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Supporting Information

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Assembly of Near-Infrared Luminescent Lanthanide Host(Host–Guest) Complexes With a Metallacrown Sandwich Motif**

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Supporting Information Contents:

Synthesis of Picoline hydroxamic acid (picHA)

Following a modified literature method[1], picolinic acid (5 g, 40.6 mmol) and N-methylmorpholine (5.80 mL, 52.8 mmol) were mixed under nitrogen in 100 mL of dry dichloromethane at 0 °C. Ethyl chloroformate (4.64 mL, 48.7 mmol) was added dropwise via syringe, and the mixture was stirred for ten minutes. Separately, 100 mL of methanol was sparged with nitrogen for ten minutes. In separate flasks, hydroxylamine hydrochloride (4.23 g, 60.9 mmol) and 85% potassium hydroxide (56.2 g, 60.9 mmol) were each dissolved in 50 mL of the sparged methanol. The solutions were combined and cooled at 0 °C under a stream of nitrogen for ten minutes to precipitate potassium chloride. Under an ambient atmosphere, both solutions were vacuum filtered, combined, and the flask was sealed under a nitrogen atmosphere. After stirring for one hour at room temperature, the solvent was removed under vacuum, and the residue was taken up in 150 mL of water and washed with chloroform (2 x 50 mL). The aqueous layer was dried under vacuum, and the solid was recrystallized in ~15 mL of hot water, with white needles precipitating upon cooling in an ice bath. This solid was then recrystallized in ~200 mL hot dichloromethane and filtered. ~20 mL of hexanes was added to the cloudiness point of the solution. Homogeneity was restored with a few drops of dichloromethane, and the solution was cooled at -20 °C to yield white to faint pink needles. The product was isolated by vacuum filtration, ground into a fine powder, and thoroughly dried under vacuum. Yield = 3.13 g, 56%. m.p. 116.5 °C (dec. Above 121 °C). ^{1}H NMR [$(CD_3)_2SO$, 500 Mhz, TMS], δ 11.45 (br, 1H) 9.11 (br, 1H), 8.60 (d, ^{3}J(H,H)=6 Hz, 1H, ph), 7.98(m, 2H, ph), 7.58 ppm (m, 1H, ph), ^{13}C NMR [$(CD_3)_2SO$, 100 Mhz, $(CD_3)_2SO$] δ 161.4, 150.1, 148.5, 137.6, 126.3, 121.8 ppm. IR (KBr): *v* = 3173 (b, O-H, N-H), 2860 (m, C-C), 1657 (s, C=O) 1591 (m), 1570 (m), 1495 (m), 1431 (m), 1178 (w), 1026 (w), 1000 (w), 823 (w), 703 (w), 624 cm^{-1} (w). CHN found (calc'd for $C_6H_6N_2O_2$) C: 52.10 (52.17), H: 4.34 (4.38), N: 20.32 (20.28).

We have utilized a slightly modified workup when performing the reaction with a brand new ethyl chloroformate sample (Acros, 97%). After evaporating the reaction mixture to dryness under vacuum, the residue was taken up in 15 mL of water and stirred, resulting in the precipitate of a white powder. This powder was cooled in an ice bath, vacuum filtered, and rinsed with 5 mL of cold water. Recrystallizations in water and dichloromethane and thorough drying as described above yielded the pure picoline hydroxamic acid product with a 52% yield.

Instruments and Materials

General Details*:* ^{1}H NMR spectra were recorded on a Varian Inova 500 MHz spectrometer. Chemical shifts (δ) are reported in ppm and referenced to tetramethylsilane (TMS). Coupling constants (*J*) are listed in hertz (Hz). ESI-MS was performed on a Micromass LCT Time-of-Flight mass spectrometer. ~10 μM sample solutions were injected via syringe pump with a cone voltage of 50 V. IR spectra were taken on a Perkin-Elmer Spectrum BX FT-IR spectrometer. CHN analysis was performed by Atlantic Microlabs, Inc. All materials were used as received unless specifically noted. The Picoline hydroxamic acid (picHA) synthesis was monitored by thin layer chromatography (TLC) using basic alumina TLC plates (Selecto Scientific, Alumina B F-254, 200 micron) and a 1:1:1 dichloromethane:methanol:hexanes eluent. Dry dichloromethane used in the synthesis of picHA was dried on a Glass Contours solvent purification system.

Photophysical Procedures: Stock solutions of the Ln-**1** complexes were made using *ca.* 5.0 mg of sample in 5 mL of dry HPLC grade methanol. Typical sample concentrations for absorption and fluorescence measurements were *ca*. 3×10^{-7} to 5×10^{-6} M. Measurements were collected 1.0 cm cells in quartz Spectrosil® or equivalent (Starna Cells, Inc.). UV-Visible absorption spectra were recorded on a HP 8542 diode array absorption spectrometer equipped with a temperature controller at 25.0 °C. Emission spectra were acquired on a HORIBA Jobin Yvon IBH FluoroLog-3 spectrofluorometer equipped with a temperature controller at 25.0 °C. Spectra were reference corrected for both the excitation light source variation (lamp and grating) and the emission spectral response (detector and grating). Quantum yields were determined by the optically dilute method using the following equation;

$$\frac{\Phi_x}{\Phi_r} = \left[\frac{A_r(\lambda_r)}{A_x(\lambda_x)}\right]\left[\frac{I(\lambda_r)}{I(\lambda_x)}\right]\left[\frac{n_x^2}{n_r^2}\right]\left[\frac{D_x}{D_r}\right]$$

where *A* is the absorbance at the excitation wavelength (λ), *I* is the intensity of the excitation light at the same wavelength, *n* is the refractive index and *D* is the integrated luminescence intensity (900-1100 nm). The subscripts '*x*' and '*r*' refer to the sample and reference, respectively. A quantum yield standard, $Yb(dipicolinate)_3^{3-}$, in 0.1 M TRIS buffer pH = 7.4 (Φ_r = 0.015 ± 0.02 %) was used as a reference[2] and prepared according to the literature.[3]

Luminescence lifetimes were determined with a HORIBA Jobin Yvon IBH FluoroLog-3 spectrofluorometer, adapted for time-resolved measurements. For steady-state emission spectroscopy a 450 W Xenon lamp was used as the excitation source. A thermoelectrically cooled single photon

detection module (Hamamatsu, Inc. H9170-75 NIR PMT) at -61°C and -900 V was used as the detector. Spectral selection of the emission was achieved by passage through a double grating emission monochromator (600 grooves/mm) blazed at 1 µm, the observed emission signals were not corrected for the efficiency of the grating.

