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Supplemental Information

Th(IV) and Ce(IV) Napthylsalophen Sandwich Complexes: Characterization of Unusual Thorium Fluorescence in Solution and Solid-state

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Experimental Details

General considerations

Caution! Standard precautions for handling radioactive materials or heavy metals, such as $Th(NO_3)_4 \bullet 6H_2O$ as used in this study, were followed.

Any solvents not specifically identified were ACS grade, purchased from EMD, and used as received without further purification. The reagents toluene (HPLC grade, BDH), dimethylsulfoxide (99%, Macron), dimethylformamide (99.9%, EMD), acetonitrile (99.5%, BDH), chloroform (99.8%, BDH), methanol (HPLC grade, EMD), 1,2-diaminobenzene (99.5%, Aldrich), 2-hydroxynapthaldehyde (98%, Alpha Aesar), and $Th(NO_3)_4 \bullet 6H_2O$ (99%, Fluka) were used as received without further purification. Anhydrous dichloromethane (BDH) was purchased, stored under argon, and dispensed from a solvent purification system. Triethylamine (99%, Alpha Aesar) was distilled and stored under argon until use.

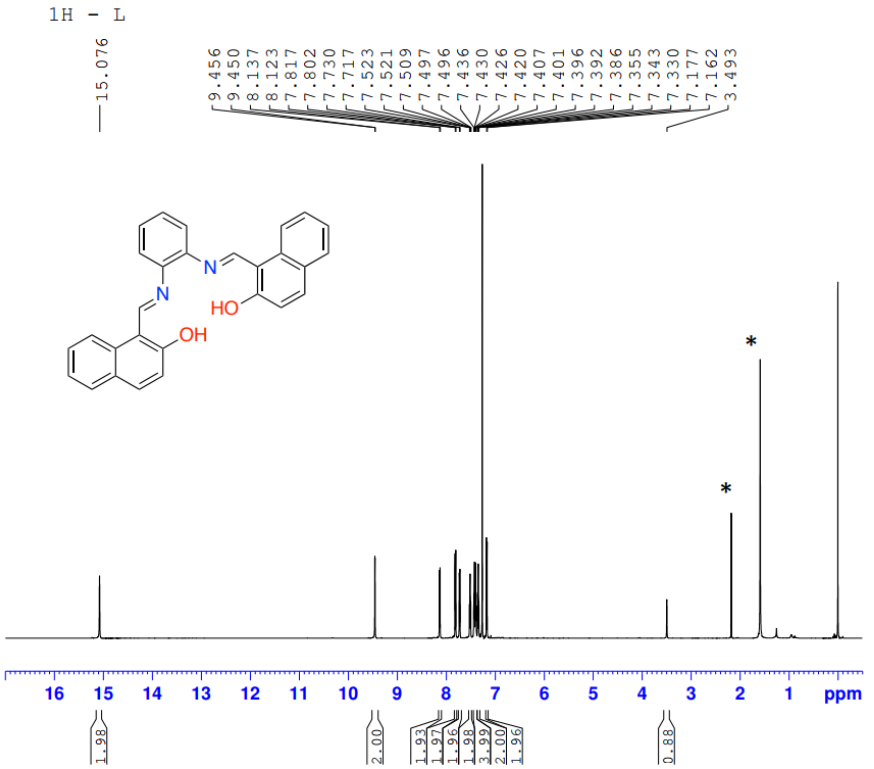
NMR Spectroscopy: ^{1}H NMR spectra were recorded with a Bruker AC400 spectrometer at 600 MHz. ^{13}C NMR spectra were recorded with a Bruker AC400 spectrometer at 151 MHz. NMR spectroscopic data were collected using deuterated chloroform ($CDCl_3$).

X-ray Diffraction: Suitable crystals were selected and mounted on a glass fiber using paratone-n oil and data collection was completed on a 'Bruker APEX CCD' diffractometer using Mo Kα radiation. The crystals were kept at 180(2) K during unit cell and data collection. SMART (v. 5.624) were used for preliminary determination of cell constatns and data collection control. Determination of integrated intensities and global cell refinements were performed with the Bruker SAINT software package, and empirical absorption corrections (SADABS) were applied. The structure was solved with the ShelXS structure solution program using Direct Methods[1] and refined with the olex2.refine[2] refinement package using Gauss-Newton minimisation. Projections were created on Olex2 software.[3]

Synthetic Procedures:

L: 1,2-diaminobenzene (0.433 g, 7.23 mmol) and 2-hydroxynapthaldehyde (1.32 g, 15.0 mmol) were added to 150 mL of MeOH, heated to reflux temperature, and stirred at for 6 hours. The solution was observed to change from yellow to orange and a precipitate formed. The solution was allowed to cool to room temperature. The resulting solid was filtered and washed with hexanes to yield an orange powder (2.54 g, 84 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.177 (d, 2H, *J* = 9.2 Hz), 7.343 (t, 2H, *J* = 7.4 Hz), 7.435-7.386 (m, 4H), 7.509 (t, 2H, *J* = 8.2 Hz), 7.730 (d, 2H, *J* = 7.9 Hz), 7.817 (d, 2H, *J* = 9.2 Hz), 8.137 (d, 2H, *J* = 8.5 Hz), 9.456 (d, 2H, *J* = 3.6 Hz), 15.076 (s, 2OH); ^{13}C NMR (151 MHz, $CDCl_3$) δ 109.40, 119.03, 119.15, 122.09, 123.63, 127.42, 127.51, 128.08, 129.41, 133.21, 136.67, 139.73, 156.17, 169.08; TOF MS (ESI) m/z (M^+ + 1) Cald 417.1525, Found 417.1550.

^{1}H NMR spectrum of L (residual acetone and water denoted by an asterisk)



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PROCNO                  1

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TD                 65536
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DE                10.00 usec
TE                308.2 K
D1           10.00000000 sec
TD0                    1

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NUC1                  1H
P1                  9.50 usec
PLW1          4.90000010 W

F2 - Processing parameters
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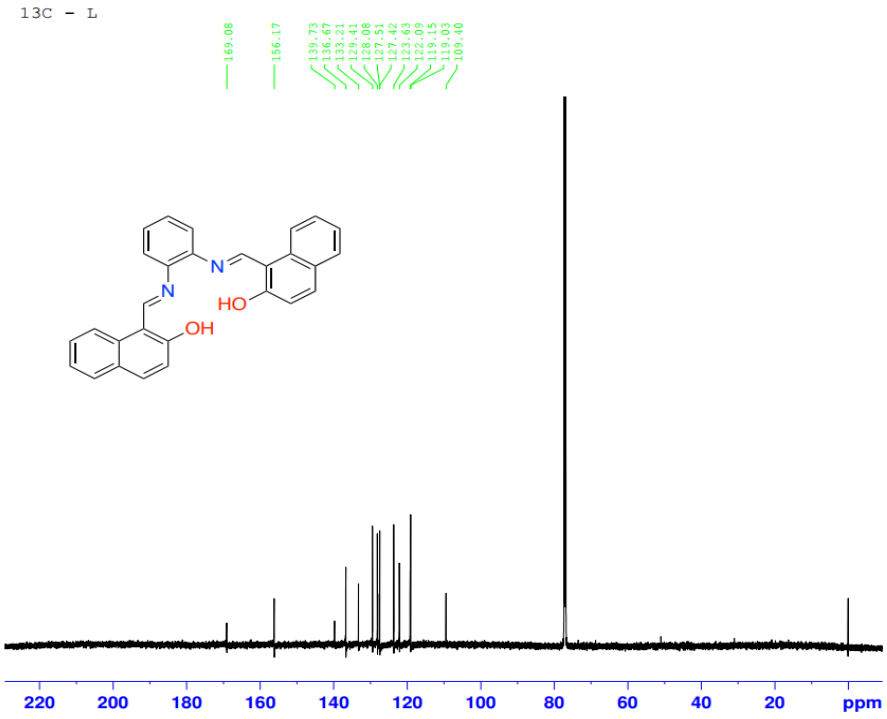

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NUC1                 13C
P1                 15.00 usec
PLW1        110.00000000 W

======== CHANNEL f2 ========
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NUC2                  1H
CPDPRG[2          waltz16
PCPD2              70.00 usec
PLW2          4.90000010 W
PLW12         0.09025000 W
PLW13         0.04422300 W

