2	112.55(15)	O6	C9A	C10	117.6(8)
O5	P1	O6	107.63(15)	N1S	C1S	C2S	178.6(5)
O5	P1	C2	107.36(15)				

[1]1/2-X,1/2-Y,1-Z

Table 6 Hydrogen Bonds for TB(NO3)3-1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
C2	H2A	O12	0.99	2.43	3.075(4)	122.4
C4	H4A	N1S	0.99	2.37	3.277(5)	152.3
C4	H4B	O15	0.99	2.55	3.204(5)	123.3
C2S	H2SB	O12	0.98	2.50	3.284(5)	137.0
N1	H1	O13[1]	0.80(4)	2.09(4)	2.881(4)	172(4)
N2	H2	N1S	0.81(4)	2.33(4)	3.070(5)	152(4)

[1]+X,1-Y,-1/2+Z

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for TB(NO3)3-1.

Atom	*x*	*y*	*z*	U(eq)
H2A	3754	5562	5037	29
H2B	4009	4932	4538	29
H4A	1985	4829	3937	34
H4B	1998	3966	4668	34
H5A	3061	2307	4128	28
H5B	3217	2090	3344	28
H6A	2677	3417	2434	28
H6B	2435	2402	2634	28
H7A	4878	5845	5357	45
H7B	5262	5214	6207	45
H8A	5031	7401	6197	73
H8B	5510	6956	6265	73
H8C	5380	6786	7092	73
H9A	4704	2561	6816	46
H9B	5178	3124	6967	46
H10A	4687	1646	5558	83
H10B	5154	1382	6442	83
H10C	5159	2210	5705	83
H10D	5075	2115	5536	83
H10E	4893	1186	5965	83
H10F	5235	2080	6608	83
H11A	1397	4230	1733	52
H11B	1602	5311	2294	52

H12A	1119	5735	781	77
H12B	895	6174	1412	77
H12C	703	5100	841	77
H13A	1296	5905	3918	54
H13B	1216	5710	4803	54
H14A	506	5936	3018	112
H14B	639	6806	3807	112
H14C	417	5692	3884	112
H9AA	4318	2386	5321	44
H9AB	4502	2438	6395	44
H2SA	3196	7880	4336	64
H2SB	3160	7562	5247	64
H2SC	2785	8342	4525	64
H1	3531(13)	3720(30)	3630(30)	18(10)
H2	2434(14)	4360(30)	3250(30)	30(11)

Table 8 Atomic Occupancy for TB(NO3)3-1.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C9	0.610(12)	H9A	0.610(12)	H9B	0.610(12)
H10A	0.610(12)	H10B	0.610(12)	H10C	0.610(12)
H10D	0.390(12)	H10E	0.390(12)	H10F	0.390(12)
C9A	0.390(12)	H9AA	0.390(12)	H9AB	0.390(12)

Crystal structure determination of [TB(NO3)3-1]

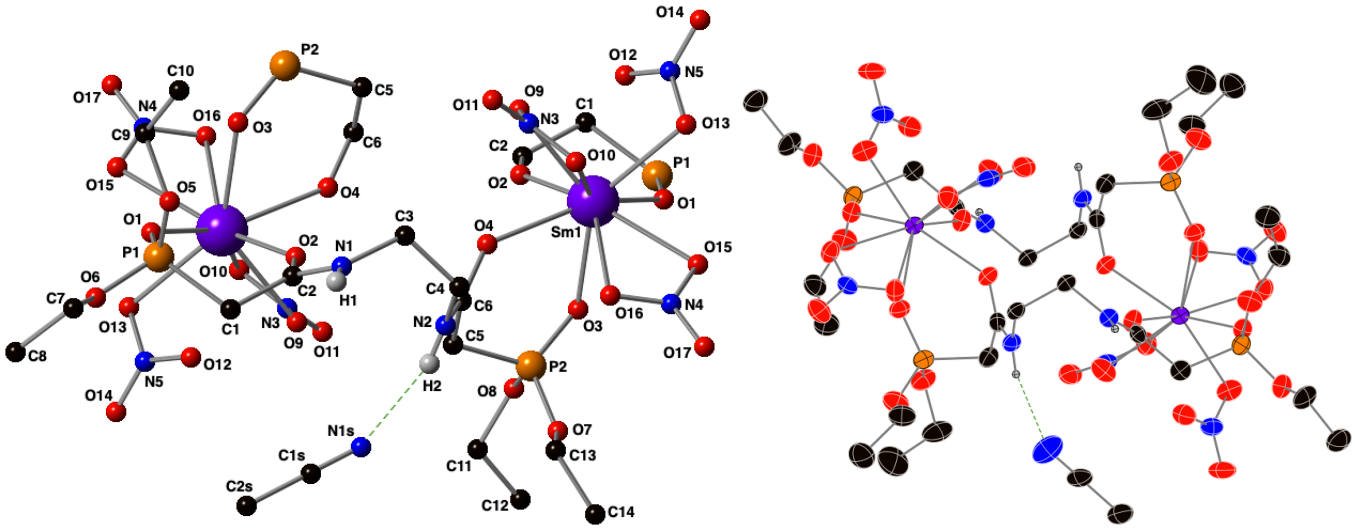
Crystal Data for $C_{32}H_{66}N_{12}O_{34}P_4Tb_2$ (M =1604.68 g/mol): monoclinic, space group C2/c (no. 15), a = 32.3189(5) Å, b = 12.5255(2) Å, c = 16.4158(3) Å, β = 116.1620(10)°, V = 5964.48(18) Å^3, Z = 4, T = 173.02 K, μ(CuKα) = 13.430 mm^{-1}, *Dcalc* = 1.787 g/cm^3, 44653 reflections measured (6.094° ≤ 2Θ ≤ 140.374°), 5582 unique (R_{int} = 0.0588, R_{sigma} = 0.0348) which were used in all calculations. The final R_1 was 0.0287 (I > 2σ(I)) and wR_2 was 0.0653 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.
Details:
1. Fixed Uiso
At 1.2 times of:
All C(H,H) groups
At 1.5 times of:
All C(H,H,H) groups, All C(H,H,H,H,H,H) groups
2. Others
Sof(H10D)=Sof(H10E)=Sof(H10F)=Sof(C9A)=Sof(H9AA)=Sof(H9AB)=1-FVAR(1)
Sof(C9)=Sof(H9A)=Sof(H9B)=Sof(H10A)=Sof(H10B)=Sof(H10C)=FVAR(1)
3.a Secondary CH2 refined with riding coordinates:
C2(H2A,H2B), C4(H4A,H4B), C5(H5A,H5B), C6(H6A,H6B), C7(H7A,H7B), C9(H9A,H9B), C11(H11A,H11B), C13(H13A,H13B), C9A(H9AA,H9AB)
3.b Idealised Me refined as rotating group:
C8(H8A,H8B,H8C), C10(H10A,H10B,H10C), C10(H10D,H10E,H10F), C12(H12A,H12B, H12C), C14(H14A,H14B,H14C), C2S(H2SA,H2SB,H2SC)

E. $Sm(NO_3)_3$-1

The figure on the left depicts the atom numbering scheme of the 2:2 **$Sm(NO_3)_3$-1** complex using a ball and stick model with standard CPK colors (Sm atoms are colored purple). The electron density corresponding to the methylene carbon C9 was disordered, and modeled over two positions. The occupancy of this atom was refined against a free variable to give a ratio of 62.9:37.1. The N1-H1 bond was restrained using a DFIX in ShelXL command to give a bond length that agrees with known values. Hydrogen atoms bonded to carbon atoms are not shown for clarity, and hydrogen bonds are depicted with green, dashed lines. The figure on the right depicts the thermal ellipsoids of all atoms of the 2:2 complex, which are shown at the 40% probability level.



Experimental

Single crystals of $C_{32}H_{66}N_{12}O_{34}P_4Sm_2$ **[SM(NO3)3-1]** were grown by slow diffusion of diethyl ether into an acetonitrile solution of the complex. A suitable crystal was selected and mounted using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [SM(NO3)3-1]

Crystal Data for $C_{32}H_{66}N_{12}O_{34}P_4Sm_2$ (M =1587.54 g/mol): monoclinic, space group C2/c (no. 15), a = 32.318(11) Å, b = 12.538(4) Å, c = 16.447(6) Å, β = 116.217(4)°, V = 5979(4) Å^3, Z = 4, T = 173(2) K, μ(MoKα) = 2.154 mm^{-1}, *Dcalc* = 1.764 g/cm^3, 26038 reflections measured (3.54° ≤ 2Θ ≤ 52.802°), 6120 unique (R_{int} = 0.0770, R_{sigma} = 0.0704) which were used in all calculations. The final R_1 was 0.0532 (I > 2σ(I)) and wR_2 was 0.1487 (all data).

Table 1 Crystal data and structure refinement for SM(NO3)3-1.