For time-resolved luminescent lifetime measurements, either a sub-microsecond Xenon flash lamp (Jobin Yvon, 5000XeF) or a Sirah Cobra Stretch dye laser (CSTR-LG24, Plasmatechnik Gmbh) pumped by a QuantaRay INDI-HG Nd:YAG (SpectraPhysics, Inc.) were used as the excitation sources for the Yb(III) and Nd(III) complexes, respectively. The Xenon flash lamp was coupled to a double grating excitation monochromator for spectral selection. The Xenon flash lamp was coupled to a double grating excitation monochromator for spectral selection. The input pulse energy (100 nF discharge capacitance) was *ca*. 50 mJ, yielding an optical pulse duration of less than 300 ns at FWHM for the Xenon flash lamp. The dye laser pulse 8-10 ns, with an approximate energy of 10 mJ/pulse (λ_{EX} = 376, Exalite 376 Dye), was routed directly into the sample chamber of the Fluorolog. A portion of this excitation was sampled with a 10% beam splitter, which was focused onto the entrance of a UV-sensitive photodiode (DET210, Thor Laboratories). The small amplitude analogue output from the photodiode was processed into a TAC Start signal (NIM) using a TB-01 pulse converter module from IBH. The output signal from the PMT was processed using a TB-02 0.5 GHz preamplifier module from IBH, and a 100 MHz Constant Fraction Discriminator (CFD) (Model 6915, Phillips Scientific), yielding appropriate TAC Stop signals (NIM). These were acquired using a 2 ns PCI Multi Channel Scaling (MCS) card (Model P7888-1E, FAST ComTec GmbH) Signals were acquired using an IBH DataStation Hub photon counting module and data analysis was performed using the commercially available DAS 6 decay analysis software package from HORIBA Jobin Yvon IBH. Goodness of fit was assessed by minimizing the reduced chi squared function, χ^2, and a visual inspection of the weighted residuals. Each trace contained at least 10,000 points and the reported lifetime values result from at least three independent measurements.

Synthesis and Characterization of Ln-1 complexes

Yb-**1** was prepared using a modified procedure for Tb-**1**. PicHA (150 mg, 1.09 mmol) and sodium hydroxide (2.186 mL of a 0.9937 M solution in methanol, 2.17 mmol) were stirred in 20 mL of methanol. Once dissolved, zinc trifluoromethanesulfonate (395 mg, 1.09 mmol) was added, turning the solution cloudy. Ytterbium nitrate (30.5 mg, 0.068 mmol) was then added and the solution gradually clarified. After twenty minutes, 5 mL of pyridine was added. After another 20 minutes, 5 mL of water was added. After another twenty minutes, the solution was gravity filtered and set to slowly evaporate, yielding yellow crystals within two weeks. Yield = 22.9 mg, 7 %. ESI-MS (methanol): 1132.5^{3+} [1132.4 calcd. For $YbZn_{16}(C_6H_4N_2O_2)_{16}^{3+}$]. CHN found (calc'd for $YbZn_{16}(C_6H_4N_2O_2)_{16}(C_5H_5N)_8(CF_3SO_3)_3(H_2O)_2(CH_4O)_4$) C: 37.40 (37.01), H: 2.50 (2.69), N: 11.85 (12.07).

All other complexes were prepared using the procedure for Tb-**1**, though substituting the appropriate lanthanide nitrate salt for Terbium nitrate.

La-***1***. Yield = 51.7 mg, 16%. ESI-MS (methanol): 1120.8^{3+} [1120.7 calcd. For $LaZn_{16}(C_6H_4N_2O_2)_{16}^{3+}$]. CHN found (calc'd for $LaZn_{16}(C_6H_4N_2O_2)_{16}(C_5H_5N)_8(CF_3SO_3)(H2O)_4(CH_4O)$) C: 37.09 (37.00), H: 2.40 (2.78), N: 12.36 (12.07).

Sm-***1***. Yield = 159.7 mg, 50%. ESI-MS (methanol): 1124.3^{3+} [1124.4 calcd. For $SmZn_{16}(C_6H_4N_2O_2)_{16}^{3+}$]. CHN found (calc'd for $SmZn_{16}(C_6H_4N_2O_2)_{16}(C_5H_5N)_8(CF_3SO_3)_3(H2O)_{12}$) C: 35.49 (35.75), H: 2.26 (2.76), N: 12.00 (11.83).

Eu-***1***. Yield = 62.9 mg, 20%. ESI-MS (methanol): 1125.2^{3+} [1125.4 calcd. For $EuZn_{16}(C_6H_4N_2O_2)_{16}^{3+}$]. CHN found (calc'd for $EuZn_{16}(C_6H_4N_2O_2)_{16}(C_5H_5N)_8(CF_3SO_3)_3(H2O)_9$) C: 35.95 (36.15), H: 2.44 (2.66), N: 11.94 (12.13).

Dy-***1***. Yield = 99.3 mg, 31%. ESI-MS (methanol): 1128.5^{3+} [1128.7 calcd. For $DyZn_{16}(C_6H_4N_2O_2)_{16}^{3+}$]. CHN found (calc'd for $DyZn_{16}(C_6H_4N_2O_2)_{16}(C_5H_5N)_8(CF_3SO_3)_3(H2O)_{11}$) C: 35.66 (35.79), H: 2.41 (2.72), N: 11.81 (12.01).

H-H COSY NMR Spectrum

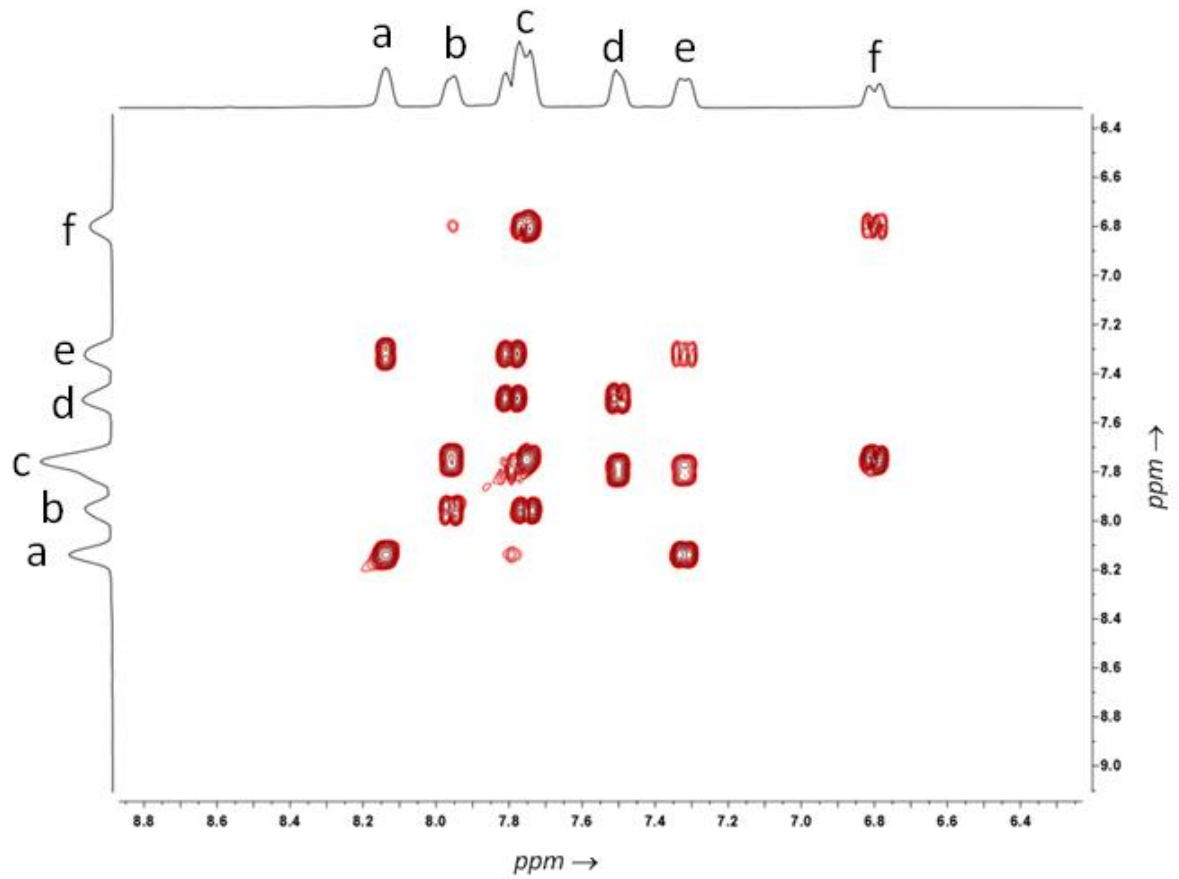


Figure S1: H-H COSY NMR spectrum of Y-**1**(pyridine-D_5)$_8$(Otf)$_3$ in deuterated methanol at 25.0 °C. 1-D ^{1}H NMR spectrum peak details: (500 MHz, TMS): a: δ = 8.14 (d, J=5 Hz, 1H), b: δ = 7.96 (d, J=8 Hz, 1H), c: δ = 7.77 (m, 3H), d: δ = 7.50 (d, J=8 Hz, 1H), e: δ = 7.32 (t, J=6 Hz, 1H), f: δ = 6.80 (t, J=6 Hz, 1H).

