Heterodinuclear (Sm, Tb) lanthanide pivalates with heterocyclic N-donors: synthesis, structure, thermal behavior, magnetic and photoluminescence properties

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Fig. S1[†] Synthetic details and analytical data for complex $[SmTb(piv)_6(bath)_2] \cdot EtOH$ (**2b·EtOH**).

Synthesis of $[SmTb(piv)_6(bath)_2] \cdot EtOH$ (2b·EtOH). Single crystals of **2b·2EtOH** (30 mg) were kept over anhydrous $CaCl_2$ at 20 ºC for 2 h. The single crystals that were obtained after the desolvation retained the habit and color, remained transparent, and were suitable for X-ray diffraction. The single phase of **2b·2EtOH** was confirmed by X-ray powder diffraction. The yield of **2b·EtOH** was quantitative. The evaluated stoichiometry of Sm and Tb atoms in the crystal of **2b·EtOH** is 1.02 ± 0.05 : 1.03 ± 0.05. Found (%): C, 59.23; H, 6.01; N, 3.54. $C_{80}H_{92}Sm_{1.0}N_4O_{13}Tb_{1.0}$. Calculated (%): C, 59.06; H, 5.70; N, 3.45. FT-IR (KBr), v/cm^{-1}: 3426 m, 3082 w, 3064 m, 3032 w, 2960 s, 2924 m, 2904 m, 2864 m, 1624 s, 1594 s, 1580 m, 1564 s, 1532 s, 1522 s, 1484 s, 1458 m, 1445 m, 1424 s, 1390 m, 1376 s, 1360 s, 1286 m, 1228 s, 1160 w, 1110 w, 1092 m, 1074 w, 1028 w, 1020 w, 1002 w, 986 w, 976 w, 938 w, 894 m, 878 w, 866 w, 856 m, 834 m, 806 m, 796 m, 790 m, 764 m, 744 m, 704 s, 664 w, 628 m, 606 m, 598 s, 574 m, 564 m, 550 m, 496w, 488 w, 475 w, 434 w.

Table S1†. Crystallographic parameters and structure refinement statistics for compounds **1**, **2a**·1.75EtOH, **2b**·2EtOH, and **2b**·EtOH.

Identification code	1	2a·1.75EtOH	2b·2EtOH	2b·EtOH
Empirical formula	$C_{54}H_{70}N_4O_{12}SmTb$	$C_{81.50}H_{96.5}N_4O_{13.75}SmTb$	$C_{82}H_{98}N_4O_{14}SmTb$	$C_{80}H_{92}N_4O_{13}SmTb$
Formula weight	1276.41	1661.39	1672.91	1626.85
Temperature, K	150(2)	120(2)	173(2)	296(2)
Wavelength, Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$\bar{}$	$\bar{}$	C2/c	C2/c
a, Å	10.288(2)	12.2129(10)	30.978(6)	31.2102(8)
b, Å	11.9691(12)	14.3749(12)	14.701(3)	14.7436(4)
c, Å	12.7440(13)	23.947(2)	18.594(3)	18.7990(5)
α, deg	113.092(2)	100.5730(10)	90	90
β, deg	99.678(3)	90.8990(10)	106.894(4)	107.2480(10)
γ, deg	96.877(3)	97.9340(10)	90	90
Volume, Å^3	1392.8(3)	4089.5(6)	8102(3)	8261.4(4)
Z	1	2	4	4
Density (calc), mg/m^3	1.522	1.349	1.371	1.308
Abs. coefficient, mm^{-1}	2.364	1.63	1.646	1.611
F(000)	645	1701	3428	3324
Crystal size, mm^3	0.32 x 0.12 x 0.03	0.24 x 0.08 x 0.05	0.13 x 0.09 x 0.07	0.35 x 0.3 x 0.28
Theta range	2.827 to 26.258°	2.314 to 27.562°	2.592 to 25.995°	2.57 to 28.32°.
Index ranges	-12<=h<=12	-15<=h<=15	-38<=h<=38	-41<=h<=41
	-14<=k<=14	-18<=k<=18	-17<=k<=18	-19<=k<=19
	-15<=l<=15	-30<=l<=31	-22<=l<=19	-24<=l<=25
Reflections collected	10023	40985	26072	51828
Independent reflections, R(int)	5390, 0.0564	18812, 0.035	7947, 0.1031	10193, 0.0409
Completeness	97.7 %	99.9 %	99.9 %	99.2 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.745 and 0.571	0.7456 and 0.5906	0.7456 and 0.5688	0.6471 and 0.5166
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/ restraints/ parameters	5390 / 122 / 379	18812 / 420 / 1081	7947 / 54 / 494	10193 / 2 / 436

Goodness-of-fit on F^2	1.00	1.015	1.127	0.976
R1, wR2 [I>2σ(I)]	0.0502, 0.1014	0.0401, 0.0931	0.0729, 0.1826	0.0368, 0.1126
R1, wR2 (all data)	0.08, 0.1129	0.0708, 0.1089	0.1221, 0.2058	0.0589, 0.1382
Largest diff. peak and hole, e.Å^{-3}	1.028 and -1.522	1.319 and -0.621	1.920 and -2.123	1.462 and -0.615

Table S2†. Mass spectra of complexes [SmTb(piv)$_6$(phen)$_2$] (**1**) and [SmTb(piv)$_6$(bath)$_2$]·1.75EtOH (**2a**·1.75EtOH).