F2 - Processing parameters
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SF           150.9028090 MHz
WDW                   EM
SSB       0
LB                  1.00 Hz
GB        0
PC                  1.40
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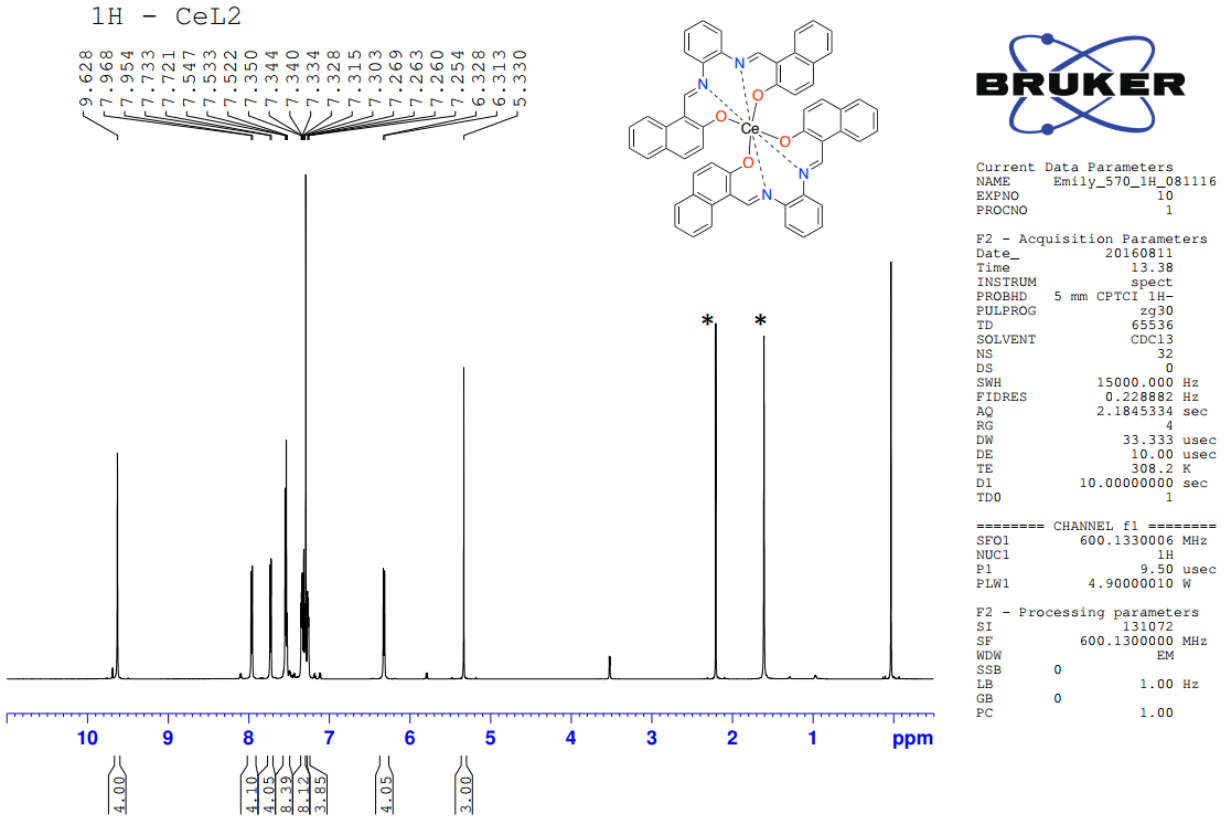
Ce**L**$_2$:

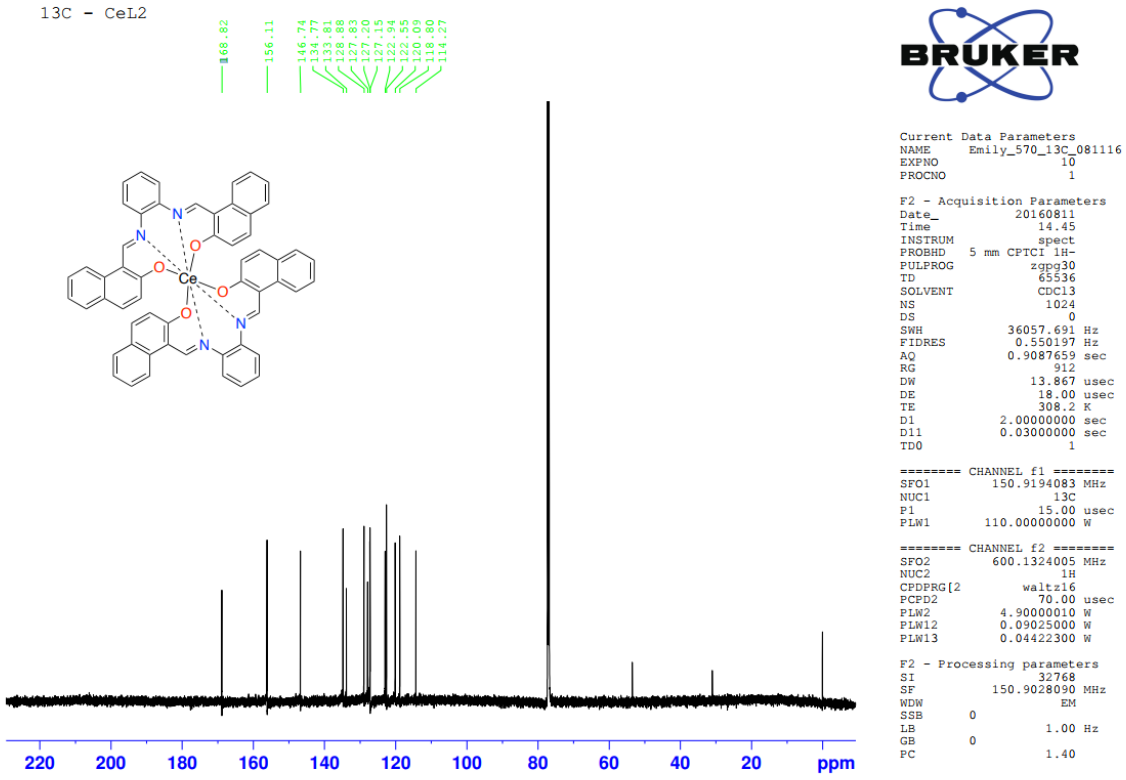
The napthylsalophen ligand (**L**) (867 mg, 2.08 mmol) and NEt_3 (1.0 mL) were added to minimal amount of DCM (120 mL) and allowed to dissolve in a 250 mL round bottom flask. $Ce(OAc)_3 \bullet H_2O$ (342 mg, 1.08 mmol) was then added to the flask with minimal amount (80 mL) of MeOH to dissolve the salt after some stirring. The reaction was heated to 40 °C and stirred for 6 hours. The solution volume was reduced by half by rotary evaporation, and the precipitate, a reddish brown solid, was filtered off and collected. Crystals suitable for x-ray diffraction were grown in five days from layering a saturated toluene solution of Ce**L**$_2$ with hexanes. (976 mg, 94 %).

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.328 (d, 4H, *J* = 9.0 Hz), 7.254-7.269 (m, 4H), 7.303-7.350 (m, 8H), 7.533 (s, 4H), 7.547 (s, 4H), 7.733 (d, 4H, *J* = 7.7 Hz), 7.968 (d, 4H, *J* = 8.4 Hz), 9.628 (s, 4H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 114.27, 118.80, 120.09, 122.55, 122.94, 127.15, 127.20, 127.83, 128.88, 133.81, 134.77, 146.74, 156.11, 168.82 ppm; TOF MS (ESI) m/z (M^+ + 1) Cald 969.1791, Found 969.1705.