H-H COSY NMR Peak Assignment

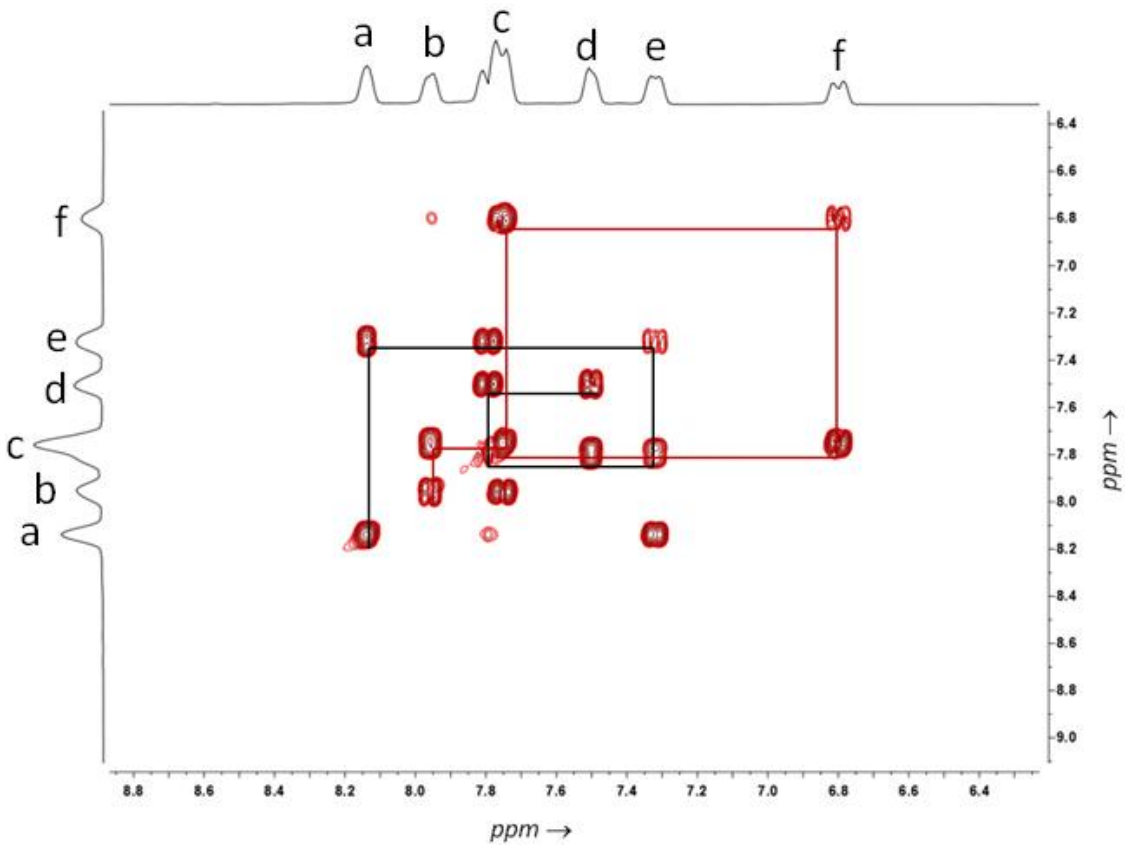
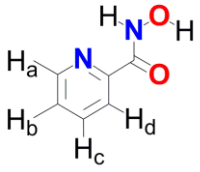
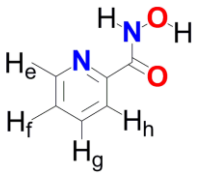


Figure S2: H-H COSY NMR spectrum of Y-**1**(pyridine-D_5)$_8$(Otf)$_3$ in deuterated methanol at 25.0 °C. Correlations between proton resonances are depicted with black(picHA 1) or red(picHA 2) lines.





<u>picHA 1</u>

H_a = peak a

H_b = peak e

H_c = peak c

H_d = peak d

<u>picHA 2</u>

H_e = peak b

H_f = peak c

H_g = peak f

H_h = peak c

We have tentatively assigned picHA 1 as the ligand on the [12-MC-4] subunit due to its more downfield chemical shifts.

^{1}H STE NMR

^{1}H stimulated echo (STE) NMR was performed with the DOSY gradient compensated stimulated echo with spin lock and convection compensation (DgcsteSL_cc) pulse sequence at 298 K. A diffusion delay of 150 ms, diffusion gradient length of 3.0 ms, and a gradient strength array of 15 increments from ~90 to 28 %. The gradient field strength was calibrated with D_2O by the University of Michigan NMR facility staff. The data was fit according to equation 1 to solve for D (the diffusion coefficient), where I = intensity or integral of the peak at a given G, I_0 = intensity or integral of the peak at G = 0, γ = magnetogyric constant of the nucleus (for ^{1}H, g = 2.675 x 108 T^{-1} s^{-1}), δ = diffusion gradient length, Δ = diffusion delay, G = gradient field strength.

$$\ln(I/I_0)=-\gamma^2\delta^2G^2(\Delta-\delta/3)D \qquad (1)$$

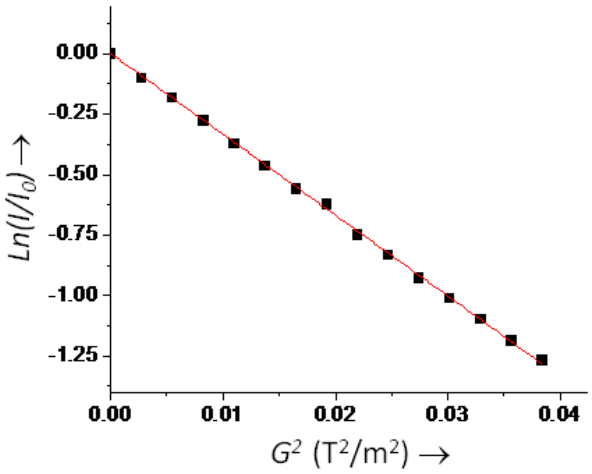


Figure S3: Stejskal-Tanner attenuation plot of Y-**1**(pyridine-D_5)$_8$(Otf)$_3$ in deuterated methanol at 25.0 °C. From the plot, diffusion coefficients ranging from 3.45 ± 0.01 x 10^{-9} to 3.51 ± 0.01 x 10^{-9} m^2/s were calculated for the six phenyl proton resonances.