Ion	**1**	**2a**·1.75EtOH
	I_{rel}	I_{rel}
[SmTb(piv)$_2$]$^+$	$6 \cdot 10^{-2}$	$9 \cdot 10^{-2}$
[SmTb(piv)$_2$OH]$^+$	$7 \cdot 10^{-2}$	$8 \cdot 10^{-2}$
[Sm$_2$(piv)$_2$OH]$^+$	$1 \cdot 10^{-2}$	$<1 \cdot 10^{-2}$
[Tb$_2$(piv)$_2$OH]$^+$	$<1 \cdot 10^{-2}$	$<1 \cdot 10^{-2}$
[SmTb(piv)$_3$O]$^+$	0.12	0.1
[SmTb(piv)$_3$CO]$^+$	1.0	0.6
[SmTb(piv)$_3$O$_2$H]$^+$	0.15	0.16
[SmTb(piv)$_3$CCO$_2$H]$^+$	-	0.24
[SmTb(piv)$_3$CCO$_2$]$^+$	0.11	-
[Sm$_2$(piv)$_4$]$^+$	0.1	-
[SmTb(piv)$_4$]$^+$	0.43	0.58
[SmTb(piv)$_4$O$_2$H]$^+$	0.2	0.1
[SmTb(piv)$_5$-CH$_3$]$^+$	$6 \cdot 10^{-2}$	$5 \cdot 10^{-3}$
[SmTb(piv)$_5$]$^+$	0.75	1.0
[Tb$_2$(piv)$_5$]$^+$	0.25	0.15
[SmTb(piv)$_5$O$_2$H]$^+$	$<1 \cdot 10^{-2}$	$<1 \cdot 10^{-2}$
[Sm$_2$(piv)$_6$-3(CH$_3$)]$^+$	$<1 \cdot 10^{-2}$	-
[Sm$_2$Tb$_2$(piv)$_2$CCO]$^+$	$6 \cdot 10^{-2}$	$4 \cdot 10^{-2}$
[Sm$_4$(piv)$_3$-CH$_3$]$^+$	$<1 \cdot 10^{-2}$	-

Table S3†. Selected bond lengths and Ln…Ln distances (Å) in compounds [(SmTb(piv)$_6$(phen)$_2$] (**1**), [SmTb(piv)$_6$(bath)$_2$]·1.75EtOH (**2a**·1.75EtOH), [SmTb(piv)$_6$(bath)$_2$]·2EtOH (**2b**·2EtOH), and [SmTb(piv)$_6$(bath)$_2$]·EtOH (**2b**·EtOH)

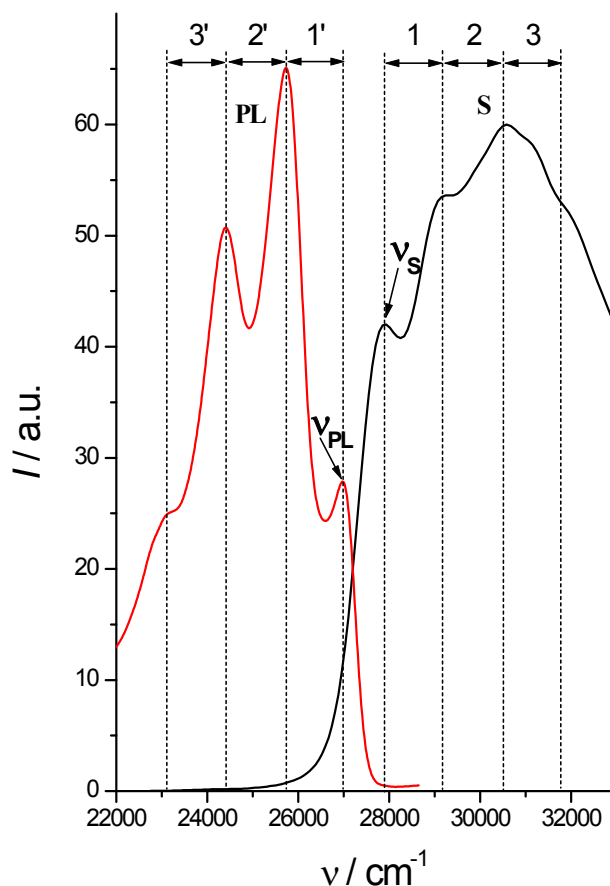| Identification code	**1**	**2a**·1.75EtOH	**2b**·2EtOH	**2b**·EtOH
Ln…Ln1'	5.391(1)	3.9909(4)	4.294(1)	4.2844(3)
Ln1—O1	2.254(5)	2.413(3)	2.411(6)	2.395(2)
Ln1—O2	2.342(5)	2.766(3)	2.284(6)	2.295(2)
Ln1—O3	2.403(5)	2.352(3)	2.402(7)	2.391(2)
Ln1—O4	2.385(5)		2.265(6)	2.282(2)
Ln1—O5	2.420(5)	2.379(3)	2.436(7)	2.435(2)
Ln1—O6	2.411(5)		2.462(7)	2.461(2)
Ln1—O7		2.360(3)		
Ln1—O9		2.444(3)		
Ln1—O10		2.469(3)		
Ln1—N1	2.550(6)	2.647(3)	2.716(7)	2.702(3)
Ln1—N1'	5.391(1)	2.615(3)	2.591(8)	2.597(3)
Ln2—O2		2.339(3)		
Ln2—O4		2.364(3)		
Ln2—O6		2.384(3)		
Ln2—O7		2.782(3)		
Ln2—O8		2.400(3)		
Ln2—O11		2.566(3)		
Ln2—O12		2.408(3)		
Ln2—N3		2.611(3)		
Ln2—N4		2.643(3)		