CCDC code	2003370
Empirical formula	$C_{32}H_{66}N_{12}O_{34}P_4Sm_2$
Formula weight	1587.54
Temperature/K	173(2)

Crystal system	monoclinic
Space group	C2/c
a/Å	32.318(11)
b/Å	12.538(4)
c/Å	16.447(6)
α/°	90
β/°	116.217(4)
γ/°	90
Volume/Å^3	5979(4)
Z	4
ρ_{calc}g/cm^3	1.764
μ/mm^{-1}	2.154
F(000)	3192.0
Crystal size/mm^3	0.279 × 0.218 × 0.082
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.54 to 52.802
Index ranges	-40 ≤ h ≤ 40, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	26038
Independent reflections	6120 [R_{int} = 0.0770, R_{sigma} = 0.0704]
Data/restraints/parameters	6120/1/402
Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0532, wR_2 = 0.1296
Final R indexes [all data]	R_1 = 0.0776, wR_2 = 0.1487
Largest diff. peak/hole / e Å^{-3}	3.54/-0.79

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for SM(NO3)3-1. U_{eq} is defined as 1/3 of of the trace of the 34rthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Sm1	3493.7(2)	6067.2(2)	6793.8(2)	26.46(13)
P1	4370.3(6)	5416.9(14)	6087.5(12)	32.6(4)
P2	1288.1(6)	6079.8(12)	3387.0(13)	33.1(4)
O1	4219.4(15)	5659(4)	6795(3)	34.2(10)
O2	3353.9(16)	6242(3)	5248(3)	33.5(11)
O3	1157.7(15)	7211(3)	3204(3)	38.0(11)
O4	2128.7(15)	7651(3)	3774(3)	36.1(10)
O5	4626.9(18)	6338(4)	5873(3)	46.4(13)
O6	4692.7(16)	4429(4)	6367(3)	38.7(11)
O7	1104.8(18)	5343(4)	2543(3)	50.0(13)
O8	1071.7(17)	5581(4)	3982(3)	46.2(13)
O9	2706.5(18)	5181(4)	5924(3)	51.0(13)
O10	2882.1(17)	5486(4)	7308(3)	45.3(12)

O11	2170.7(17)	5111(4)	6370(4)	51.7(14)
O12	3504.9(19)	4050(4)	6209(3)	45.3(13)
O13	3694.6(18)	4297(4)	7623(3)	41.7(12)
O14	3593.9(19)	2701(4)	7091(4)	54.8(14)
O15	4088.9(16)	6248(4)	8440(3)	39.0(11)
O16	3487.0(16)	7236(4)	8092(3)	41.8(12)
O17	4061.9(17)	7346(4)	9429(3)	49.1(13)
N1	3438.7(18)	6505(4)	3976(3)	29.6(12)
N2	2409.2(19)	6265(5)	3297(4)	31.8(13)
N3	2575(2)	5262(4)	6537(5)	40.0(14)
N4	3884.1(19)	6961(4)	8673(3)	32.6(12)
N5	3595(2)	3649(5)	6958(4)	36.6(14)
C1	3897(2)	5131(5)	5011(4)	34.4(15)
C2	3535(2)	6012(5)	4744(4)	27.8(14)
C3	3100(2)	7363(5)	3620(4)	30.5(14)
C4	2637(2)	6966(5)	2920(4)	30.4(14)
C5	1900(2)	5919(5)	4000(5)	36.9(16)
C6	2167(2)	6676(5)	3693(4)	30.6(14)
C7	5038(3)	4188(6)	6042(6)	49(2)
C8	5253(3)	3171(6)	6408(6)	61(2)
C9	4894(4)	7158(10)	6509(9)	47(4)
C10	4979(3)	8057(6)	6010(6)	61(2)
C11	1087(3)	4445(6)	4135(6)	61(2)
C12	626(4)	3967(7)	3667(9)	91(4)
C13	1320(3)	5111(6)	1956(5)	51(2)
C14	974(3)	4454(7)	1175(6)	66(2)
C9A	4576(7)	7409(14)	5892(15)	41(6)
N1S	2480(3)	3888(6)	3780(6)	70(2)
C1S	2704(3)	3185(6)	4140(5)	45.1(18)
C2S	2985(3)	2286(6)	4603(5)	54(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for SM(NO3)3-1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sm1	29.8(2)	26.4(2)	26.9(2)	1.48(13)	15.88(16)	1.64(13)
P1	30.5(9)	36.6(9)	33.4(9)	3.6(7)	16.5(8)	4.3(8)
P2	34.6(10)	29.3(9)	40.8(10)	2.3(7)	21.5(8)	1.4(7)
O1	35(3)	41(3)	29(2)	1(2)	17(2)	5(2)
O2	35(3)	43(3)	31(2)	5(2)	22(2)	10(2)
O3	35(3)	31(2)	53(3)	3(2)	23(2)	-1(2)
O4	39(3)	31(3)	38(3)	4(2)	18(2)	9(2)
O5	56(3)	46(3)	50(3)	2(2)	34(3)	-8(3)

O6	38(3)	47(3)	40(3)	7(2)	25(2)	9(2)
O7	49(3)	55(3)	55(3)	-12(3)	31(3)	-11(3)
O8	49(3)	40(3)	62(3)	13(2)	37(3)	6(2)
O9	51(3)	55(3)	54(3)	-16(3)	28(3)	-13(3)
O10	42(3)	48(3)	47(3)	5(2)	19(3)	-3(2)
O11	33(3)	41(3)	83(4)	-3(3)	28(3)	-5(2)
O12	59(3)	43(3)	34(3)	-1(2)	21(3)	-8(2)
O13	60(3)	40(3)	41(3)	6(2)	37(3)	5(2)
O14	78(4)	28(3)	59(3)	-5(2)	31(3)	-5(3)
O15	41(3)	44(3)	31(3)	1(2)	15(2)	12(2)
O16	34(3)	51(3)	36(3)	-5(2)	12(2)	4(2)
O17	48(3)	63(3)	36(3)	-14(2)	18(3)	-5(3)
N1	34(3)	33(3)	28(3)	-1(2)	20(3)	1(2)
N2	28(3)	31(3)	40(3)	0(3)	18(3)	4(2)
N3	39(4)	26(3)	64(4)	2(3)	31(3)	1(3)
N4	39(3)	35(3)	27(3)	-5(2)	17(3)	-8(3)
N5	43(4)	30(3)	46(4)	-1(3)	28(3)	-3(3)
C1	43(4)	39(4)	28(3)	-1(3)	22(3)	3(3)
C2	29(3)	33(3)	22(3)	-2(3)	11(3)	-4(3)
C3	34(4)	27(3)	35(4)	3(3)	19(3)	5(3)
C4	35(4)	28(3)	29(3)	1(3)	15(3)	8(3)
C5	34(4)	36(4)	45(4)	10(3)	21(3)	4(3)
C6	26(3)	34(4)	29(3)	7(3)	10(3)	1(3)
C7	36(4)	51(4)	72(6)	6(4)	35(4)	14(4)
C8	43(5)	46(5)	97(7)	4(5)	32(5)	9(4)
C9	38(8)	50(8)	56(9)	-5(6)	23(7)	-7(6)
C10	58(5)	46(5)	78(6)	10(4)	28(5)	-7(4)
C11	71(6)	41(5)	88(7)	21(4)	52(6)	8(4)
C12	82(8)	72(7)	121(10)	11(6)	45(7)	-30(6)
C13	66(6)	44(4)	53(5)	-9(4)	36(4)	-6(4)
C14	76(7)	64(6)	48(5)	-8(4)	20(5)	-1(5)
C9A	46(14)	36(11)	47(13)	29(9)	25(12)	16(9)
N1S	93(6)	64(5)	72(5)	14(4)	54(5)	25(4)
C1S	69(5)	33(4)	38(4)	-8(3)	28(4)	4(4)
C2S	67(6)	37(4)	58(5)	-1(4)	29(5)	5(4)

Table 4 Bond Lengths for SM(NO3)3-1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Sm1	O1	2.400(4)	O7	C13	1.447(8)
Sm1	O2	2.387(4)	O8	C11	1.444(9)
Sm1	$O3^{1}$	2.434(4)	O9	N3	1.260(7)
Sm1	$O4^{1}$	2.417(4)	O10	N3	1.249(7)

Sm1	O9	2.557(5)	O11	N3	1.225(7)
Sm1	O10	2.574(5)	O12	N5	1.239(7)
Sm1	O12	2.712(5)	O13	N5	1.284(7)
Sm1	O13	2.535(5)	O14	N5	1.209(7)
Sm1	O15	2.546(5)	O15	N4	1.268(7)
Sm1	O16	2.598(5)	O16	N4	1.263(7)
Sm1	N3	2.984(6)	O17	N4	1.216(6)
Sm1	N4	2.992(5)	N1	C2	1.314(8)
P1	O1	1.478(4)	N1	C3	1.460(8)
P1	O5	1.551(5)	N2	C4	1.449(8)
P1	O6	1.552(5)	N2	C6	1.323(8)
P1	C1	1.792(7)	C1	C2	1.525(9)
P2	O3	1.473(4)	C3	C4	1.514(8)
P2	O7	1.551(5)	C5	C6	1.511(9)
P2	O8	1.563(5)	C7	C8	1.450(10)
P2	C5	1.792(7)	C9	C10	1.489(14)
O2	C2	1.242(7)	C10	C9A	1.47(2)
O4	C6	1.242(7)	C11	C12	1.468(12)
O5	C9	1.448(12)	C13	C14	1.519(11)
O5	C9A	1.355(18)	N1S	C1S	1.128(9)
O6	C7	1.465(8)	C1S	C2S	1.437(10)

[1]1/2-X,3/2-Y,1-Z

Table 5 Bond Angles for SM(NO3)3-1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O1	Sm1	O3[1]	74.78(15)	O16	Sm1	N3	86.45(16)
O1	Sm1	O4[1]	142.01(15)	O16	Sm1	N4	24.85(14)
O1	Sm1	O9	129.64(16)	N3	Sm1	N4	102.25(16)
O1	Sm1	O10	146.23(16)	O1	P1	O5	114.9(3)
O1	Sm1	O12	68.60(16)	O1	P1	O6	110.0(3)
O1	Sm1	O13	78.17(15)	O1	P1	C1	112.6(3)
O1	Sm1	O15	74.89(15)	O5	P1	O6	107.8(3)
O1	Sm1	O16	118.88(14)	O5	P1	C1	103.5(3)
O1	Sm1	N3	147.02(16)	O6	P1	C1	107.6(3)
O1	Sm1	N4	96.50(15)	O3	P2	O7	115.4(3)
O2	Sm1	O1	75.24(14)	O3	P2	O8	110.3(3)
O2	Sm1	O3[1]	77.88(15)	O3	P2	C5	111.6(3)
O2	Sm1	O4[1]	78.09(14)	O7	P2	O8	102.9(3)
O2	Sm1	O9	76.73(16)	O7	P2	C5	109.1(3)
O2	Sm1	O10	124.33(16)	O8	P2	C5	106.9(3)
O2	Sm1	O12	74.57(15)	P1	O1	Sm1	134.9(3)
O2	Sm1	O13	122.43(14)	C2	O2	Sm1	140.0(4)