^{1}H NMR spectrum of Ce**L**$_2$ (residual water and acetone are denoted by an asterisk):

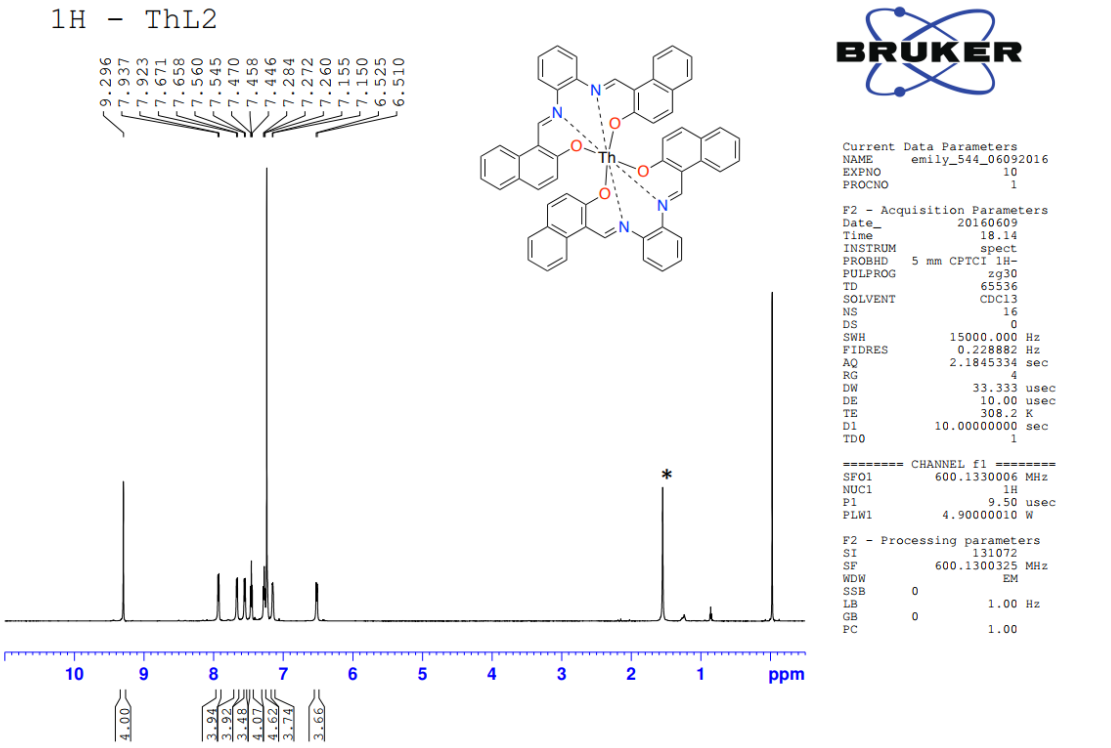


^{13}C NMR spectrum of CeL_2:

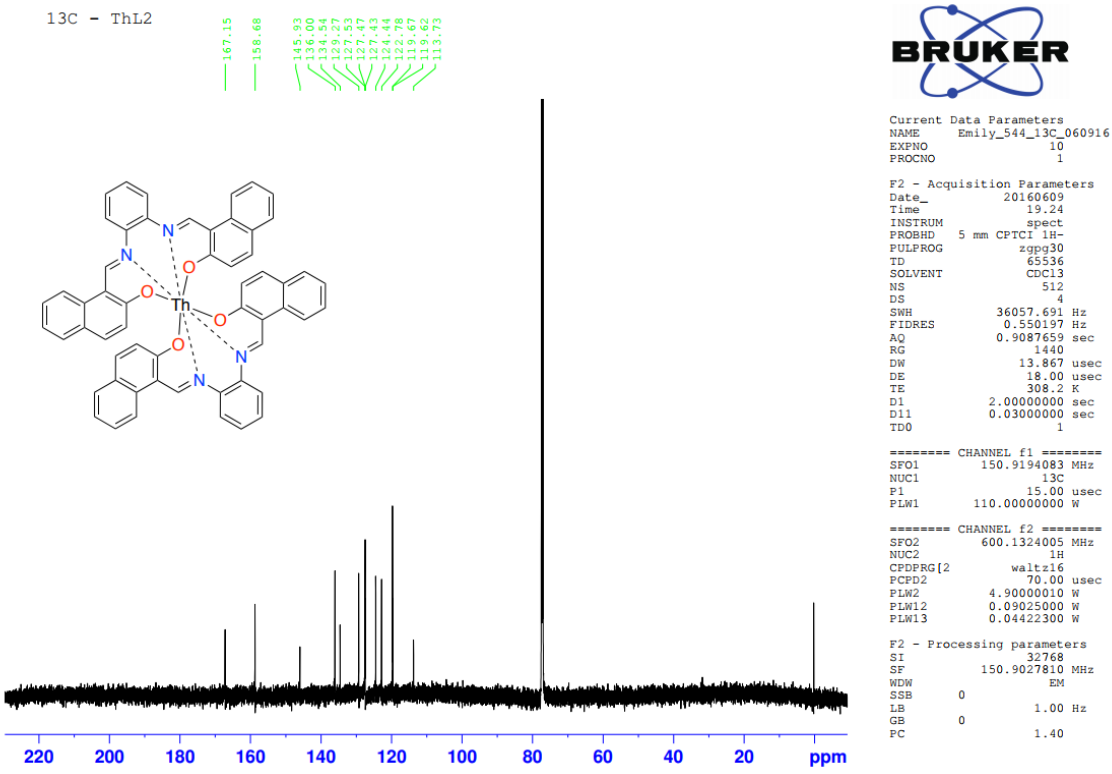


Th**L**$_2$: The napthylsalophen ligand (**L**) (414 mg, 0.995 mmol) and NEt_3 (1.0 mL) were added to 100 mL of DCM and 50 mL of MeOH in a 250 mL round bottom flask. The mixture was stirred until all the solids were dissolved. Thorium nitrate (214 mg, 0.415 mmol) was then added to the flask. The reaction was heated to 40 °C and heated with stirring for 5.5 hours. The solution volume was reduced by half by rotary evaporation, and subsequently put in ice for 30 minutes. A yellow solid precipitated. This was filtered off and rinsed with hexanes (333 mg, 76 %). Crystals suitable for x-ray diffraction were grown in 3 days from layering a saturated toluene solution of ThL_2 with hexanes. ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.525 (d, 4H, *J* = 9.0 Hz), 7.150 (s, 4H), 7.272 (t, 4H, *J* = 7.2 Hz), 7.458 (t, 4H, *J* = 7.2 Hz), 7.560 (d, 4H, *J* = 9.0 Hz), 7.671 (d, 4H, *J* = 7.8 Hz), 7.937 (d, 4H, *J* = 8.4 Hz), 9.296 (s, 4H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 113.73, 119.62, 119.67, 122.78, 124.44, 127.43, 127.47, 127.53, 129.27, 134.54, 136.00, 145.93, 158.68, 167.15 ppm; TOF MS (ESI) m/z (M^+ + 1) Cald 1061.3195, Found 1061.3199.

^{1}H NMR spectrum of ThL$_2$ (residual water denoted with an asterisk):



^{13}C NMR Spectrum of ThL2:



Electronic Spectroscopy

Absorbance Spectroscopy: All solution phase absorbance spectra were collected on a VARIAN Cary 50 WinUV Spectrometer with a xenon lamp with absorbance spectra from 200 nm to 900 nm with a 1 cm width quartz cuvette. Solid-state absorbance spectra were collected on a 20/20 PV CRAIC microspectrophotometer with a xenon lamp for transmission/absorbance measurements, with optimized exposure times from single crystals of each respective complex.

Fluorescence Spectroscopy: All solution phase fluorescence spectra were collected on a Shimadzu RF-5301 PC fluorospectrophotometer with a xenon lamp and a 1 cm width quartz cuvette with an excitation of 365 nm and an emission spectrum of 375–900 nm. Slit widths were set so that the maximum emission of the ligand could be seen, and held constant throughout. Solid-state fluorescence spectra were collected on a 20/20 PV CRAIC microspectrophotometer with a mercury lamp for fluorescence measurements. Samples were excited with 365 nm light with optimized exposure times from single crystals of each respective complex.

Thorium Titration Procedure

Serial titrations of ThL_2 was completed by introducing a known amount $Th(NO_3)_2$ to a solution of free base in methanol. Solutions were 2.0 mL of 31 μM ligand, and 1/10 equivalent of metal salt were added per addition (12μL additions). The solutions were shaken for 3 seconds, replaced in the spectrometer, and the UV-vis spectrum was collected.