Figure S2† PL spectra (black, λ_{ex} = 337 nm, 77 K) and scattering (red, 300 K) spectra of gadolinium complex **7**.

Because of the complexity of the molecules from the point of view of a set of oscillators, the use of the scattering spectrum instead of the absorption spectrum, and the fact that the PL and scattering spectra were measured at different temperatures, the mirror symmetry of the curves is not visible in Figure S3. As can be seen from Figure S2, the frequency ranges 1, 2, and 3 in the scattering spectrum coincide with the corresponding ranges 1′, 2′, and 3′ in the PL spectrum. The corresponding peaks reflect the vibrational structure, which has a mirror symmetry with respect to the vertical line that passes through $\nu_0=(\nu_{PL}+\nu_S)/2$ and determines, according to the symmetry conditions for frequencies [Levshin, V. L. *Photoluminescence of Liquids and Solids*, Gos. Izd. Tekhniko-teoreticheskoi literatury, Moscow, Leningrad, 1951, p. 104 (in Russian)], the position of the S_1 energy level of the bath ligand.
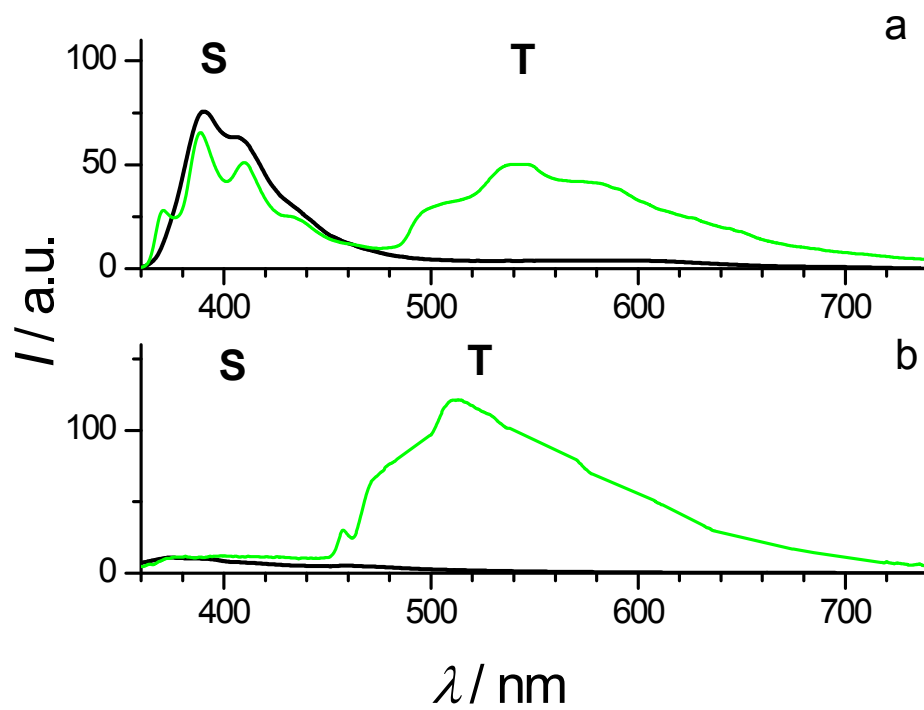
Figure S3† PL spectra of the gadolinium complexes (λ_{ex} = 337 nm; black, 300 K; green, 77 K): (a) **7**, (b) **8**.