O2	Sm1	O15	145.37(16)	P2	O3	Sm1[1]	139.8(3)
O2	Sm1	O16	139.22(15)	C6	O4	Sm1[1]	135.9(4)
O2	Sm1	N3	99.90(17)	C9	O5	P1	124.9(6)
O2	Sm1	N4	149.37(15)	C9A	O5	P1	130.6(9)
O3[1]	Sm1	O9	137.03(16)	C7	O6	P1	125.1(4)
O3[1]	Sm1	O10	132.27(15)	C13	O7	P2	127.7(5)
O3[1]	Sm1	O12	138.50(15)	C11	O8	P2	120.9(5)
O3[1]	Sm1	O13	140.10(16)	N3	O9	Sm1	97.0(4)
O3[1]	Sm1	O15	77.73(15)	N3	O10	Sm1	96.4(4)
O3[1]	Sm1	O16	70.76(15)	N5	O12	Sm1	93.4(4)
O3[1]	Sm1	N3	136.99(15)	N5	O13	Sm1	100.8(4)
O3[1]	Sm1	N4	71.49(15)	N4	O15	Sm1	97.7(3)
O4[1]	Sm1	O3[1]	73.53(15)	N4	O16	Sm1	95.3(3)
O4[1]	Sm1	O9	67.69(16)	C2	N1	C3	123.4(5)
O4[1]	Sm1	O10	71.75(15)	C6	N2	C4	119.8(6)
O4[1]	Sm1	O12	128.50(16)	O9	N3	Sm1	58.3(3)
O4[1]	Sm1	O13	139.64(15)	O10	N3	Sm1	59.0(3)
O4[1]	Sm1	O15	117.43(14)	O10	N3	O9	115.6(6)
O4[1]	Sm1	O16	68.59(15)	O11	N3	Sm1	168.5(4)
O4[1]	Sm1	N3	64.17(15)	O11	N3	O9	120.8(7)
O4[1]	Sm1	N4	92.83(15)	O11	N3	O10	123.6(6)
O9	Sm1	O10	48.88(16)	O15	N4	Sm1	57.5(3)
O9	Sm1	O12	64.03(16)	O16	N4	Sm1	59.8(3)
O9	Sm1	O16	109.74(15)	O16	N4	O15	117.1(5)
O9	Sm1	N3	24.78(15)	O17	N4	Sm1	176.5(4)
O9	Sm1	N4	127.03(15)	O17	N4	O15	121.0(6)
O10	Sm1	O12	89.12(16)	O17	N4	O16	121.8(5)
O10	Sm1	O16	66.64(16)	O12	N5	O13	116.8(6)
O10	Sm1	N3	24.57(15)	O14	N5	O12	124.1(6)
O10	Sm1	N4	78.56(15)	O14	N5	O13	119.1(6)
O12	Sm1	N3	78.61(16)	C2	C1	P1	110.6(4)
O12	Sm1	N4	130.53(15)	O2	C2	N1	123.4(6)
O13	Sm1	O9	82.86(18)	O2	C2	C1	120.2(5)
O13	Sm1	O10	68.09(15)	N1	C2	C1	116.3(6)
O13	Sm1	O12	48.22(16)	N1	C3	C4	112.1(5)
O13	Sm1	O15	67.18(15)	N2	C4	C3	113.1(5)
O13	Sm1	O16	98.32(15)	C6	C5	P2	113.1(4)
O13	Sm1	N3	77.43(16)	O4	C6	N2	123.0(6)
O13	Sm1	N4	83.18(15)	O4	C6	C5	118.9(6)
O15	Sm1	O9	137.02(16)	N2	C6	C5	117.9(6)
O15	Sm1	O10	90.30(16)	C8	C7	O6	109.5(6)
O15	Sm1	O12	109.75(15)	O5	C9	C10	109.6(10)
O15	Sm1	O16	49.63(14)	O8	C11	C12	111.3(7)
O15	Sm1	N3	114.70(17)	O7	C13	C14	106.5(7)

O15	Sm1	N4	24.83(14)	O5	C9A	C10	116.2(14)
O16	Sm1	O12	145.46(15)	N1S	C1S	C2S	179.4(9)

[1]1/2-X,3/2-Y,1-Z

Table 6 Hydrogen Bonds for SM(NO3)3-1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1	H1	O13[1]	0.877(10)	2.03(2)	2.877(7)	161(6)
N2	H2	N1S	0.85(10)	2.24(10)	3.067(9)	163(9)

[1]+X,1-Y,-1/2+Z

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for SM(NO3)3-1.

Atom	*x*	*y*	*z*	U(eq)
H1	3580(19)	6300(50)	3650(40)	30(18)
H2	2390(30)	5590(80)	3310(70)	100(40)
H1A	4010.68	5068.88	4544.12	41
H1B	3755.57	4441.7	5042.96	41
H3A	3216.68	7913.58	3341.24	37
H3B	3060.79	7700.63	4125.33	37
H4A	2434.54	7586.16	2635.43	37
H4B	2680.82	6579.61	2438.81	37
H5A	1993.77	6035.26	4652.94	44
H5B	1982.26	5176.94	3923.81	44
H7A	4888.09	4159.52	5371.52	59
H7B	5274.46	4756.94	6236.14	59
H8A	5479.72	3003.69	6180.79	92
H8B	5017.1	2612.03	6218.02	92
H8C	5408.32	3210.08	7070.74	92
H9A	5191.63	6858.09	6952.66	56
H9B	4724.07	7420.11	6843.87	56
H10A	4690.72	8447.77	5669.08	92
H10B	5092.49	7776.02	5590.16	92
H10C	5209.67	8539.84	6443.57	92
H10D	4948.71	8281.34	5415.63	92
H10E	5260.57	7633.42	6319.26	92
H10F	4995.61	8688.6	6374.79	92
H11A	1212.9	4304.11	4793.1	73
H11B	1295.44	4109.21	3913.26	73
H12A	488.74	4164.17	3024.83	137
H12B	430.75	4228.82	3940.89	137

H12C	651.61	3188.87	3724.36	137
H13A	1608.61	4703.97	2287.86	61
H13B	1393.47	5780.03	1727.73	61
H14A	867.77	3854.43	1414.49	98
H14B	1121.85	4182.54	808.25	98
H14C	710.62	4902.88	797.26	98
H9AA	4495.01	7580.3	6391.05	49
H9AB	4312.42	7626.22	5318.13	49
H2SA	3208.07	2144.49	4362.68	80
H2SB	2788.43	1657.56	4510.03	80
H2SC	3149.62	2441.64	5252.61	80

Table 8 Atomic Occupancy for SM(NO3)3-1.

Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C9	0.629(19)	H9A	0.629(19)	H9B	0.629(19)
H10A	0.5	H10B	0.5	H10C	0.5
H10D	0.5	H10E	0.5	H10F	0.5
C9A	0.371(19)	H9AA	0.371(19)	H9AB	0.371(19)

Refinement model description

Number of restraints – 1, number of constraints – unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H,H) groups

At 1.5 times of:

All C(H,H,H) groups, All C(H,H,H,H,H,H) groups

2. Restrained distances

N1-H1

0.88 with sigma of 0.01

3. Others

Sof(C9A)=Sof(H9AA)=Sof(H9AB)=1-FVAR(1)

Sof(C9)=Sof(H9A)=Sof(H9B)=FVAR(1)

Fixed Sof: H10A(0.5) H10B(0.5) H10C(0.5) H10D(0.5) H10E(0.5) H10F(0.5)

4.a Secondary CH2 refined with riding coordinates:

C1(H1A,H1B), C3(H3A,H3B), C4(H4A,H4B), C5(H5A,H5B), C7(H7A,H7B), C9(H9A,H9B), C11(H11A,H11B), C13(H13A,H13B), C9A(H9AA,H9AB)

4.b Idealised Me refined as rotating group:

C8(H8A,H8B,H8C), C10(H10A,H10B,H10C), C10(H10D,H10E,H10F), C12(H12A,H12B, H12C), C14(H14A,H14B,H14C), C2S(H2SA,H2SB,H2SC)

F. $Tb(NO_3)_3$-2 (water solvate)

The figure on the left depicts the atom numbering scheme of the 2:2 **$Tb(NO_3)_3$-2 • (3 H_2O)** complex using a ball and stick model with standard CPK colors (Tb atoms are colored green). All phenyl rings and hydrogen atoms bonded to carbon atoms are not shown for clarity. Only one complete ligand (except for the pendant phenyl rings) is shown, although every atom in the inner coordination sphere of both metals has been included. The figure on the right depicts the thermal ellipsoids of all atoms of the 2:2 complex, which are shown at the 40% probability level. Hydrogen bonds are depicted with green, dashed lines.