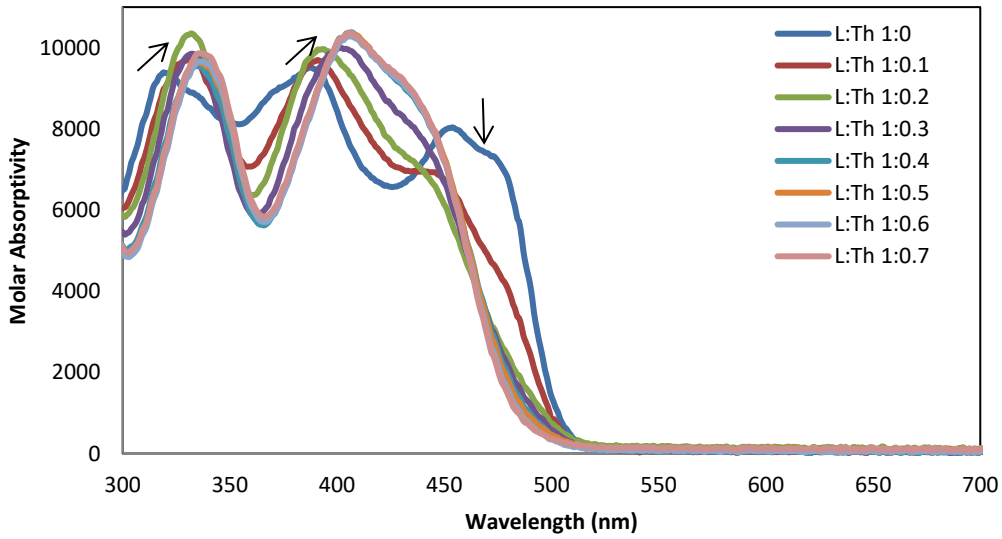


Figure SI1: Solution phase absorbance of L (λ_{max}=324, 394, and 446 nm) with increasing [Th^{4+}] to form ThL_2 (λ_{max}=342, and 411 nm with a shoulder at 440 nm).

Cerium UV Procedure

The oxidation of Ce(III) to Ce(IV) was observed spectrophotometrically by adding 1 equivalent of Ce(III) acetate to a 31 μM solution of free base in dimethylformamide. One equivalent of metal salt was added (120 μL). The solution was then heated and a UV-visible spectra was recorded every two minutes for 36 minutes. The charge transfer band of the CeL_2 solution was observed to grown in slowly, after heating and exposure to oxygen in a mildly basic solvent.

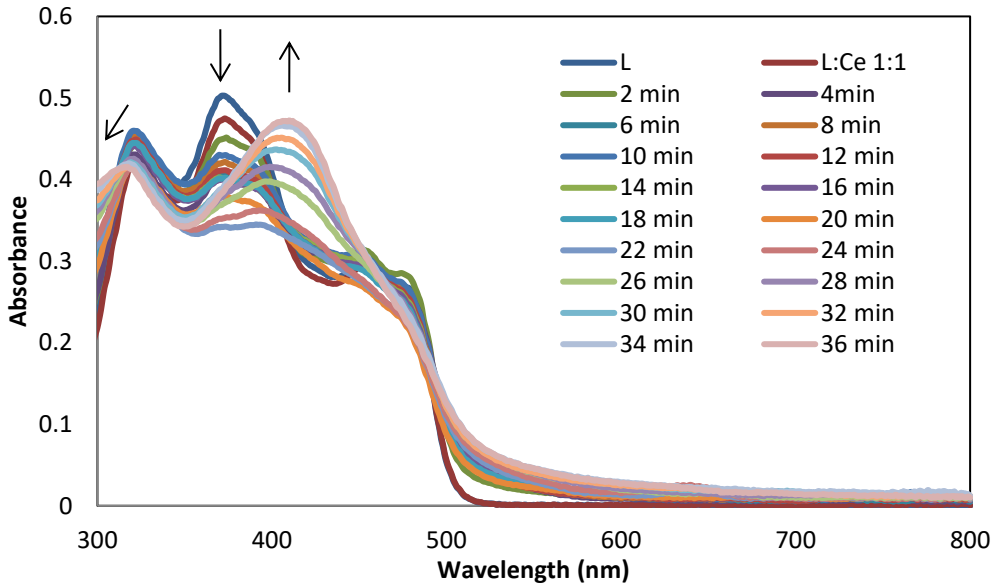


Figure SI2: Solution phase absorbance of L (λ_{max}=324, 394, and 446 nm) and spectrophotometric observation of the formation of Ce(IV)L_2 (λ_{max}=317, and 417 nm).

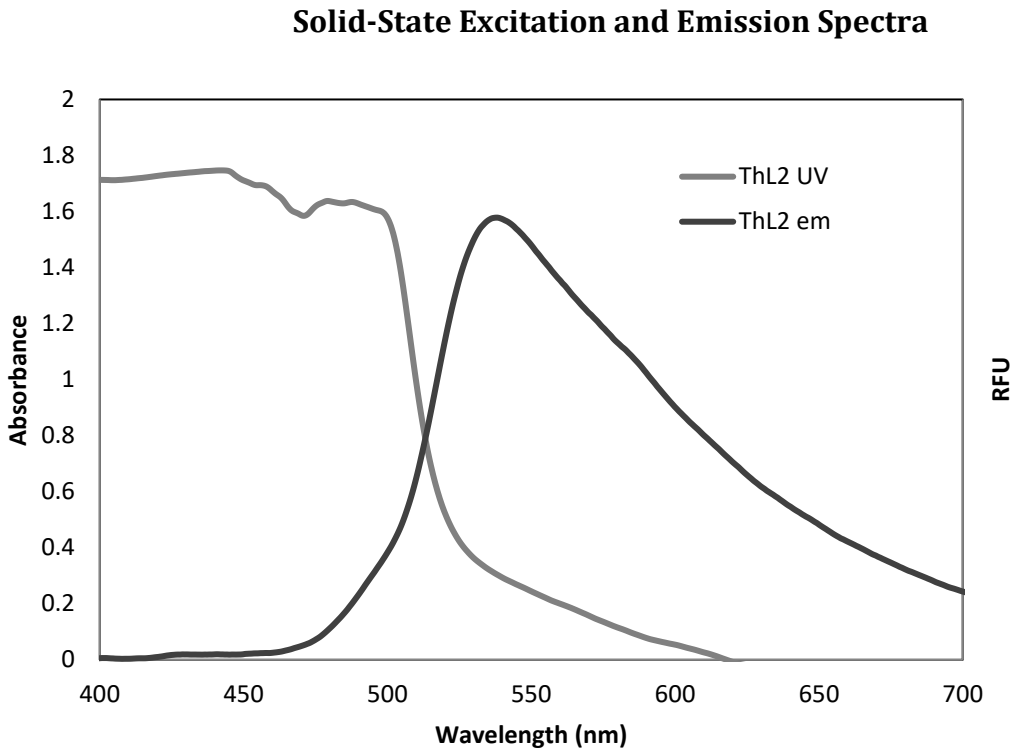


Figure SI3: Solid-state absorbance and emission spectra with excitation at 365 nm of ThL_2. An absorbance peak centered at 488 nm and an emission peak at 537 nm are observed.

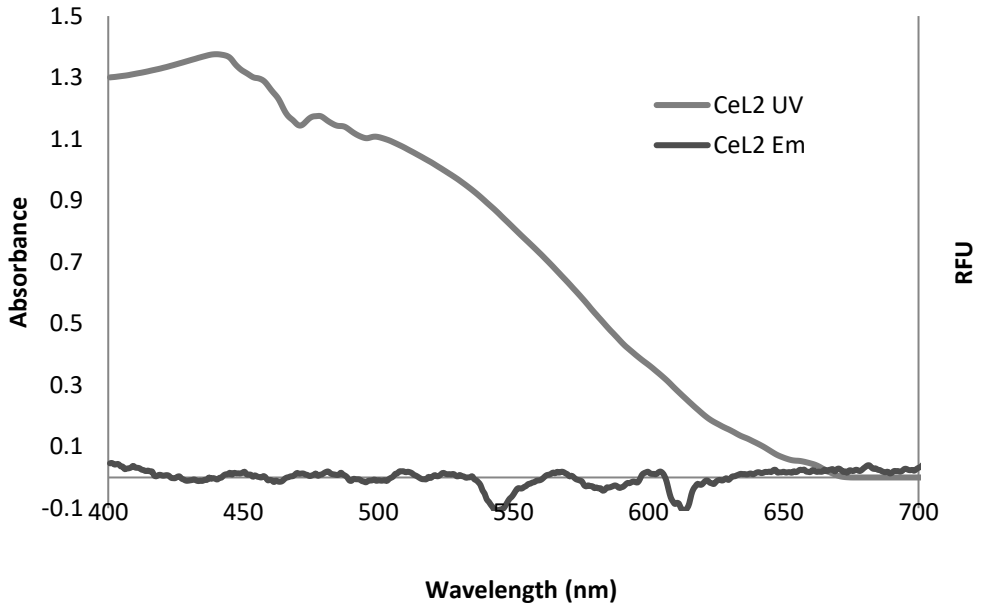


Figure SI4: Solid-state absorbance and emission spectra with excitation at 365 nm of CeL_2. Broad absorbance peak is observed, but all emission is quenched.