With the diffusion coefficient, the hydrodynamic radius was calculated using the Stokes-Einstein equation (2), where k_b = Boltzman constant, 1.3806 x 10-23 kg·m^2/(s^2·K^1), T = temperature, η = viscosity of the solution at temperature T, D = diffusion coefficient. Using the value for η for methanol at 298 K of 5.44x10^{-4} kg/(m·s)[4] (ignoring isotope effects), giving r_H = 11.6 ± 0.2 Å.

$$r_H = \frac{k_b T}{6\pi\eta D} \qquad (2)$$

Photophysical Characterization of Ln-1 complexes.

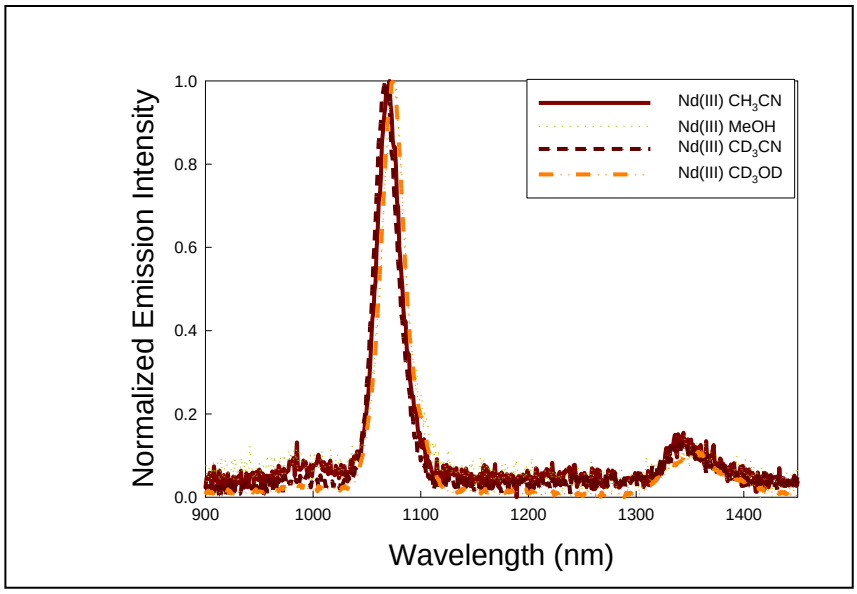


Figure S4. Normalized emission of Nd-**1** in deuterated and non-deuterated methanol and acetonitrile. Emission spectra were collected with absorbance of ~0.1 at 320 nm and excitation at 320 nm (14.5 nm bandpass) at 25.0 °C.

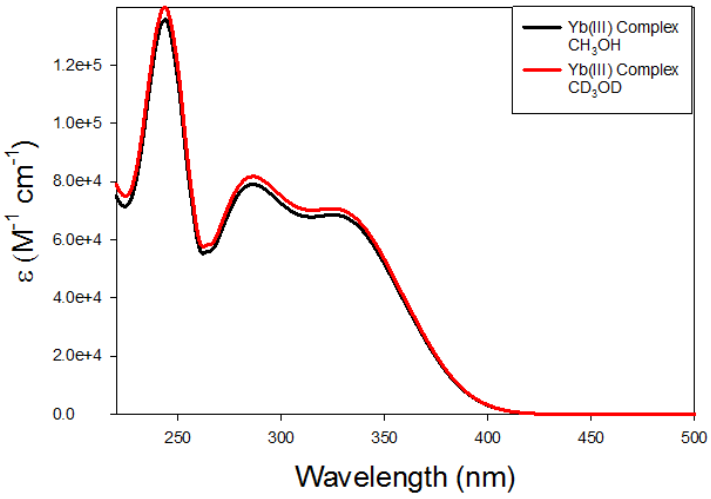


Figure S5. Absorption spectra of Yb-**1** in methanol (black) and deuterated methanol (red). As expected, Yb-**1** displays a nearly identical absorption spectrum in either solvent collected at 25.0 °C.

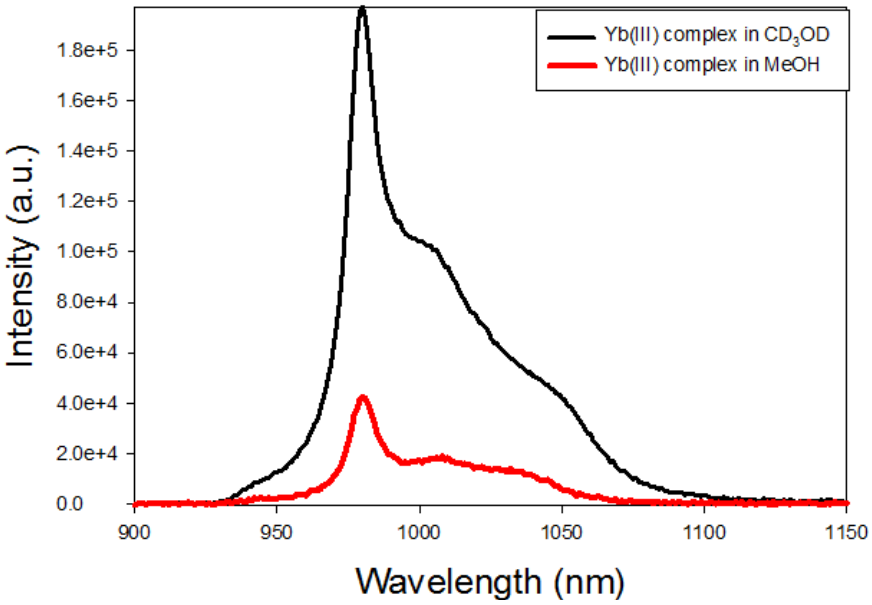


Figure S6. Emission spectra (4 nm bandpass) of Yb-**1** at 25.0 °C in MeOH (-) and CD_3OD (-). Emission spectra were collected with absorbance of ~0.1 at 280 nm by excitation at 280 nm (14.5 nm bandpass).

Color Images of Tb-1 from Figure 2.

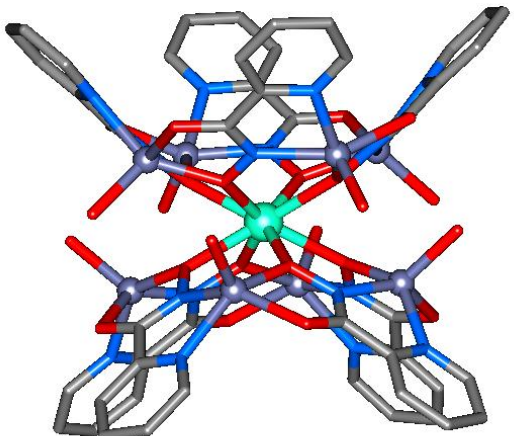


Figure S6: Image from the crystal structure of Tb-**1** highlighting the Tb[12-$MC_{Zn(II),\ picHA}$-4]$^{3+}$ sandwich complex. Color scheme: Red = oxygen, blue = nitrogen, light gray = carbon, dark gray = zinc, blue-green = terbium.