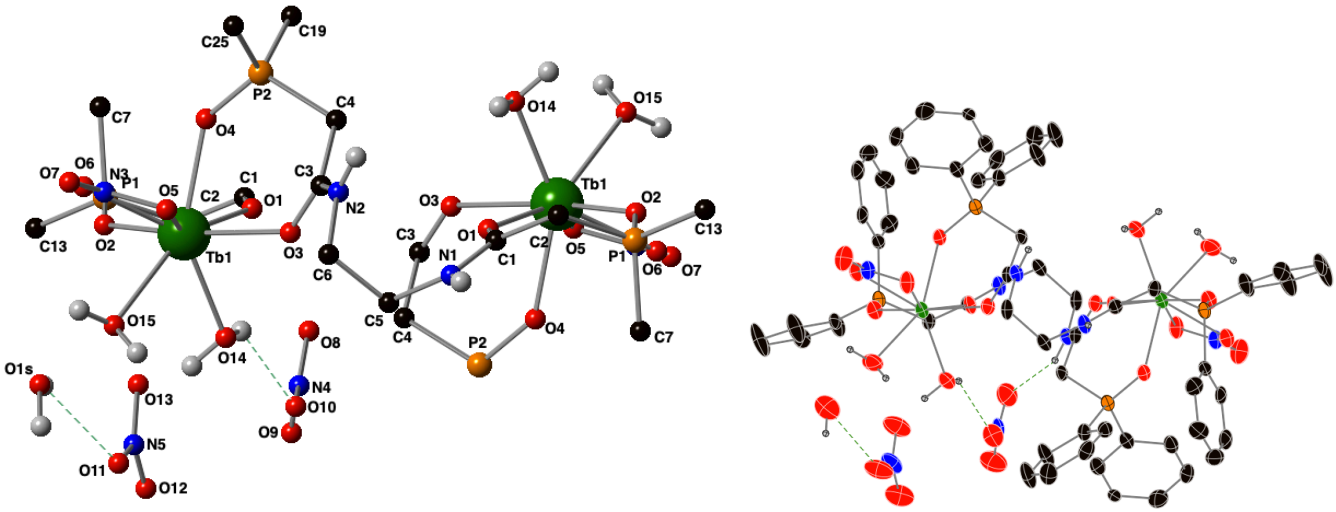
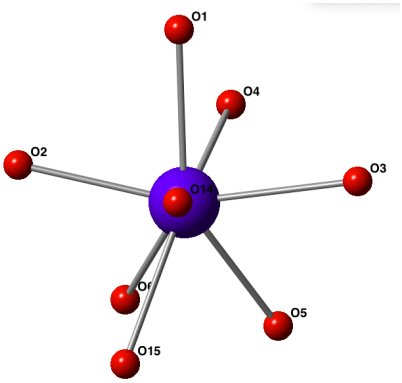


Figure showing only atoms of inner coordination sphere:



Experimental

Single crystals of $C_{60}H_{72}N_{10}O_{32}P_4Tb_2$ **[$Tb(NO_3)_3$-2 (water solvate)** were grown by slow evaporation of an acetonitrile solution of the complex. A suitable crystal was selected and mounted on a nylon loop using a small amount of paratone oil on a Bruker APEX-II CCD diffractometer. The crystal was kept at 173(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimization.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of $Tb(NO_3)_3$-2 (water solvate)

Crystal Data for $C_{60}H_{72}N_{10}O_{32}P_4Tb_2$ (M =1886.99 g/mol): triclinic, space group P-1 (no. 2), a = 11.438(2) Å, b = 12.724(2) Å, c = 14.681(3) Å, α = 91.784(2)°, β = 106.593(2)°, γ = 113.139(2)°, V = 1857.8(6) Å^3, Z = 1, T = 173(2) K, μ(MoKα) = 2.068 mm^{-1}, *Dcalc* = 1.687 g/cm^3, 18678 reflections measured (3.528° ≤ 2Θ ≤ 50.95°), 6825 unique (R_{int} = 0.0585, R_{sigma} = 0.0735) which were used in all calculations. The final R_1 was 0.0626 (I > 2σ(I)) and wR_2 was 0.1717 (all data).

Table 1 Crystal data and structure refinement for $Tb(NO_3)_3$-2 (water solvate).

CCDC code	2003374
Empirical formula	$C_{60}H_{72}N_{10}O_{32}P_4Tb_2$
Formula weight	1886.99
Temperature/K	173(2)
Crystal system	triclinic
Space group	P-1
a/Å	11.438(2)
b/Å	12.724(2)
c/Å	14.681(3)
α/°	91.784(2)
β/°	106.593(2)
γ/°	113.139(2)
Volume/Å^3	1857.8(6)
Z	1
ϱ_{calc}g/cm^3	1.687
μ/mm^{-1}	2.068
F(000)	948.0
Crystal size/mm^3	0.187 × 0.11 × 0.038
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.528 to 50.95
Index ranges	-13 ≤ h ≤ 13, -12 ≤ k ≤ 15, -17 ≤ l ≤ 16
Reflections collected	18678
Independent reflections	6825 [R_{int} = 0.0585, R_{sigma} = 0.0735]
Data/restraints/parameters	6825/0/492
Goodness-of-fit on F^2	1.024
Final R indexes [I>=2σ (I)]	R_1 = 0.0626, wR_2 = 0.1578
Final R indexes [all data]	R_1 = 0.0791, wR_2 = 0.1717
Largest diff. peak/hole / e Å^{-3}	3.52/-1.60

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for TB(NO3)3-2 (WATER SOLVATE). U_{eq} is defined as 1/3 of of the trace of the orthogonalized U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Tb1	6061.6(3)	1484.1(3)	3059.3(3)	26.32(16)
P1	4885.7(19)	3581.4(16)	2350.5(14)	25.8(4)
P2	7121.3(18)	942.7(16)	7505.1(14)	24.7(4)
O4	6159(5)	-199(4)	7663(3)	26.7(11)

O1	4765(5)	1973(5)	3897(4)	30.5(12)
O2	5786(5)	2976(4)	2353(4)	32.5(12)
O3	4135(5)	-65(5)	5934(4)	30.6(12)
O6	5911(5)	1047(5)	1380(4)	34.6(12)
N4	7303(6)	4569(5)	6193(5)	26.0(13)
O14	7569(5)	2715(5)	4513(4)	42.4(14)
O7	6482(7)	-242(6)	867(5)	52.3(17)
O5	6335(6)	-118(5)	2307(4)	39.8(14)
N1	3219(6)	2474(6)	4216(4)	29.7(14)
N2	4568(6)	1827(5)	6013(4)	27.6(13)
N3	6251(6)	213(6)	1483(5)	31.9(15)
O10	8039(7)	4075(6)	6156(5)	56.3(17)
O15	8290(6)	2357(7)	2930(5)	63(2)
O11	281(7)	3827(6)	5259(6)	69(2)
O8	6158(8)	4187(6)	5896(5)	62.9(19)
O13	2227(6)	3845(6)	5490(6)	70(2)
O12	502(7)	2513(6)	4447(6)	69(2)
C4	6439(7)	1295(6)	6340(5)	26.1(16)
C5	2586(7)	1443(6)	4610(5)	28.5(16)
C6	3154(8)	1626(7)	5702(5)	32.2(17)
N5	1028(7)	3396(7)	5073(6)	51(2)
C1	4254(7)	2687(7)	3906(5)	27.4(16)
C13	5475(7)	4964(6)	1967(5)	27.5(16)
C25	7492(7)	2091(6)	8422(5)	27.3(16)
C19	8654(7)	903(7)	7456(5)	28.9(16)
C7	3223(7)	2737(7)	1527(5)	30.5(17)
O9	7966(8)	5643(7)	6633(6)	73(2)
C12	2162(8)	3024(8)	1520(6)	40(2)
C2	4790(7)	3817(7)	3537(5)	27.8(16)
C18	5043(9)	5799(7)	2151(6)	38.6(19)
C24	8902(8)	-76(7)	7707(5)	32.2(17)
C23	10047(8)	-138(8)	7635(6)	39(2)
C3	4964(7)	986(7)	6076(5)	27.2(16)
C9	1778(9)	1291(7)	129(6)	42(2)
C8	3023(8)	1886(7)	831(5)	34.0(18)
C17	5403(9)	6796(7)	1758(6)	39(2)
C29	7411(8)	2678(8)	9965(6)	40(2)
C11	916(8)	2435(8)	826(7)	45(2)
C10	738(9)	1561(8)	123(6)	48(2)
C30	7124(7)	1821(8)	9238(6)	36.1(19)
C26	8141(8)	3258(7)	8334(6)	40(2)
C16	6159(9)	6972(7)	1173(7)	44(2)
C20	9560(8)	1759(9)	7139(7)	49(2)
C22	10949(9)	739(9)	7331(7)	50(2)

C28	8050(9)	3840(8)	9879(6)	47(2)
C14	6249(11)	5135(9)	1369(8)	60(3)
C27	8396(8)	4161(8)	9085(6)	46(2)
C21	10686(9)	1670(10)	7072(8)	59(3)
O1S	872(11)	5275(9)	7092(8)	112(4)
C15	6584(13)	6144(10)	963(10)	78(4)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for TB(NO3)3-2 (WATER SOLVATE). The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Tb1	28.6(2)	23.1(2)	34.5(2)	14.24(15)	15.03(15)	14.07(16)
P1	31.9(9)	21.8(10)	30.2(10)	14.9(8)	13.2(8)	14.9(8)
P2	25.4(9)	24.3(10)	29.7(10)	13.2(8)	11.9(7)	13.0(8)
O4	28(2)	25(3)	31(3)	15(2)	12(2)	12(2)
O1	32(3)	32(3)	37(3)	19(2)	19(2)	16(2)
O2	38(3)	26(3)	44(3)	18(2)	17(2)	20(2)
O3	37(3)	28(3)	32(3)	14(2)	12(2)	17(2)
O6	41(3)	31(3)	42(3)	19(2)	17(2)	22(2)
N4	36(4)	24(3)	36(4)	17(3)	23(3)	21(3)
O14	31(3)	47(4)	46(3)	8(3)	18(3)	9(3)
O7	79(5)	53(4)	50(4)	11(3)	36(3)	42(4)
O5	57(4)	39(3)	46(3)	26(3)	27(3)	33(3)
N1	33(3)	33(4)	40(4)	20(3)	21(3)	23(3)
N2	33(3)	24(3)	35(3)	12(3)	16(3)	17(3)
N3	40(4)	31(4)	37(4)	14(3)	19(3)	23(3)
O10	61(4)	50(4)	68(5)	13(3)	31(4)	26(3)
O15	35(3)	89(6)	53(4)	-11(4)	22(3)	10(3)
O11	40(4)	60(5)	103(6)	-12(4)	20(4)	21(3)
O8	73(5)	44(4)	70(5)	21(4)	26(4)	21(4)
O13	39(4)	55(5)	108(6)	19(4)	12(4)	20(3)
O12	60(4)	41(4)	101(6)	0(4)	15(4)	27(4)
C4	31(4)	22(4)	28(4)	14(3)	12(3)	12(3)
C5	27(4)	22(4)	44(5)	16(3)	18(3)	13(3)
C6	45(4)	37(5)	34(4)	20(4)	25(4)	28(4)
N5	33(4)	45(5)	81(6)	30(4)	20(4)	18(4)
C1	26(4)	32(4)	29(4)	12(3)	8(3)	17(3)
C13	34(4)	22(4)	31(4)	15(3)	14(3)	13(3)
C25	29(4)	21(4)	39(4)	13(3)	15(3)	15(3)
C19	27(4)	37(5)	31(4)	13(3)	15(3)	18(3)
C7	30(4)	30(4)	31(4)	19(3)	9(3)	11(3)
O9	67(5)	50(5)	96(6)	-8(4)	28(4)	19(4)
C12	46(5)	35(5)	41(5)	12(4)	11(4)	21(4)