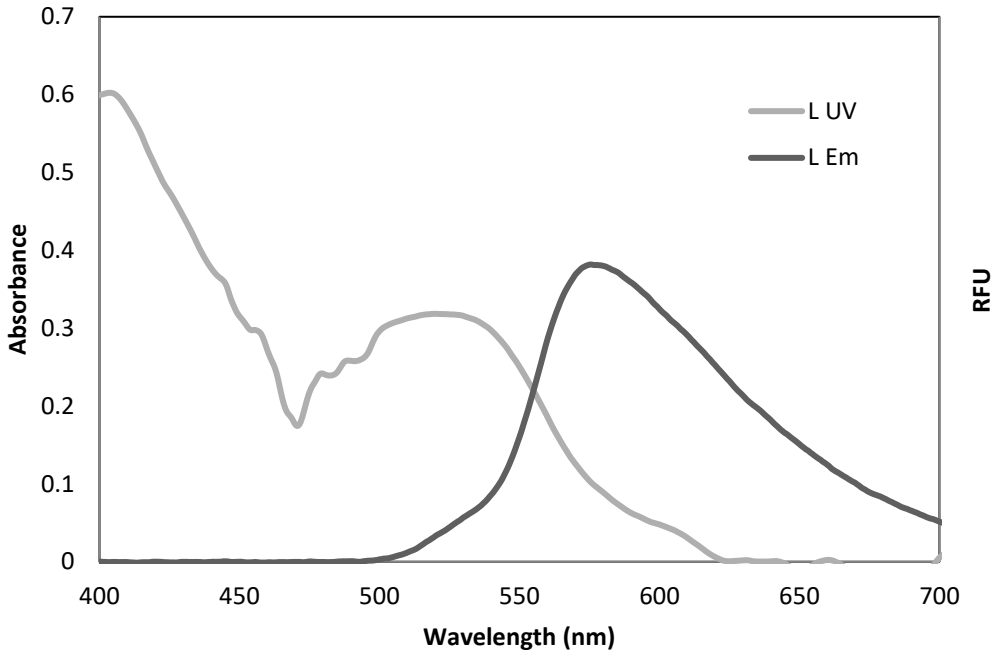


Figure SI5: Solid-state absorbance and emission spectra with excitation at 365 nm of L. An absorbance peak at 520 nm and an emission peak at 575 nm are observed.

Solution phase Excitation and Emission Spectra

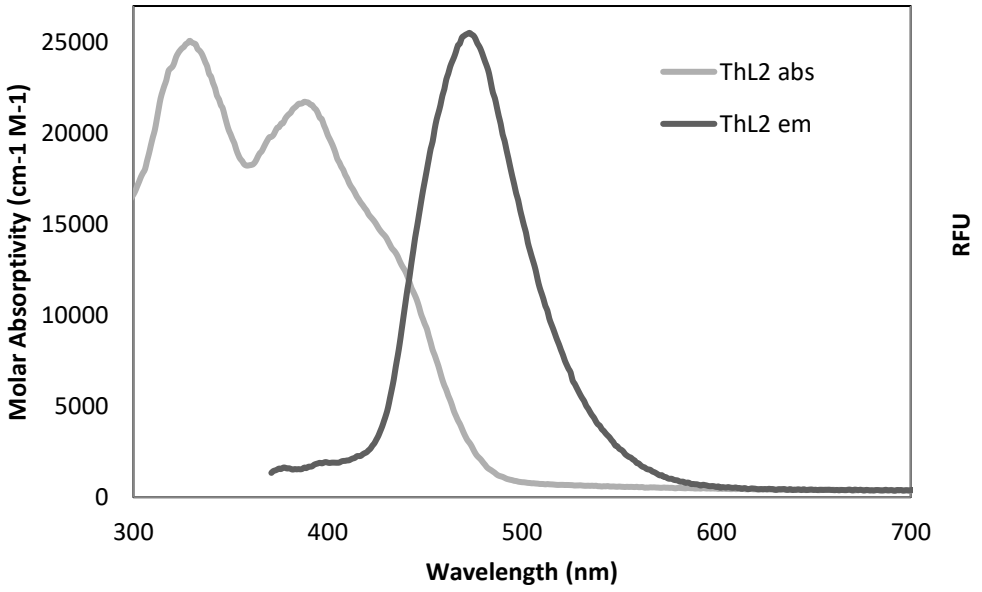


Figure SI6: Solution phase absorbance and emission spectra of ThL_2 in acetonitrile with excitation at 365 nm. Two absorbance peaks at 333 nm and 391 nm, with a shoulder centered on 440 nm are observed, with an emission peak at 473 nm.

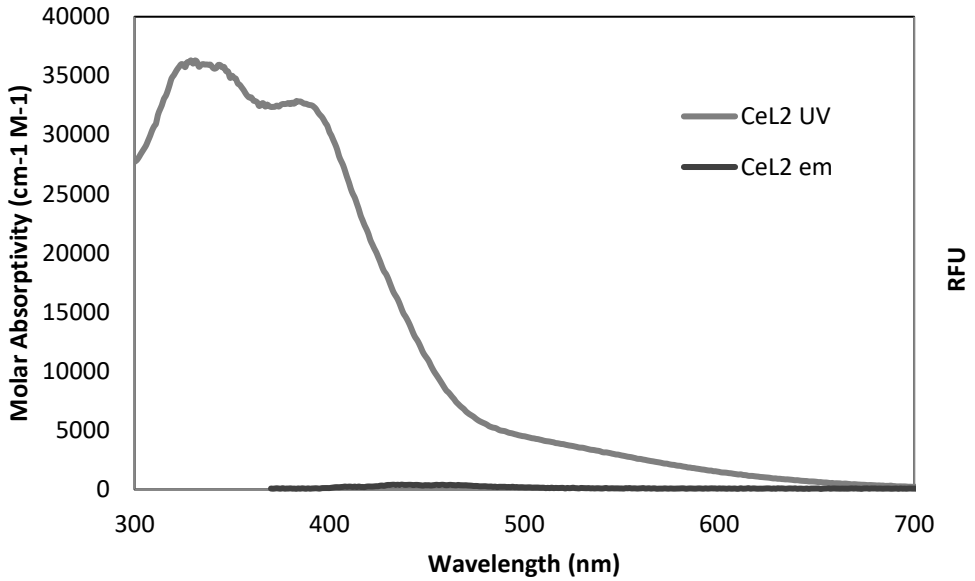


Figure SI7: Solution phase absorbance and emission spectra of CeL_2 in dichloromethane with excitation at 365 nm. Two absorbance peaks at 335 nm and 387 nm, with a shoulder centered on 440 nm are observed, all emission is quenched.