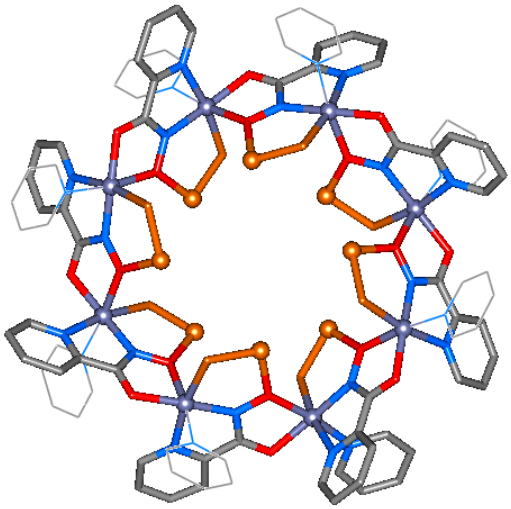
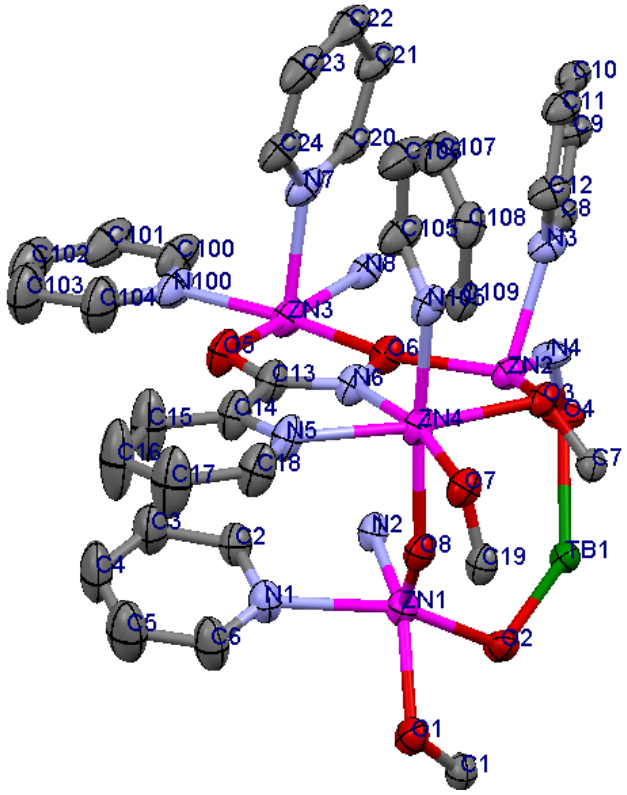


Figure S7: Image from the crystal structure of Tb-**1** highlighting the [24-$MC_{Zn(II),\ picHA}$-8]. Color scheme: Red = oxygen, blue = nitrogen, gold = Zn(II) and oxygen atoms on the Tb[12-$MC_{Zn(II),\ picHA}$-4]$^{3+}$ sandwich that bind to the [[24-MC-8], light gray = carbon, dark gray = zinc.

TEP diagram of the Tb-1 asymmetric unit with the atom labeling scheme

Figure S9. TEP diagram of the asymmetric unit of Tb-**1** that displays the atom labeling scheme. Ellipsoids are displayed at the 50% probability level.



1. A. S. Reddy, M. S. Kumar, G. R. Reddy, *Tet. Lett.* **2000**, *41*, 6285.
2. A, Aebischer, F. Gumy, J.-C. G. Bünzli, *Phys. Chem. Chem. Phys.* **2009**, *11*, 1346–1353.
2. P. A. Brayshaw, J.-C. G. Bünzli,; P. Froidevaux, J. M. Harrowfield, Y. Kim, A. N. Sobolev, *Inorg. Chem.* **1995**, *34*, 2068.
3. *CRC Handbook of Chemistry and Physics, 88th edition.* (Ed. D. Lide) CRC Press, Boca Raton. **1992**.

Crystal data and structure refinement for Tb-1.

Empirical formula	C139 H152 F8 N40 O64 S3 Tb Zn16
Formula weight	4860.03
Temperature	85(2) K
Wavelength	1.54178 A
Crystal system, space group	Tetragonal, P(4)/nnc
Unit cell dimensions	a = 27.3594(4) Å alpha = 90 deg. b = 27.3594(4) Å beta = 90 deg. c = 28.025(2) Å gamma = 90 deg.
Volume	20977.6(16) $Å^3$
Z, Calculated density	4, 1.539 Mg/m^3
Absorption coefficient	4.637 mm^{-1}
F(000)	9772
Crystal size	0.23 x 0.20 x 0.13 mm
Theta range for data collection	3.23 to 68.26 deg.
Limiting indices	-32<=h<=32, -32<=k<=32, -33<=l<=33
Reflections collected / unique	281538 / 9625 [R(int) = 0.1071]

Completeness to theta = 68.26 99.9 %

Absorption correction Semi-empirical from equivalents

Max. and min. transmission 0.5839 and 0.4152

Refinement method Full-matrix least-squares on F^2

Data / restraints / parameters 9625 / 126 / 742

Goodness-of-fit on F^2 1.090

Final R indices [I>2sigma(I)] $R_1 = 0.0535$, $wR^2 = 0.1729$

R indices (all data) $R_1 = 0.0550$, $wR^2 = 0.1743$

Largest diff. peak and hole 0.910 and -0.843 e. $Å^{-3}$

Bond lengths [A] and angles [deg] for Tb-1.

Tb(1)-O(2)#1	2.349(3)
Tb(1)-O(2)	2.349(3)
Tb(1)-O(2)#2	2.349(3)
Tb(1)-O(2)#3	2.349(3)
Tb(1)-O(4)#3	2.356(3)
Tb(1)-O(4)	2.356(3)
Tb(1)-O(4)#2	2.356(3)
Tb(1)-O(4)#1	2.356(3)
Zn(1)-O(8)	1.981(3)
Zn(1)-O(2)	2.033(3)
Zn(1)-N(2)	2.065(4)
Zn(1)-O(1)	2.132(3)
Zn(1)-N(1)	2.202(4)
Zn(2)-O(6)	1.980(3)
Zn(2)-O(4)#2	1.999(3)
Zn(2)-N(4)	2.056(4)
Zn(2)-N(3)	2.137(4)
Zn(2)-O(3)	2.151(3)
Zn(3)-O(5)	2.003(3)
Zn(3)-N(8)	2.035(4)
Zn(3)-O(6)	2.135(3)
Zn(3)-N(100)	2.188(4)
Zn(3)-N(7)	2.200(4)
Zn(3)-O(1)#1	2.296(3)
Zn(4)-O(7)	2.016(3)
Zn(4)-N(6)	2.054(4)
Zn(4)-O(8)	2.153(3)
Zn(4)-N(105)	2.181(4)
Zn(4)-N(5)	2.211(4)

Zn(4)-O(3)	2.243(3)
N(1)-C(6)	1.344(6)
N(1)-C(2)	1.343(6)
N(2)-C(1)#1	1.287(6)
N(2)-O(2)#1	1.373(5)
N(3)-C(12)	1.341(5)
N(3)-C(8)	1.355(5)
N(4)-C(7)#1	1.299(6)
N(4)-O(4)	1.373(4)
N(5)-C(18)	1.328(6)
N(5)-C(14)	1.348(6)
N(6)-C(13)	1.305(6)
N(6)-O(6)	1.387(5)
N(7)-C(20)	1.337(6)
N(7)-C(24)	1.347(6)
N(8)-C(19)#1	1.313(6)
N(8)-O(8)#1	1.391(5)
O(1)-C(1)	1.314(5)
O(1)-Zn(3)#2	2.296(3)
O(2)-N(2)#2	1.373(5)
O(3)-C(7)	1.304(5)
O(4)-Zn(2)#1	1.999(3)
O(5)-C(13)	1.290(6)
O(7)-C(19)	1.292(6)
O(8)-N(8)#2	1.391(5)
C(1)-N(2)#2	1.287(6)
C(1)-C(2)#2	1.487(6)
C(2)-C(3)	1.386(7)
C(2)-C(1)#1	1.487(6)
C(3)-C(4)	1.376(8)
C(4)-C(5)	1.389(10)
C(5)-C(6)	1.369(8)