C2	32(4)	32(4)	27(4)	9(3)	14(3)	18(3)
C18	56(5)	23(4)	53(5)	17(4)	34(4)	22(4)
C24	33(4)	36(5)	32(4)	10(3)	12(3)	17(3)
C23	45(5)	56(6)	31(4)	14(4)	13(4)	34(4)
C3	35(4)	28(4)	25(4)	11(3)	15(3)	16(3)
C9	60(5)	30(5)	35(5)	19(4)	19(4)	14(4)
C8	46(4)	28(4)	28(4)	16(3)	16(3)	11(4)
C17	54(5)	23(4)	47(5)	11(4)	18(4)	19(4)
C29	48(5)	48(6)	31(4)	7(4)	23(4)	21(4)
C11	36(4)	44(5)	58(6)	22(5)	8(4)	24(4)
C10	48(5)	37(5)	40(5)	12(4)	1(4)	8(4)
C30	32(4)	39(5)	40(5)	16(4)	18(3)	13(4)
C26	44(5)	30(5)	41(5)	12(4)	15(4)	7(4)
C16	66(6)	23(4)	54(6)	26(4)	34(5)	17(4)
C20	38(5)	53(6)	78(7)	45(5)	34(5)	27(4)
C22	37(4)	80(7)	52(6)	27(5)	22(4)	35(5)
C28	58(5)	38(5)	40(5)	-4(4)	13(4)	18(4)
C14	86(7)	37(5)	97(8)	39(6)	65(7)	39(5)
C27	33(4)	45(5)	28(4)	15(4)	1(3)	-11(4)
C21	50(5)	70(7)	83(8)	56(6)	41(5)	34(5)
O1S	96(7)	93(8)	99(8)	28(6)	24(6)	-4(6)
C15	108(9)	57(7)	126(11)	58(7)	95(9)	48(7)

Table 4 Bond Lengths for TB(NO3)3-2 (WATER SOLVATE).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Tb1	O4[1]	2.310(5)	O13	N5	1.210(9)
Tb1	O1	2.412(5)	O12	N5	1.247(11)
Tb1	O2	2.277(5)	C4	C3	1.499(10)
Tb1	O3[1]	2.352(5)	C5	C6	1.521(11)
Tb1	O6	2.452(6)	C1	C2	1.510(10)
Tb1	O14	2.356(5)	C13	C18	1.384(11)
Tb1	O5	2.455(6)	C13	C14	1.381(12)
Tb1	N3	2.889(7)	C25	C30	1.389(11)
Tb1	O15	2.414(6)	C25	C26	1.405(11)
P1	O2	1.509(5)	C19	C24	1.418(11)
P1	C13	1.792(7)	C19	C20	1.377(11)
P1	C7	1.798(7)	C7	C12	1.396(11)
P1	C2	1.799(7)	C7	C8	1.369(11)
P2	O4	1.511(5)	C12	C11	1.384(11)
P2	C4	1.815(7)	C18	C17	1.372(11)
P2	C25	1.786(8)	C24	C23	1.376(11)
P2	C19	1.796(7)	C23	C22	1.378(13)

O1	C1	1.261(8)	C9	C8	1.388(11)
O3	C3	1.266(9)	C9	C10	1.360(13)
O6	N3	1.265(8)	C17	C16	1.350(12)
N4	O10	1.244(8)	C29	C30	1.371(12)
N4	O8	1.141(9)	C29	C28	1.397(13)
N4	O9	1.308(9)	C11	C10	1.405(13)
O7	N3	1.202(8)	C26	C27	1.447(13)
O5	N3	1.284(8)	C16	C15	1.382(14)
N1	C5	1.456(9)	C20	C21	1.367(12)
N1	C1	1.320(9)	C22	C21	1.372(13)
N2	C6	1.462(9)	C28	C27	1.360(12)
N2	C3	1.312(9)	C14	C15	1.394(13)
O11	N5	1.264(10)			

[1]1-X,-Y,1-Z

Table 5 Bond Angles for TB(NO3)3-2 (WATER SOLVATE).

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O4[1]	Tb1	O1	72.89(18)	O8	N4	O9	119.2(7)
O4[1]	Tb1	O3[1]	79.05(17)	N3	O5	Tb1	96.1(4)
O4[1]	Tb1	O6	76.62(18)	C1	N1	C5	124.9(6)
O4[1]	Tb1	O14	142.21(19)	C3	N2	C6	123.1(7)
O4[1]	Tb1	O5	79.35(19)	O6	N3	Tb1	57.4(4)
O4[1]	Tb1	N3	78.85(18)	O6	N3	O5	114.5(6)
O4[1]	Tb1	O15	147.0(2)	O7	N3	Tb1	172.7(6)
O1	Tb1	O6	136.89(16)	O7	N3	O6	123.5(7)
O1	Tb1	O5	144.65(19)	O7	N3	O5	122.0(6)
O1	Tb1	N3	151.38(18)	O5	N3	Tb1	57.7(4)
O1	Tb1	O15	137.8(2)	C3	C4	P2	112.8(5)
O2	Tb1	O4[1]	93.84(17)	N1	C5	C6	112.3(6)
O2	Tb1	O1	77.64(18)	N2	C6	C5	110.7(6)
O2	Tb1	O3[1]	159.75(19)	O13	N5	O11	120.1(9)
O2	Tb1	O6	74.75(18)	O13	N5	O12	121.4(8)
O2	Tb1	O14	92.6(2)	O12	N5	O11	118.5(7)
O2	Tb1	O5	126.38(19)	O1	C1	N1	121.9(7)
O2	Tb1	N3	100.16(19)	O1	C1	C2	120.7(6)
O2	Tb1	O15	84.6(2)	N1	C1	C2	117.4(6)
O3[1]	Tb1	O1	82.14(17)	C18	C13	P1	122.1(6)
O3[1]	Tb1	O6	120.99(18)	C14	C13	P1	118.1(6)
O3[1]	Tb1	O14	82.15(19)	C14	C13	C18	119.3(7)
O3[1]	Tb1	O5	71.32(18)	C30	C25	P2	119.2(6)
O3[1]	Tb1	N3	97.04(18)	C30	C25	C26	119.4(8)
O3[1]	Tb1	O15	111.7(2)	C26	C25	P2	121.5(6)

O6	Tb1	O5	51.82(17)	C24	C19	P2	118.5(6)
O6	Tb1	N3	25.77(17)	C20	C19	P2	122.2(6)
O14	Tb1	O1	72.27(18)	C20	C19	C24	119.2(7)
O14	Tb1	O6	140.73(19)	C12	C7	P1	120.6(6)
O14	Tb1	O5	124.5(2)	C8	C7	P1	119.7(6)
O14	Tb1	N3	136.18(19)	C8	C7	C12	119.3(7)
O14	Tb1	O15	70.7(2)	C11	C12	C7	120.0(8)
O5	Tb1	N3	26.23(17)	C1	C2	P1	111.3(5)
O15	Tb1	O6	71.2(2)	C17	C18	C13	120.3(8)
O15	Tb1	O5	75.4(2)	C23	C24	C19	119.1(8)
O15	Tb1	N3	69.1(2)	C24	C23	C22	120.7(8)
O2	P1	C13	112.2(3)	O3	C3	N2	121.6(7)
O2	P1	C7	110.5(3)	O3	C3	C4	120.0(6)
O2	P1	C2	110.7(3)	N2	C3	C4	118.3(7)
C13	P1	C7	106.5(3)	C10	C9	C8	119.8(9)
C13	P1	C2	107.6(4)	C7	C8	C9	121.1(8)
C7	P1	C2	109.2(4)	C16	C17	C18	120.9(8)
O4	P2	C4	111.5(3)	C30	C29	C28	120.0(8)
O4	P2	C25	110.8(3)	C12	C11	C10	119.4(8)
O4	P2	C19	112.4(3)	C9	C10	C11	120.3(8)
C25	P2	C4	108.7(3)	C29	C30	C25	120.9(8)
C25	P2	C19	109.8(4)	C25	C26	C27	119.6(8)
C19	P2	C4	103.4(3)	C17	C16	C15	120.1(8)
P2	O4	Tb1[1]	137.3(3)	C21	C20	C19	120.4(8)
C1	O1	Tb1	139.1(5)	C21	C22	C23	119.7(8)
P1	O2	Tb1	133.7(3)	C27	C28	C29	121.9(8)
C3	O3	Tb1[1]	131.3(4)	C13	C14	C15	119.5(9)
N3	O6	Tb1	96.8(4)	C28	C27	C26	118.1(8)
O10	N4	O9	113.6(7)	C20	C21	C22	120.9(9)
O8	N4	O10	127.3(8)	C16	C15	C14	119.9(9)

[1]1-X,-Y,1-Z

Table 6 Hydrogen Bonds for TB(NO3)3-2 (WATER SOLVATE).

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
O14	H14A	O1	0.88	2.44	2.811(7)	105.6
O14	H14A	O10	0.88	2.13	2.714(9)	123.5
O14	H14B	O11[1]	0.88	2.15	2.709(9)	121.3
N1	H1	O13	0.88	2.60	3.225(10)	128.5
N1	H1	O12	0.88	2.70	3.240(9)	121.0
N1	H1	O9[2]	0.88	2.48	3.301(10)	154.6
N2	H2	O8	0.88	2.06	2.876(10)	154.4
O15	H15B	O12[1]	0.91	1.97	2.785(10)	147.9

O1S H1SA O11	0.87	2.41	2.960(14)	121.6
O1S H1SB O10[3]	0.87	2.00	2.856(13)	165.8

[1]1+X,+Y,+Z; [2]1-X,1-Y,1-Z; [3]-1+X,+Y,+Z

Table 7 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for TB(NO3)3-2 (WATER SOLVATE).