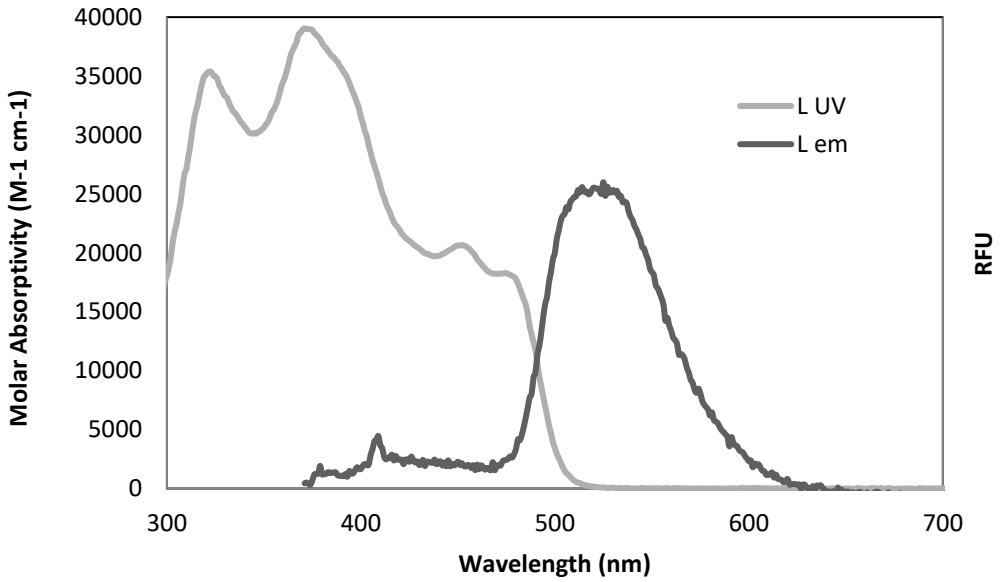


Figure SI8: Solution phase absorbance and emission spectra of ThL_2 in acetonitrile with excitation at 365 nm of. Four absorbance peaks at 326 nm, 375 nm, 456, and 476 nm are observed, with an emission peak at 517 nm.

Quantum Yield Calculations

Quantum Yields in **Table 1** were calculated via equation 1,

$$\Phi_X = \Phi_{ST}\left(\frac{Slope_X}{Slope_{ST}}\right)\left(\frac{\eta_X^2}{\eta_{ST}^2}\right) \quad (1)$$

Where the subscripts ST and X denote standard (anthracene) and unknown (ThL_2) respectively, Φx is the fluorescence quantum yield, Slope is the slope from the plot of fluorescence intensity vs absorbance, and η the refractive index of the solvent. In this case the solvent for the standard was methanol and the solvent for the samples were variable, and Φ_{ST} was equal to 24 %.[5]

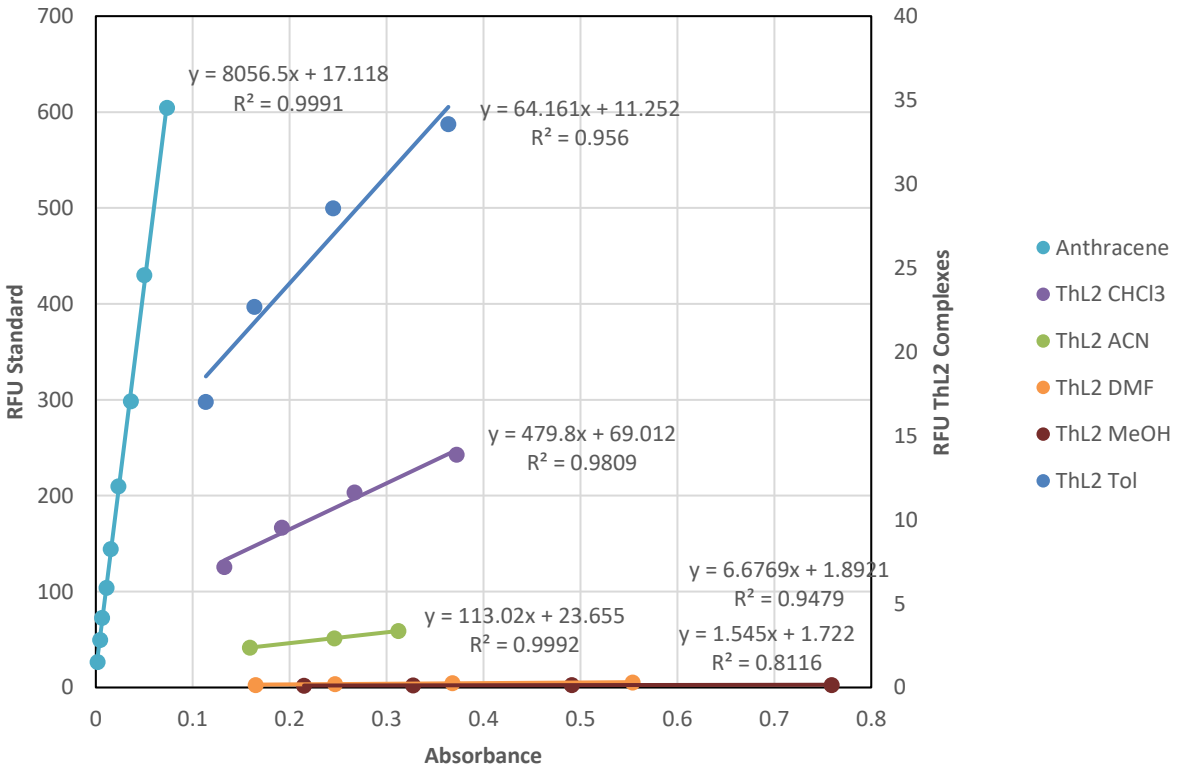


Figure SI9: ThL_2 fluorescence after excitation at 365 nm vs. absorbance value at 365 nm of 31.2, 21.8, 14.5, 9.7 µM solutions in indicated solvent and anthracene fluorescence after excitation at 365 nm vs. absorbance value at 365 nm of 35.7, 23.8, 15.8, 10.6, 7.1, 4.7, 3.1, 2.0, 1.0 µM solutions in methanol.

Crystallographic Tables

ThL2_FINAL

Table 1 Crystal data and structure refinement for ThL2_FINAL

Identification code	ThL2_FINAL
Empirical formula	$C_{66.5}H_{47.5}N_4O_4Th$
Formula weight	1198.68
Temperature/K	180.45
Crystal system	triclinic
Space group	P-1
a/Å	11.4987(3)
b/Å	14.3613(4)
c/Å	16.2765(5)
α/°	106.2205(11)
β/°	90.8258(11)
γ/°	94.1516(11)
Volume/Å^3	2572.39(13)
Z	2
ρ_{calc}mg/mm^3	1.5474
m/mm^{-1}	2.955
F(000)	1180.2
Crystal size/mm^3	0.18 × 0.12 × 0.08
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	2.6 to 48.22°
Index ranges	$-13 \leq h \leq 13$, $-16 \leq k \leq 16$, $-18 \leq l \leq 18$
Reflections collected	53501
Independent reflections	8180 [R_{int} = 0.0498, R_{sigma} = 0.0396]
Data/restraints/parameters	8180/3/686
Goodness-of-fit on F^2	1.060
Final R indexes [I>=2σ (I)]	R_1 = 0.0242, wR_2 = 0.0489
Final R indexes [all data]	R_1 = 0.0330, wR_2 = 0.0516
Largest diff. peak/hole / e Å^{-3}	0.92/-0.91

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for ThL2_FINAL. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Th1	105.71(10)	5047.97(10)	2558.78(8)	18.78(5)
O1	-621.3(17)	5380.9(16)	1388.0(13)	21.4(5)
O3	207.8(18)	5808.6(16)	3993.1(13)	22.8(5)
O4	1803.9(18)	4430.9(17)	2831.8(14)	28.0(6)
N3	399(2)	6951(2)	2905.6(16)	18.6(6)
N4	1928(2)	5814(2)	1950.7(16)	18.8(6)
N2	-1484(2)	4086(2)	3193.3(16)	18.5(6)
N1	-1985(2)	5709.5(19)	2808.4(16)	17.9(6)
O2	-246.0(19)	3440.0(18)	1737.1(14)	28.9(6)
C40	890(3)	7271(2)	2228(2)	19.2(8)
C19	-1227(3)	2380(2)	2444(2)	22.0(8)
C10	-2247(3)	6345(2)	1563(2)	19.7(8)
C45	1692(3)	6681(2)	1726(2)	20.6(8)
C48	4540(3)	4377(2)	1675.8(19)	18.2(8)
C12	-2506(3)	5541(2)	3549.0(19)	17.4(8)
C11	-2588(3)	6117(2)	2344(2)	19.9(8)
C2	-1056(3)	6097(2)	302(2)	24.7(8)
C9	-3009(3)	6884(2)	1186(2)	20.8(8)
C16	-2592(3)	4539(3)	4525(2)	24.5(8)
C4	-2758(3)	7004(2)	368(2)	24.8(8)
C20	-1533(3)	1392(2)	2472(2)	24.2(8)
C27	-348(3)	1748(3)	1072(2)	34.8(10)
C29	-178(3)	6562(3)	4549(2)	22.2(8)
C17	-2208(3)	4717(2)	3771(2)	19.0(8)
C56	2837(3)	4204(3)	2534(2)	24.0(8)
C13	-3240(3)	6165(3)	4075(2)	26.8(9)
C31	-806(3)	7235(3)	5994(2)	31.7(10)
C1	-1287(3)	5941(2)	1111(2)	18.7(8)
C53	5055(3)	3642(3)	1945(2)	24.3(8)
C41	600(3)	8106(3)	2019(2)	26.2(9)
C47	3411(3)	4683(2)	2000(2)	19.7(8)
C3	-1760(3)	6609(2)	-48(2)	28.0(9)
C39	97(3)	7608(3)	3584(2)	22.5(8)
C50	6196(3)	4433(2)	773(2)	25.7(9)