C(7)-N(4)#2	1.299(6)
C(7)-C(8)#2	1.491(6)
C(8)-C(9)	1.380(6)
C(8)-C(7)#1	1.491(6)
C(9)-C(10)	1.389(6)
C(10)-C(11)	1.379(7)
C(11)-C(12)	1.385(6)
C(13)-C(14)	1.474(6)
C(14)-C(15)	1.389(7)
C(15)-C(16)	1.383(9)
C(16)-C(17)	1.390(9)
C(17)-C(18)	1.396(8)
C(19)-N(8)#2	1.313(6)
C(19)-C(20)#2	1.488(6)
C(20)-C(21)	1.388(7)
C(20)-C(19)#1	1.488(6)
C(21)-C(22)	1.391(6)
C(22)-C(23)	1.377(8)
C(23)-C(24)	1.376(8)
N(100)-C(104)	1.320(8)
N(100)-C(100)	1.335(7)
C(100)-C(101)	1.376(7)
C(101)-C(102)	1.358(10)
C(102)-C(103)	1.372(10)
C(103)-C(104)	1.393(8)
N(105)-C(109)	1.340(6)
N(105)-C(105)	1.344(6)
C(105)-C(106)	1.386(7)
C(106)-C(107)	1.385(8)
C(107)-C(108)	1.366(8)
C(108)-C(109)	1.391(7)
S(250)-O(251)	1.395(13)

S(250)-O(252)	1.401(11)
S(250)-O(250)	1.402(12)
S(250)-C(250)	1.802(12)
C(250)-F(251)	1.305(12)
C(250)-F(250)	1.316(12)
C(250)-F(252)	1.319(13)

O(2)#1-Tb(1)-O(2)	77.62(7)
O(2)#1-Tb(1)-O(2)#2	124.82(16)
O(2)-Tb(1)-O(2)#2	77.61(7)
O(2)#1-Tb(1)-O(2)#3	77.61(7)
O(2)-Tb(1)-O(2)#3	124.82(16)
O(2)#2-Tb(1)-O(2)#3	77.62(7)
O(2)#1-Tb(1)-O(4)#3	141.14(10)
O(2)-Tb(1)-O(4)#3	70.13(10)
O(2)#2-Tb(1)-O(4)#3	68.84(11)
O(2)#3-Tb(1)-O(4)#3	139.25(10)
O(2)#1-Tb(1)-O(4)	68.84(11)
O(2)-Tb(1)-O(4)	139.25(10)
O(2)#2-Tb(1)-O(4)	141.14(10)
O(2)#3-Tb(1)-O(4)	70.13(10)
O(4)#3-Tb(1)-O(4)	126.39(15)
O(2)#1-Tb(1)-O(4)#2	70.13(10)
O(2)-Tb(1)-O(4)#2	68.84(11)
O(2)#2-Tb(1)-O(4)#2	139.25(10)
O(2)#3-Tb(1)-O(4)#2	141.13(10)
O(4)#3-Tb(1)-O(4)#2	78.26(6)
O(4)-Tb(1)-O(4)#2	78.27(6)
O(2)#1-Tb(1)-O(4)#1	139.25(10)
O(2)-Tb(1)-O(4)#1	141.14(10)
O(2)#2-Tb(1)-O(4)#1	70.13(10)
O(2)#3-Tb(1)-O(4)#1	68.84(11)

O(4)#3-Tb(1)-O(4)#1	78.27(6)
O(4)-Tb(1)-O(4)#1	78.27(6)
O(4)#2-Tb(1)-O(4)#1	126.39(15)
O(8)-Zn(1)-O(2)	120.29(12)
O(8)-Zn(1)-N(2)	117.13(14)
O(2)-Zn(1)-N(2)	86.30(13)
O(8)-Zn(1)-O(1)	102.47(12)
O(2)-Zn(1)-O(1)	77.05(11)
N(2)-Zn(1)-O(1)	140.16(14)
O(8)-Zn(1)-N(1)	97.85(14)
O(2)-Zn(1)-N(1)	141.85(14)
N(2)-Zn(1)-N(1)	74.56(15)
O(1)-Zn(1)-N(1)	96.80(13)
O(6)-Zn(2)-O(4)#2	117.92(13)
O(6)-Zn(2)-N(4)	111.51(13)
O(4)#2-Zn(2)-N(4)	87.69(13)
O(6)-Zn(2)-N(3)	98.24(13)
O(4)#2-Zn(2)-N(3)	143.75(13)
N(4)-Zn(2)-N(3)	75.93(13)
O(6)-Zn(2)-O(3)	103.33(11)
O(4)#2-Zn(2)-O(3)	78.13(11)
N(4)-Zn(2)-O(3)	145.06(13)
N(3)-Zn(2)-O(3)	97.02(12)
O(5)-Zn(3)-N(8)	170.10(14)
O(5)-Zn(3)-O(6)	79.30(11)
N(8)-Zn(3)-O(6)	94.06(12)
O(5)-Zn(3)-N(100)	92.55(14)
N(8)-Zn(3)-N(100)	94.23(15)
O(6)-Zn(3)-N(100)	171.71(14)
O(5)-Zn(3)-N(7)	95.47(15)
N(8)-Zn(3)-N(7)	77.06(14)
O(6)-Zn(3)-N(7)	89.97(12)

N(100)-Zn(3)-N(7)	92.35(14)
O(5)-Zn(3)-O(1)#1	94.37(13)
N(8)-Zn(3)-O(1)#1	93.39(13)
O(6)-Zn(3)-O(1)#1	93.89(11)
N(100)-Zn(3)-O(1)#1	85.14(13)
N(7)-Zn(3)-O(1)#1	169.94(13)
O(7)-Zn(4)-N(6)	167.00(14)
O(7)-Zn(4)-O(8)	78.91(12)
N(6)-Zn(4)-O(8)	91.79(13)
O(7)-Zn(4)-N(105)	92.80(13)
N(6)-Zn(4)-N(105)	96.68(14)
O(8)-Zn(4)-N(105)	171.51(12)
O(7)-Zn(4)-N(5)	94.34(13)
N(6)-Zn(4)-N(5)	76.72(14)
O(8)-Zn(4)-N(5)	91.72(14)
N(105)-Zn(4)-N(5)	90.75(15)
O(7)-Zn(4)-O(3)	94.86(11)
N(6)-Zn(4)-O(3)	94.47(12)
O(8)-Zn(4)-O(3)	91.67(11)
N(105)-Zn(4)-O(3)	87.15(12)
N(5)-Zn(4)-O(3)	170.65(13)
C(6)-N(1)-C(2)	118.9(4)
C(6)-N(1)-Zn(1)	127.8(4)
C(2)-N(1)-Zn(1)	113.2(3)
C(1)#1-N(2)-O(2)#1	114.3(4)
C(1)#1-N(2)-Zn(1)	120.9(3)
O(2)#1-N(2)-Zn(1)	124.3(3)
C(12)-N(3)-C(8)	118.7(4)
C(12)-N(3)-Zn(2)	127.4(3)
C(8)-N(3)-Zn(2)	113.5(3)
C(7)#1-N(4)-O(4)	114.5(3)
C(7)#1-N(4)-Zn(2)	119.8(3)