Atom	*x*	*y*	*z*	U(eq)
H14A	7165.98	3054.23	4759.97	64
H14B	8218.12	3289.63	4396.14	64
H1	2887.25	2994.65	4181.49	36
H2	5183.99	2546.62	6166.14	33
H15A	8305.09	2113.97	2341.63	95
H15B	8860.39	2110.68	3342.33	95
H4A	6921.91	2136.1	6349.55	31
H4B	6596.63	877.44	5840.89	31
H5A	2720.64	794.3	4335.57	34
H5B	1607.58	1224.07	4415.22	34
H6A	3065.26	2299.58	5979.42	39
H6B	2633.57	934.55	5942.93	39
H12	2294.75	3624.43	1992.53	48
H2A	5696.01	4324.56	3982.95	33
H2B	4195.8	4214.41	3518.54	33
H18	4495.77	5681.05	2551.65	46
H24	8285.38	-679.41	7921.72	39
H23	10217.19	-793.37	7796.95	47
H9	1652.99	696.52	-344.85	50
H8	3748.42	1698.69	827.12	41
H17	5115.66	7369.99	1900.37	47
H29	7175.49	2481.15	10526.52	47
H11	187.51	2619.3	824.87	54
H10	-112.84	1157.49	-359.04	57
H30	6667.31	1033.31	9293.11	43
H26	8409.8	3453.37	7784.01	49
H16	6398.93	7666.13	904.59	53
H20	9400.08	2415.53	6966.05	59
H22	11749.55	698.71	7300.31	60
H28	8247.82	4423.91	10390.7	56
H14	6551.37	4568.68	1235.56	72
H27	8795.21	4954.62	9024.77	56
H21	11294.83	2261.97	6842.55	71

H1SA	1102.15	4746.8	6913.51	168
H1SB	20.08	5020.92	6769.86	168
H15	7103.74	6262.52	542.15	94

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
 At 1.5 times of:
  All O(H,H) groups

2.a Free rotating group:
 O1S(H1SA,H1SB)

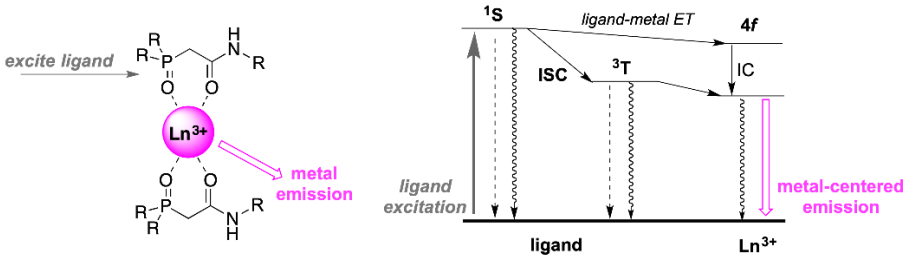
2.b Rotating group:
 O14(H14A,H14B), O15(H15A,H15B)

2.c Secondary CH2 refined with riding coordinates:
 C4(H4A,H4B), C5(H5A,H5B), C6(H6A,H6B), C2(H2A,H2B)

2.d Aromatic/amide H refined with riding coordinates:
 N1(H1), N2(H2), C12(H12), C18(H18), C24(H24), C23(H23), C9(H9), C8(H8),
 C17(H17), C29(H29), C11(H11), C10(H10), C30(H30), C26(H26), C16(H16), C20(H20),
  C22(H22), C28(H28), C14(H14), C27(H27), C21(H21), C15(H15)

II. Luminescence Data

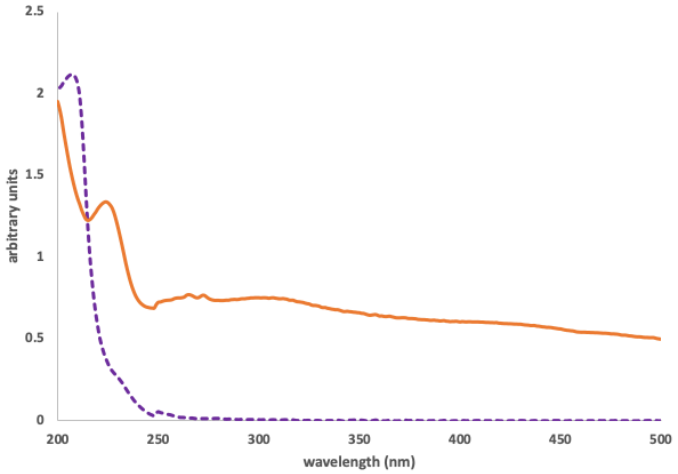
A. Diagram of a possible mechanism for the sensitization process for lanthanide luminescence using an abbreviated Jablonski diagram: dashed arrows = fluorescence (from ^{1}S) and phosphorescence (from ^{3}T) of ligand, squiggly arrows = non-radiative decay pathways, IC = internal conversion, ISC = inter-system crossing, ET = energy transfer.



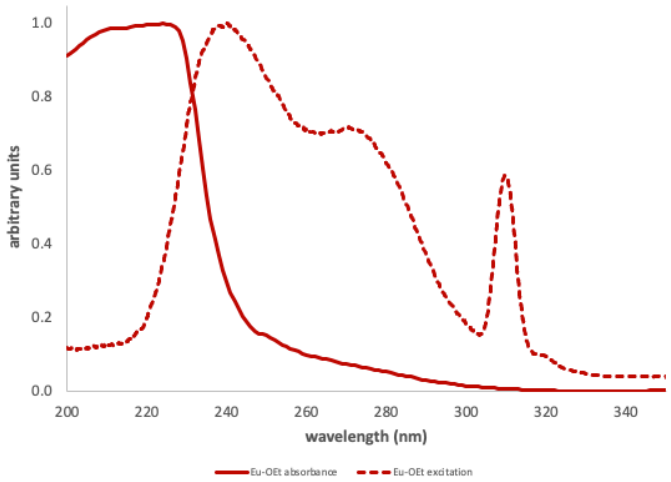
B. Absorption and Excitation spectra

The absorption and excitation spectra for each Ln-ligand complex are shown below. For a given complex, the spectra are presented on the same set of axes and the intensity values have been normalized to 1 for ease of comparison. Absorption spectra are shown with solid lines, while excitation spectra are shown with dashed lines.

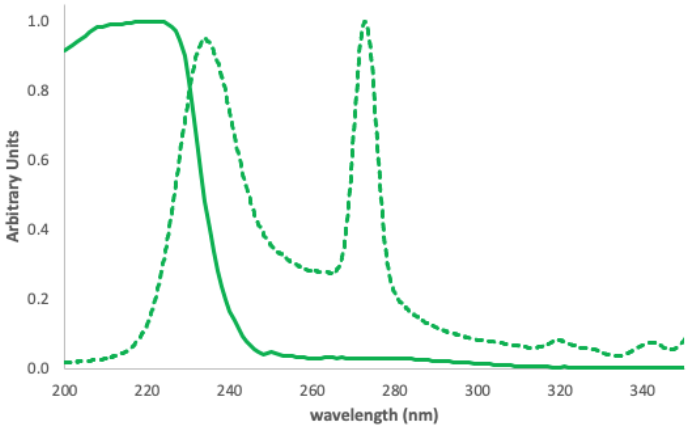
1. Absorption spectra of free ligands **1** and **2** (acetonitrile, 1.0 mM, 1.0 nm slits). Note: ligand **2** has quite poor solubility in acetonitrile, and there was some undissolved ligand in the cuvette. We attribute the high baseline of the UV-VIS spectrum to this feature. No attempt was made to correct for this. Purple dashed line: ethoxy-substituted ligand **1**, orange solid line: phenyl-substituted ligand **2**.



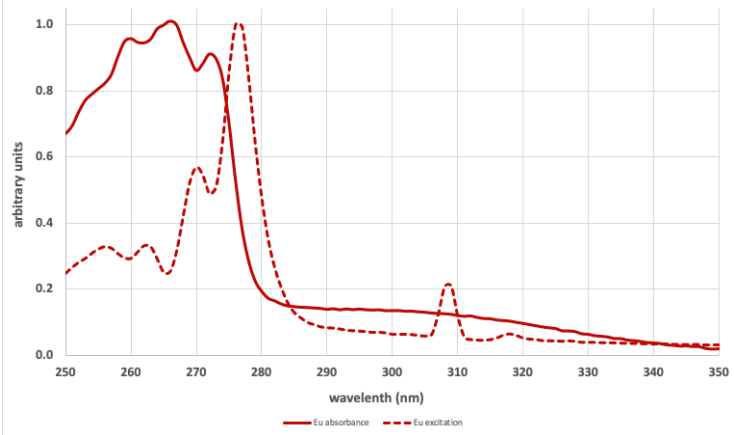
2. Eu(NO$_3$)$_3$-1 (excitation spectrum monitored at 620 nm, 2.0 nm excitation and emission slits)



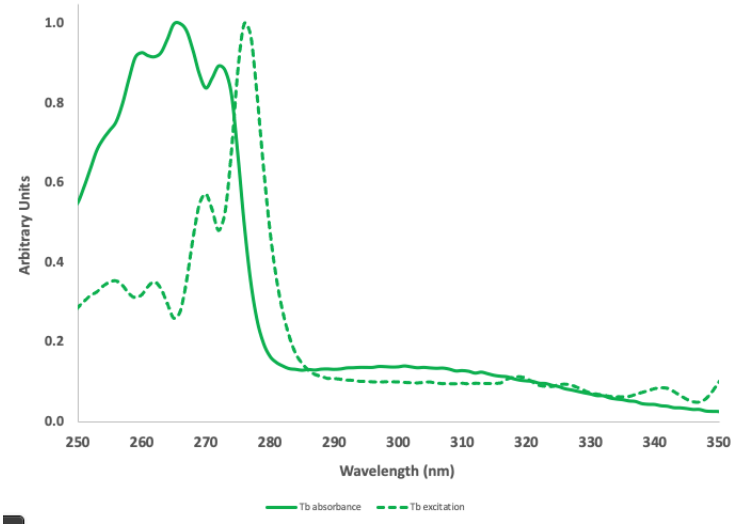
3. Tb(NO$_3$)$_3$-1 (excitation spectrum monitored at 545 nm, 2.0 nm excitation and emission slits)