C8	-4024(3)	7291(2)	1572(2)	29.3(9)
C49	5137(3)	4750(2)	1062(2)	23.6(8)
C54	4446(3)	3211(3)	2516(2)	31.0(9)
C51	6724(3)	3733(3)	1068(2)	29.4(9)
C28	-587(3)	2559(3)	1769(2)	25.4(9)
C44	2168(3)	6944(3)	1042(2)	26.3(9)
C18	-1714(3)	3159(3)	3054(2)	20.5(8)
C38	-335(3)	7442(2)	4361(2)	20.2(8)
C37	-811(3)	8231(3)	4995(2)	25.3(9)
C46	2965(3)	5519(2)	1817.4(19)	19.1(8)
C15	-3328(3)	5161(3)	5029(2)	33.9(10)
C32	-1016(3)	8128(3)	5827(2)	27.4(9)
C52	6149(3)	3336(3)	1632(2)	29.0(9)
C55	3384(3)	3468(3)	2796(2)	28.0(9)
C25	-1285(3)	609(3)	1763(2)	30.7(9)
C35	-1566(3)	9826(3)	5458(3)	41(1)
C21	-2047(3)	1164(3)	3174(2)	34.7(10)
C30	-424(3)	6480(3)	5384(2)	27.2(9)
C43	1899(3)	7787(3)	855(2)	32.5(9)
C24	-1626(3)	-351(3)	1772(3)	40.9(11)
C36	-1124(3)	9090(3)	4833(2)	33.6(9)
C5	-3507(3)	7510(3)	-21(2)	33.8(10)
C42	1106(3)	8369(3)	1343(2)	30.5(9)
C14	-3659(3)	5958(3)	4801(2)	33.7(9)
C22	-2345(3)	217(3)	3162(3)	43.7(11)
C33	-1448(3)	8894(3)	6459(2)	40.3(11)
C26	-700(3)	826(3)	1072(2)	39.8(10)
C7	-4732(3)	7771(3)	1169(3)	35.5(10)
C34	-1714(3)	9725(3)	6279(3)	45.4(12)
C6	-4473(3)	7868(3)	364(3)	37.5(10)
C23	-2153(3)	-542(3)	2459(3)	44.6(11)
C58S	4787(4)	8330(3)	5026(3)	50.8(12)
C59S	3832(4)	7670(3)	4740(3)	65.3(14)
C63S	5255(4)	8778(4)	4452(3)	64.5(14)
C62S	4763(5)	8614(4)	3643(3)	73.7(16)
C57S	5301(5)	8528(4)	5915(3)	81.7(17)
C60S	3348(4)	7486(4)	3946(4)	83.7(18)
C61S	3809(5)	7978(4)	3390(3)	77.3(16)

C66S	-6167(6)	9853(5)	-21(7)	105(3)
C64S	-6210(14)	10433(9)	1544(8)	136(6)
C67S	-5552(9)	9616(5)	-796(6)	111(3)
C65S	-5610(8)	10226(5)	764(6)	104(2)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for ThL2_FINAL. 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_{12}**	**U_{13}**	**U_{23}**
Th1	17.92(8)	22.71(8)	19.14(8)	5.72(5)	5.11(5)	10.30(6)
O1	19.7(12)	29.6(15)	18.0(12)	8.4(11)	4(1)	10.2(11)
O3	26.7(13)	26.3(15)	18.6(12)	5.3(11)	3.4(10)	10.4(11)
O4	21.2(13)	38.8(16)	34.3(14)	14.7(12)	9.4(11)	23.6(13)
N3	15.6(14)	23.7(18)	18.2(15)	3.8(13)	5.2(12)	7.9(14)
N4	18.7(15)	21.5(17)	18.6(15)	5.8(13)	3.3(12)	8.2(13)
N2	17.9(15)	20.4(18)	19.7(15)	3.7(13)	1.4(12)	9.4(13)
N1	16.7(14)	19.3(16)	19.0(15)	3.6(12)	6.2(12)	6.9(13)
O2	35.3(14)	26.2(16)	26.7(14)	3.7(12)	11.7(11)	9.1(12)
C40	19.2(18)	16(2)	21.5(19)	0.3(15)	1.6(15)	4.8(16)
C19	21.5(19)	21(2)	23(2)	4.3(16)	-3.0(16)	5.8(17)
C10	19.6(18)	19(2)	20.8(19)	1.8(15)	-1.4(15)	6.1(16)
C45	18.8(18)	23(2)	22.6(19)	6.4(16)	5.1(15)	9.6(17)
C48	15.1(17)	19(2)	18.1(18)	2.0(15)	0.3(15)	1.5(16)
C12	13.8(17)	20(2)	19.1(18)	1.9(15)	2.3(14)	5.5(16)
C11	19.5(18)	16(2)	23.3(19)	2.9(15)	3.2(16)	3.9(16)
C2	28(2)	26(2)	20.3(19)	2.5(17)	4.1(16)	6.0(17)
C9	22.7(19)	15(2)	25(2)	-1.0(15)	-5.6(16)	6.6(16)
C16	29(2)	24(2)	23.7(19)	3.4(17)	9.2(16)	11.4(17)
C4	31(2)	18(2)	25(2)	-2.2(17)	-6.2(17)	7.1(17)
C20	20.5(19)	22(2)	30(2)	2.0(16)	-5.4(16)	8.2(18)
C27	43(2)	28(2)	33(2)	6.6(19)	10.4(19)	6.2(19)
C29	14.7(18)	34(2)	16.9(19)	-0.1(16)	-0.4(15)	5.1(17)
C17	15.4(17)	20(2)	19.3(18)	1.8(15)	4.9(15)	2.2(16)
C56	18.4(19)	31(2)	24(2)	4.8(16)	-0.5(16)	8.4(17)
C13	26(2)	30(2)	27(2)	11.5(17)	8.1(17)	10.2(18)
C31	19.4(19)	58(3)	17(2)	1.6(19)	2.5(16)	10(2)
C1	22.3(19)	16.3(19)	16.6(18)	-1.2(15)	-3.6(15)	4.1(15)
C53	22.3(19)	30(2)	19.5(19)	5.3(17)	-2.4(16)	4.4(17)
C41	28(2)	26(2)	27(2)	8.9(17)	10.1(17)	9.0(17)