O(4)-N(4)-Zn(2)	125.6(3)
C(18)-N(5)-C(14)	119.3(4)
C(18)-N(5)-Zn(4)	129.0(3)
C(14)-N(5)-Zn(4)	111.4(3)
C(13)-N(6)-O(6)	114.7(3)
C(13)-N(6)-Zn(4)	119.2(3)
O(6)-N(6)-Zn(4)	126.0(3)
C(20)-N(7)-C(24)	118.7(4)
C(20)-N(7)-Zn(3)	112.0(3)
C(24)-N(7)-Zn(3)	129.0(4)
C(19)#1-N(8)-O(8)#1	114.5(4)
C(19)#1-N(8)-Zn(3)	118.8(3)
O(8)#1-N(8)-Zn(3)	126.0(3)
C(1)-O(1)-Zn(1)	107.7(3)
C(1)-O(1)-Zn(3)#2	108.2(3)
Zn(1)-O(1)-Zn(3)#2	100.01(13)
N(2)#2-O(2)-Zn(1)	113.7(2)
N(2)#2-O(2)-Tb(1)	121.6(2)
Zn(1)-O(2)-Tb(1)	121.09(13)
C(7)-O(3)-Zn(2)	105.3(2)
C(7)-O(3)-Zn(4)	113.4(3)
Zn(2)-O(3)-Zn(4)	100.58(11)
N(4)-O(4)-Zn(2)#1	113.0(2)
N(4)-O(4)-Tb(1)	120.5(2)
Zn(2)#1-O(4)-Tb(1)	121.77(13)
C(13)-O(5)-Zn(3)	111.6(3)
N(6)-O(6)-Zn(2)	112.8(2)
N(6)-O(6)-Zn(3)	108.8(2)
Zn(2)-O(6)-Zn(3)	137.59(14)
C(19)-O(7)-Zn(4)	111.2(3)
N(8)#2-O(8)-Zn(1)	112.9(2)
N(8)#2-O(8)-Zn(4)	108.4(2)

Zn(1)-O(8)-Zn(4)	136.42(15)
N(2)#2-C(1)-O(1)	124.1(4)
N(2)#2-C(1)-C(2)#2	113.7(4)
O(1)-C(1)-C(2)#2	122.1(4)
N(1)-C(2)-C(3)	121.7(5)
N(1)-C(2)-C(1)#1	115.6(4)
C(3)-C(2)-C(1)#1	122.7(5)
C(4)-C(3)-C(2)	119.0(5)
C(3)-C(4)-C(5)	119.2(5)
C(6)-C(5)-C(4)	118.8(6)
N(1)-C(6)-C(5)	122.4(6)
N(4)#2-C(7)-O(3)	124.7(4)
N(4)#2-C(7)-C(8)#2	113.3(4)
O(3)-C(7)-C(8)#2	121.9(4)
N(3)-C(8)-C(9)	121.8(4)
N(3)-C(8)-C(7)#1	115.2(4)
C(9)-C(8)-C(7)#1	123.0(4)
C(8)-C(9)-C(10)	119.0(4)
C(11)-C(10)-C(9)	119.4(4)
C(10)-C(11)-C(12)	118.8(4)
N(3)-C(12)-C(11)	122.4(4)
O(5)-C(13)-N(6)	125.5(4)
O(5)-C(13)-C(14)	118.9(4)
N(6)-C(13)-C(14)	115.5(4)
N(5)-C(14)-C(15)	122.1(5)
N(5)-C(14)-C(13)	116.9(4)
C(15)-C(14)-C(13)	121.0(4)
C(16)-C(15)-C(14)	118.7(5)
C(15)-C(16)-C(17)	119.0(6)
C(16)-C(17)-C(18)	118.9(5)
N(5)-C(18)-C(17)	121.8(5)
O(7)-C(19)-N(8)#2	125.7(4)

O(7)-C(19)-C(20)#2 119.1(4)

N(8)#2-C(19)-C(20)#2 115.2(4)

N(7)-C(20)-C(21) 122.7(4)

N(7)-C(20)-C(19)#1 116.1(4)

C(21)-C(20)-C(19)#1 121.1(4)

C(20)-C(21)-C(22) 117.6(5)

C(23)-C(22)-C(21) 120.1(5)

C(24)-C(23)-C(22) 118.6(4)

N(7)-C(24)-C(23) 122.4(5)

C(104)-N(100)-C(100) 117.6(5)

C(104)-N(100)-Zn(3) 120.9(4)

C(100)-N(100)-Zn(3) 121.3(4)

N(100)-C(100)-C(101) 122.9(6)

C(102)-C(101)-C(100) 119.2(6)

C(101)-C(102)-C(103) 118.9(5)

C(102)-C(103)-C(104) 118.6(7)

N(100)-C(104)-C(103) 122.7(6)

C(109)-N(105)-C(105) 118.2(4)

C(109)-N(105)-Zn(4) 120.3(3)

C(105)-N(105)-Zn(4) 121.5(3)

N(105)-C(105)-C(106) 122.3(5)

C(107)-C(106)-C(105) 118.8(5)

C(108)-C(107)-C(106) 119.3(5)

C(107)-C(108)-C(109) 119.1(5)

N(105)-C(109)-C(108) 122.3(4)

O(251)-S(250)-O(252) 108.9(14)

O(251)-S(250)-O(250) 116.8(8)

O(252)-S(250)-O(250) 113.6(15)

O(251)-S(250)-C(250) 106.3(10)

O(252)-S(250)-C(250) 102.4(7)

O(250)-S(250)-C(250) 107.5(12)

F(251)-C(250)-F(250) 106.0(10)

F(251)-C(250)-F(252)	107.5(15)
F(250)-C(250)-F(252)	108.0(15)
F(251)-C(250)-S(250)	112.0(10)
F(250)-C(250)-S(250)	112.5(9)
F(252)-C(250)-S(250)	110.6(8)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+1/2,z #2 -y+1/2,x,z #3 -x+1/2,-y+1/2,z

Anisotropic displacement parameters (A^2 x 10^3) for Tb-1.