4. Eu(NO$_3$)$_3$-2 (excitation spectrum monitored at 617 nm, 2.0 nm excitation and emission slits)



5. $Tb(NO_3)_3$-2 (excitation spectrum monitored at 544 nm, 2.0 mm excitation and emission slits)

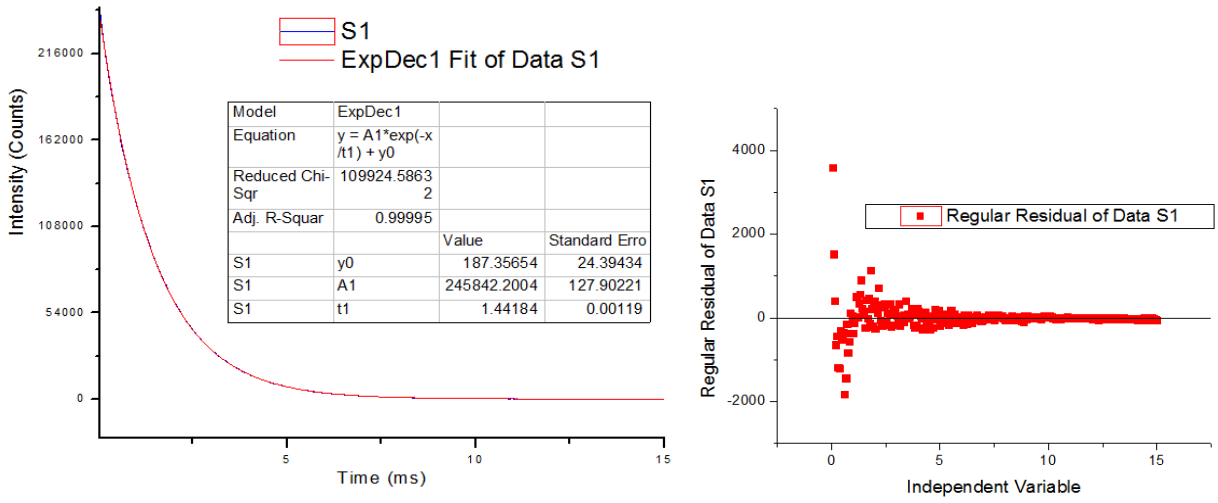


C. Lifetime decay curves

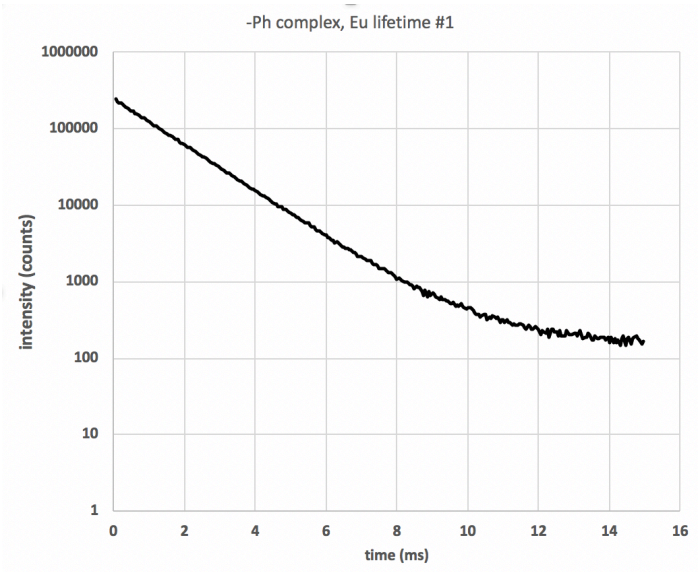
1. Ligand 2-Eu complex

Fluorimeter settings for all trials:
excitation: 260 nm; emission: 616 nm; slits: 2.0 nm; sample window: 1.5 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 15 ms; delay increment: 0.05 ms

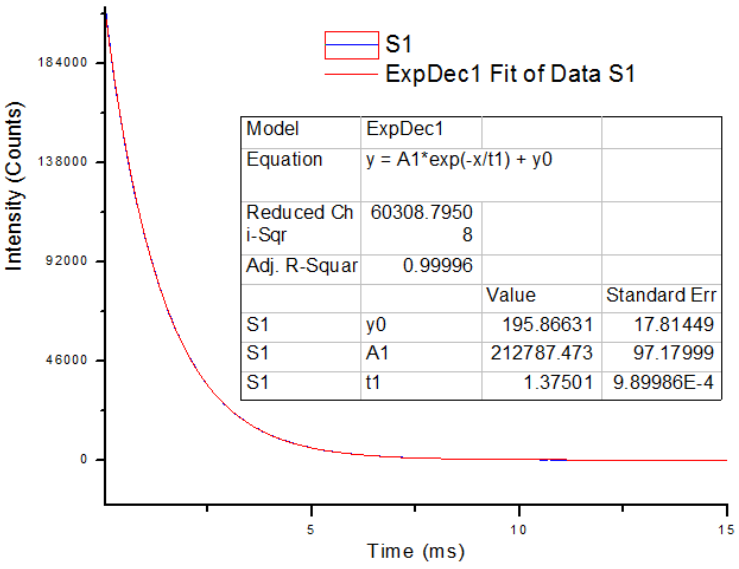
Trial #1



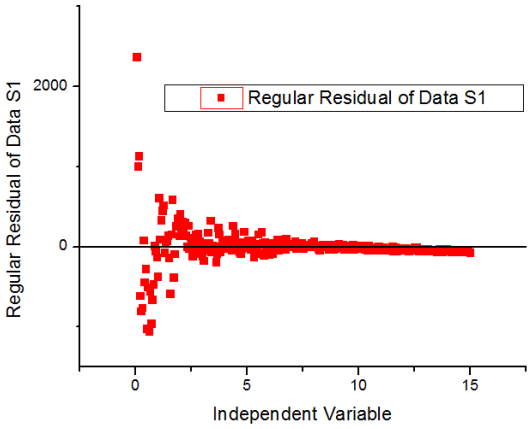
Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	109924.58632		
Adj. R-Squar	0.99995		
		Value	Standard Erro
S1	y0	187.35654	24.39434
S1	A1	245842.2004	127.90221
S1	t1	1.44184	0.00119

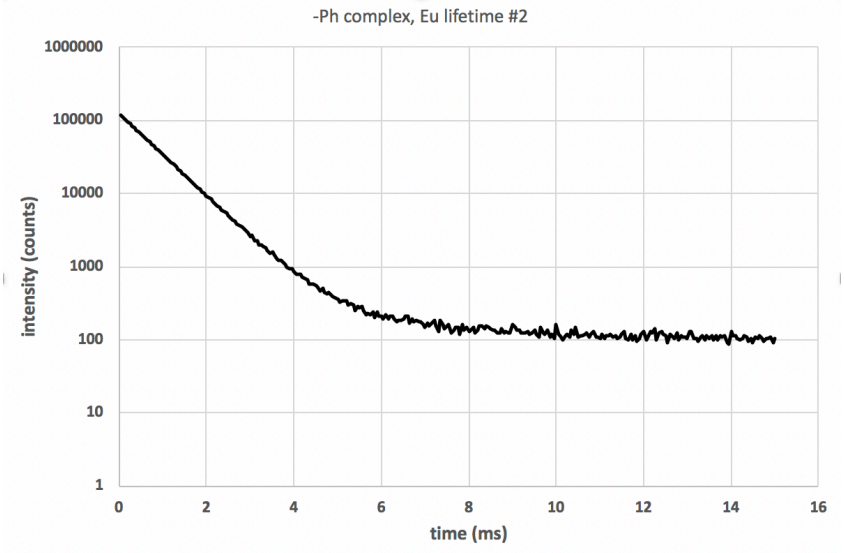


Trial #2

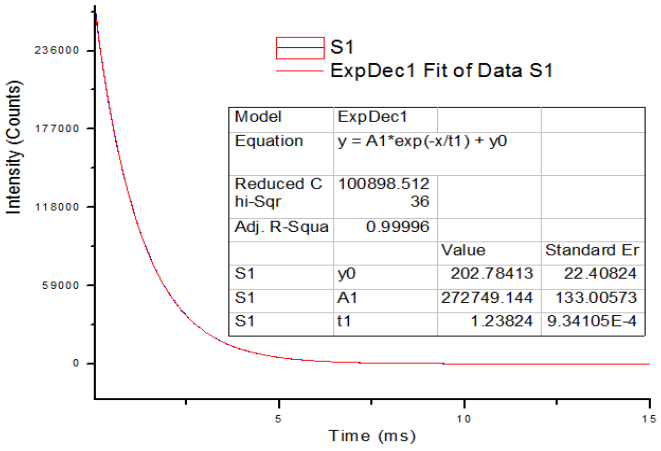


Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	60308.79508		
Adj. R-Squar	0.99996		
		Value	Standard Err
S1	y0	195.86631	17.81449
S1	A1	212787.473	97.17999
S1	t1	1.37501	9.89986E-4