The anisotropic displacement factor exponent takes the form:

-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Tb(1)	25(1)	25(1)	28(1)	0	0	0
Zn(1)	29(1)	28(1)	36(1)	2(1)	-5(1)	-1(1)
Zn(2)	25(1)	27(1)	36(1)	2(1)	1(1)	0(1)
Zn(3)	29(1)	29(1)	46(1)	10(1)	-3(1)	1(1)
Zn(4)	29(1)	28(1)	40(1)	8(1)	-4(1)	-2(1)
N(1)	45(2)	40(2)	40(2)	1(2)	-11(2)	-4(2)
N(2)	29(2)	34(2)	36(2)	3(2)	-6(2)	-3(1)
N(3)	30(2)	30(2)	40(2)	8(1)	7(1)	1(1)
N(4)	26(2)	34(2)	37(2)	-4(2)	9(1)	0(1)
N(5)	33(2)	37(2)	50(2)	11(2)	-12(2)	-6(2)
N(6)	27(2)	29(2)	44(2)	8(1)	-4(1)	-5(1)
N(7)	29(2)	33(2)	52(2)	15(2)	3(2)	3(1)
N(8)	25(2)	31(2)	42(2)	10(1)	2(1)	0(1)
O(1)	31(2)	34(2)	45(2)	-5(1)	-7(1)	-1(1)
O(2)	30(2)	31(2)	44(2)	-10(1)	-4(1)	3(1)
O(3)	27(1)	30(1)	34(1)	6(1)	0(1)	0(1)
O(4)	28(1)	32(2)	43(2)	-10(1)	13(1)	-3(1)
O(5)	37(2)	33(2)	54(2)	15(1)	-14(1)	-3(1)
O(6)	26(1)	26(1)	42(2)	6(1)	-4(1)	-4(1)
O(7)	33(2)	32(2)	44(2)	8(1)	-2(1)	-2(1)
O(8)	33(2)	27(1)	40(2)	6(1)	-6(1)	2(1)
C(1)	33(2)	36(2)	34(2)	-1(2)	-6(2)	-2(2)

C(2)	42(2)	40(2)	38(2)	7(2)	-8(2)	-2(2)
C(3)	64(4)	48(3)	56(3)	4(2)	-24(3)	1(3)
C(4)	81(4)	72(4)	67(4)	5(3)	-46(3)	-3(3)
C(5)	91(5)	60(4)	78(4)	-6(3)	-39(4)	-11(3)
C(6)	72(4)	44(3)	54(3)	0(2)	-28(3)	-11(3)
C(7)	27(2)	32(2)	28(2)	1(2)	-2(2)	0(2)
C(8)	28(2)	31(2)	33(2)	4(2)	2(2)	3(2)
C(9)	33(2)	30(2)	36(2)	3(2)	5(2)	2(2)
C(10)	33(2)	38(2)	33(2)	4(2)	6(2)	9(2)
C(11)	32(2)	40(2)	41(2)	8(2)	7(2)	4(2)
C(12)	34(2)	33(2)	43(2)	8(2)	11(2)	0(2)
C(13)	33(2)	38(2)	44(2)	7(2)	-10(2)	-4(2)
C(14)	41(3)	38(3)	55(3)	12(2)	-15(2)	-10(2)
C(15)	88(5)	52(3)	83(4)	25(3)	-52(4)	-26(3)
C(16)	105(6)	67(4)	104(5)	28(4)	-73(5)	-35(4)
C(17)	85(5)	46(3)	99(5)	19(3)	-48(4)	-28(3)
C(18)	44(3)	34(2)	72(3)	12(2)	-19(2)	-13(2)
C(19)	33(2)	28(2)	41(2)	4(2)	-10(2)	-6(2)
C(20)	27(2)	37(2)	45(2)	16(2)	5(2)	4(2)
C(21)	29(2)	44(2)	51(3)	15(2)	6(2)	4(2)
C(22)	34(2)	50(3)	53(3)	21(2)	9(2)	8(2)
C(23)	32(2)	46(3)	70(3)	30(2)	6(2)	3(2)
C(24)	27(2)	35(2)	66(3)	18(2)	2(2)	2(2)
N(100)	37(2)	44(2)	46(2)	16(2)	1(2)	8(2)
C(100)	42(3)	41(3)	64(3)	23(2)	5(2)	6(2)
C(101)	44(3)	55(3)	75(4)	33(3)	12(3)	10(2)
C(102)	62(4)	79(4)	58(3)	36(3)	9(3)	26(3)
C(103)	90(5)	74(4)	68(4)	21(3)	-31(4)	12(4)
C(104)	76(4)	59(4)	65(4)	18(3)	-25(3)	7(3)
N(105)	28(2)	35(2)	45(2)	10(2)	-3(2)	-3(1)
C(105)	39(2)	40(3)	62(3)	15(2)	6(2)	6(2)
C(106)	46(3)	52(3)	80(4)	15(3)	15(3)	13(2)

C(107) 37(2) 62(3) 53(3) 12(2) 5(2) 2(2)

C(108) 40(2) 49(3) 44(2) 12(2) -6(2) -7(2)

C(109) 31(2) 38(2) 42(2) 7(2) -6(2) -3(2)

S(250) 40(1) 42(1) 45(2) 14(1) 0(1) 7(1)

O(250) 32(5) 109(16) 42(9) 38(9) 17(7) 17(7)

O(251) 45(5) 68(11) 32(7) 8(6) 13(5) 18(5)

O(252) 136(12) 34(6) 172(14) -17(8) -92(11) 13(7)

C(250) 48(6) 82(9) 57(7) 4(6) 3(5) 28(6)

F(250) 61(7) 162(15) 99(8) 33(9) 34(6) 58(7)

F(251) 96(9) 123(12) 94(8) 46(9) 3(6) 55(8)

F(252) 62(8) 158(12) 236(18) -93(12) -60(12) 32(9)

O(255) 180(20) 69(13) 57(11) 12(9) -13(13) 42(15)

O(25A) 89(10) 198(19) 211(18) 54(15) -36(11) -53(12)

O(25B) 200(20) 36(9) 103(15) 12(9) -26(16) 9(12)

O(301) 180(30) 150(30) 67(9) 71(14) -84(14) -88(17)

O(302) 94(16) 180(20) 83(13) -23(15) -30(13) -27(16)

O(310) 214(18) 114(11) 161(13) 89(10) -114(13) -61(11)

O(312) 230(19) 125(12) 280(20) 67(14) -65(17) -83(13)

O(31A) 260(20) 69(8) 127(11) 18(8) -22(13) 1(10)

O(31B) 160(15) 134(12) 247(19) 1(14) -48(15) 7(12)

O(31C) 130(20) 150(20) 113(17) 4(17) -47(16) 7(17)

O(311) 100(20) 130(20) 170(30) 90(20) 50(20) 32(18)

O(320) 280(30) 65(12) 190(20) 17(14) -30(20) -24(16)

O(32A) 250(30) 180(20) 220(30) 120(20) 30(20) 30(20)

O(32Z) 220(30) 136(19) 250(30) 90(19) -30(20) 30(17)

O(350) 67(10) 83(12) 38(7) -31(7) 7(7) -24(9)

O(351) 70(18) 100(30) 73(10) -38(19) 22(10) -9(16)

O(352) 109(15) 47(9) 73(11) -21(8) -58(11) 24(10)

O(353) 87(14) 97(16) 106(16) -46(15) -11(13) 42(13)

Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for Tb-1.

	x	y	z	U(eq)
H(3)	464	2739	-1180	67
H(4)	96	2149	-1665	88
H(5)	341	1327	-1594	91
H(6)	921	1120	-1031	68
H(9)	1104	4099	1882	40
H(10)	438	3898	2375	41
H(11)	134	3098	2369	45
H(12)	477	2529	1850	44
H(15)	-492	2105	-640	89
H(16)	-866	1363	-851	110
H(17)	-728	669	-373	92
H(18)	-206	730	286	60
H(21)	79	4334	1431	50
H(22)	-674	3997	1675	55
H(23)	-1009	3341	1253	59
H(24)	-599	3044	588	51
H(100)	528	4314	-253	59
H(101)	254	4845	-835	69
H(102)	-279	4565	-1418	80
H(103)	-551	3755	-1384	93
H(104)	-270	3252	-770	80
H(105)	-167	2384	1116	56
H(106)	-774	2522	1683	71
H(107)	-998	1885	2200	60

H(108)	-598	1136	2143	53
H(109)	11	1032	1571	44