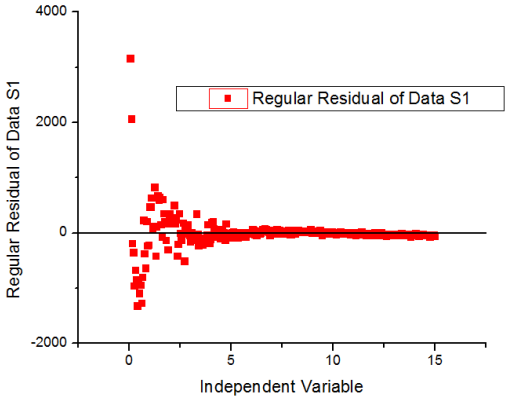


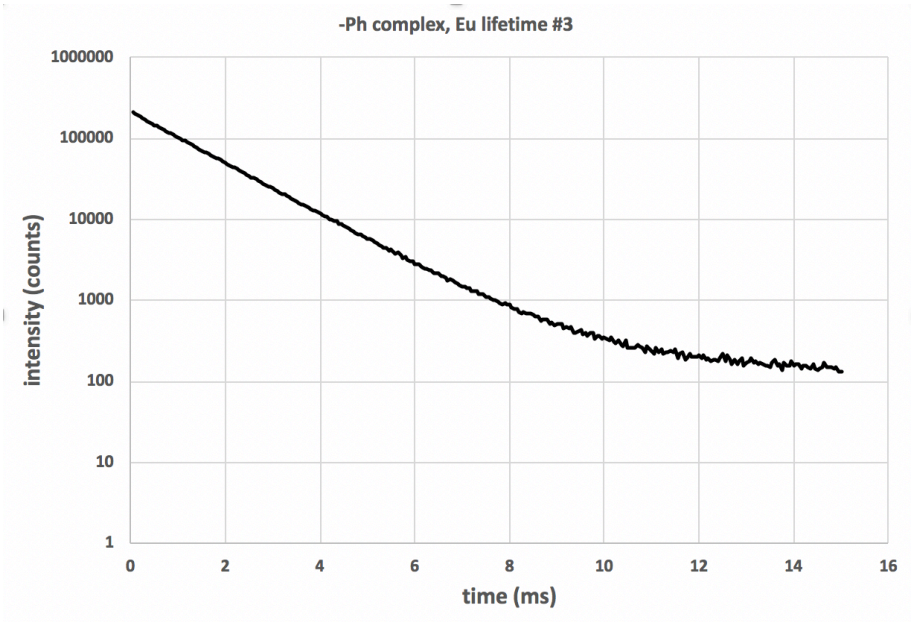


Trial #3



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	100898.51236		
Adj. R-Squa	0.99996		
		Value	Standard Er
S1	y0	202.78413	22.40824
S1	A1	272749.144	133.00573
S1	t1	1.23824	9.34105E-4



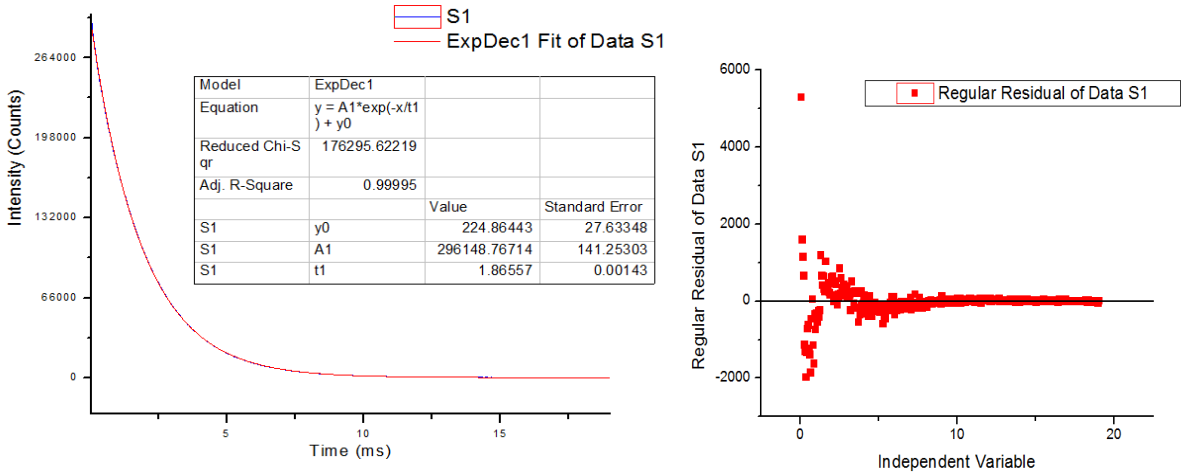


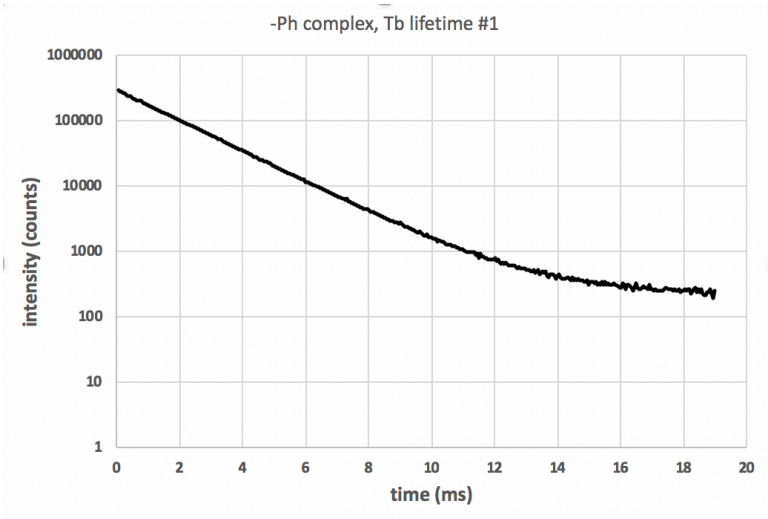
2. Ligand 2-Tb complex

Fluorimeter settings for all trials:

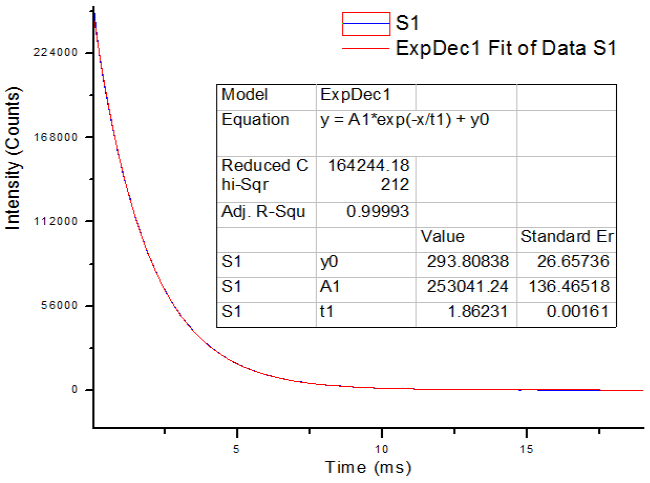
excitation: 260 nm; emission: 545 nm; slits: 2.0 nm; sample window: 1.9 ms; time between flashes: 41 ms; count (averages): 100; initial delay: 0.05 ms; max delay: 19 ms; delay increment: 0.05 ms

Trial #1

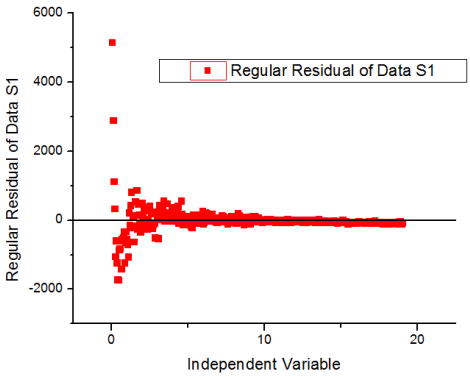


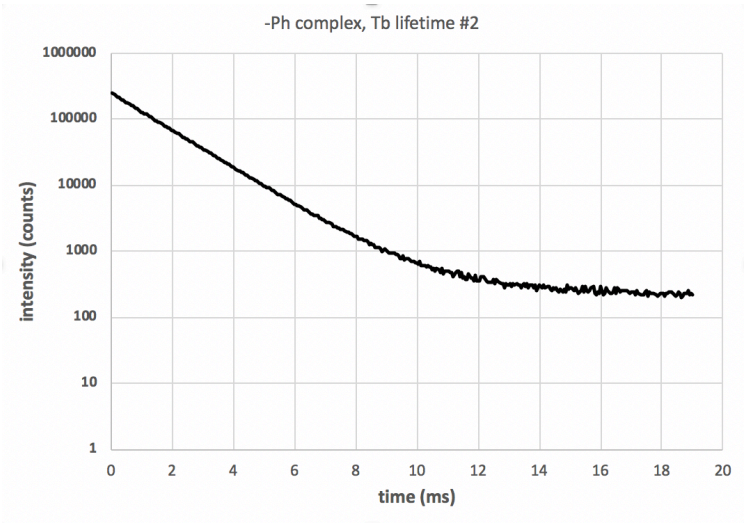


Trial #2

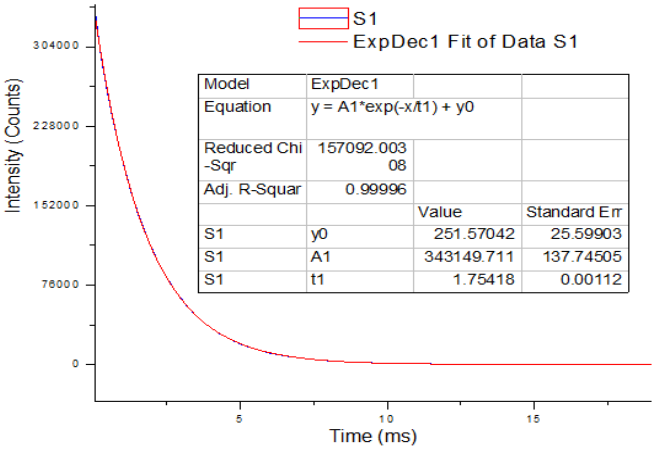


Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	164244.18212		
Adj. R-Squ	0.99993		
		Value	Standard Er
S1	y0	293.80838	26.65736
S1	A1	253041.24	136.46518
S1	t1	1.86231	0.00161





Trial #3



Model	ExpDec1		
Equation	y = A1*exp(-x/t1) + y0		
Reduced Chi-Sqr	157092.00308		
Adj. R-Squar	0.99996		
		Value	Standard Er
S1	y0	251.57042	25.59903
S1	A1	343149.711	137.74505
S1	t1	1.75418	0.00112