C47	18.2(18)	24(2)	17.7(18)	5.2(15)	0.1(15)	5.6(16)
C3	40(2)	26(2)	21(2)	-2.5(18)	-4.5(18)	11.0(17)
C39	19.4(18)	20(2)	29(2)	2.3(16)	0.0(16)	8.0(18)
C50	20.8(19)	28(2)	23(2)	-1.7(17)	5.3(16)	0.0(17)
C8	30(2)	25(2)	37(2)	4.7(17)	-1.7(18)	13.7(18)
C49	21.8(19)	23(2)	24.9(19)	3.7(16)	2.2(16)	3.7(16)
C54	30(2)	37(2)	33(2)	17.6(18)	0.0(18)	18.8(19)
C51	17.5(19)	39(2)	25(2)	8.3(18)	1.7(16)	-2.3(19)
C28	25(2)	27(2)	23(2)	7.1(17)	-0.3(17)	4.2(18)
C44	27(2)	32(2)	24(2)	13.6(17)	13.4(16)	11.5(18)
C18	19.1(18)	26(2)	18.7(19)	0.3(16)	1.3(15)	10.9(17)
C38	17.9(18)	25(2)	16.8(18)	0.3(16)	3.1(15)	5.2(16)
C37	17.1(18)	27(2)	27(2)	-4.3(16)	2.8(16)	1.1(18)
C46	20.0(19)	22(2)	17.5(18)	2.7(16)	4.0(15)	9.0(16)
C15	37(2)	44(3)	22(2)	3(2)	14.1(18)	10.9(19)
C32	18.9(19)	38(2)	21(2)	-2.5(17)	3.7(16)	2.3(18)
C52	24(2)	34(2)	28(2)	11.6(17)	-3.3(17)	4.3(18)
C55	27(2)	35(2)	31(2)	10.3(18)	6.2(17)	21.0(18)
C25	24(2)	24(2)	41(2)	2.6(17)	-4.7(18)	5.5(19)
C35	38(2)	30(3)	51(3)	2.0(19)	15(2)	4(2)
C21	39(2)	26(2)	42(2)	3.0(18)	5.4(19)	13(2)
C30	21.6(19)	44(3)	21(2)	2.6(18)	0.1(16)	16.5(19)
C43	38(2)	36(2)	32(2)	10.2(19)	15.0(18)	20.9(19)
C24	40(2)	21(2)	56(3)	5.3(19)	-4(2)	1(2)
C36	36(2)	30(2)	31(2)	-1.5(19)	13.4(18)	2.5(19)
C5	49(3)	24(2)	30(2)	2(2)	-13(2)	12.2(18)
C42	42(2)	21(2)	35(2)	11.3(18)	11.9(19)	15.1(18)
C14	34(2)	34(3)	33(2)	10.4(19)	16.4(18)	5.9(19)
C22	45(3)	33(3)	59(3)	1(2)	11(2)	23(2)
C33	34(2)	49(3)	29(2)	-3(2)	9.9(19)	-3(2)
C26	48(2)	28(3)	37(2)	8(2)	11(2)	-4(2)
C7	27(2)	26(2)	54(3)	8.6(18)	-7(2)	11(2)
C34	39(2)	42(3)	40(3)	0(2)	18(2)	-13(2)
C6	47(3)	25(2)	43(3)	5(2)	-21(2)	14(2)
C23	42(2)	22(2)	72(3)	0(2)	3(2)	16(2)
C58S	51(3)	47(3)	55(3)	3(2)	4(2)	16(2)
C59S	55(3)	59(3)	77(4)	-14(3)	14(3)	16(3)
C63S	58(3)	56(3)	70(4)	-13(3)	2(3)	7(3)

C62S	98(4)	60(4)	59(4)	-10(3)	12(3)	13(3)
C57S	90(4)	75(4)	81(4)	6(3)	-18(3)	25(3)
C60S	48(3)	103(5)	74(4)	-18(3)	-1(3)	-10(4)
C61S	81(4)	83(4)	55(3)	4(3)	-8(3)	-1(3)
C66S	70(4)	55(4)	207(8)	-11(4)	-54(6)	73(5)
C64S	260(20)	60(9)	90(10)	36(11)	67(12)	22(8)
C67S	134(8)	52(4)	157(8)	-3(5)	-68(6)	51(5)
C65S	96(6)	54(4)	175(8)	5(4)	-33(6)	57(5)

Table 4 Bond Lengths for ThL2_FINAL.

Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
Th1	O1	2.254(2)	C29	C38	1.403(5)
Th1	O3	2.282(2)	C29	C30	1.427(4)
Th1	O4	2.289(2)	C56	C47	1.395(4)
Th1	N3	2.627(3)	C56	C55	1.427(5)
Th1	N4	2.630(3)	C13	C14	1.382(5)
Th1	N2	2.608(3)	C31	C32	1.419(5)
Th1	N1	2.644(2)	C31	C30	1.354(5)
Th1	O2	2.326(2)	C53	C54	1.420(5)
O1	C1	1.311(4)	C53	C52	1.417(4)
O3	C29	1.312(4)	C41	C42	1.382(4)
O4	C56	1.318(4)	C47	C46	1.442(4)
N3	C40	1.417(4)	C39	C38	1.440(4)
N3	C39	1.307(4)	C50	C49	1.374(4)
N4	C45	1.434(4)	C50	C51	1.400(5)
N4	C46	1.295(4)	C8	C7	1.374(5)
N2	C17	1.433(4)	C54	C55	1.349(4)
N2	C18	1.293(4)	C51	C52	1.363(5)
N1	C12	1.426(4)	C44	C43	1.382(5)
N1	C11	1.297(4)	C38	C37	1.449(5)
O2	C28	1.313(4)	C37	C32	1.424(5)
C40	C45	1.408(4)	C37	C36	1.401(5)
C40	C41	1.395(4)	C15	C14	1.374(5)
C19	C20	1.451(5)	C32	C33	1.407(5)
C19	C28	1.403(5)	C25	C24	1.410(5)
C19	C18	1.427(5)	C25	C26	1.415(5)
C10	C11	1.451(4)	C35	C36	1.380(5)

C10	C9	1.447(4)	C35	C34	1.396(5)
C10	C1	1.405(4)	C21	C22	1.372(5)
C45	C44	1.381(4)	C43	C42	1.386(5)
C48	C53	1.414(4)	C24	C23	1.364(5)
C48	C47	1.459(4)	C5	C6	1.347(5)
C48	C49	1.421(4)	C22	C23	1.375(5)
C12	C17	1.394(4)	C33	C34	1.359(6)
C12	C13	1.396(4)	C7	C6	1.389(5)
C2	C1	1.422(4)	C58S	C59S	1.382(6)
C2	C3	1.351(5)	C58S	C63S	1.370(6)
C9	C4	1.421(4)	C58S	C57S	1.498(6)
C9	C8	1.418(5)	C59S	C60S	1.347(7)
C16	C17	1.393(4)	C63S	C62S	1.376(6)
C16	C15	1.381(5)	C62S	C61S	1.356(7)
C4	C3	1.414(5)	C60S	C61S	1.385(7)
C4	C5	1.416(5)	C66S	C67S	1.425(8)
C20	C25	1.416(5)	C66S	C65S	1.369(8)
C20	C21	1.401(5)	C64S	C65S	1.422(10)
C27	C28	1.427(5)	C67S	C65S[1]	1.336(9)
C27	C26	1.356(5)			

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

Table 5 Bond Angles for ThL2_FINAL.

Atom	**Atom**	**Atom**	**Angle/°**	**Atom**	**Atom**	**Atom**	**Angle/°**
O3	Th1	O1	135.40(8)	C30	C29	C38	119.2(3)
O4	Th1	O1	132.65(8)	C12	C17	N2	116.6(3)
O4	Th1	O3	84.21(8)	C16	C17	N2	122.7(3)
N3	Th1	O1	75.34(8)	C16	C17	C12	120.7(3)
N3	Th1	O3	67.17(8)	C47	C56	O4	121.9(3)
N3	Th1	O4	110.38(8)	C55	C56	O4	117.9(3)
N4	Th1	O1	76.15(7)	C55	C56	C47	120.1(3)
N4	Th1	O3	104.69(8)	C14	C13	C12	119.9(3)
N4	Th1	O4	67.66(8)	C30	C31	C32	121.9(3)
N4	Th1	N3	61.61(8)	C10	C1	O1	122.3(3)
N2	Th1	O1	110.22(7)	C2	C1	O1	118.1(3)
N2	Th1	O3	75.51(8)	C2	C1	C10	119.5(3)
N2	Th1	O4	103.54(8)	C54	C53	C48	118.7(3)

N2	Th1	N3	125.47(8)	C52	C53	C48	120.0(3)
N2	Th1	N4	170.99(8)	C52	C53	C54	121.3(3)
N1	Th1	O1	68.12(8)	C42	C41	C40	121.1(3)
N1	Th1	O3	78.30(8)	C56	C47	C48	119.0(3)
N1	Th1	O4	159.18(8)	C46	C47	C48	119.1(3)
N1	Th1	N3	73.06(8)	C46	C47	C56	121.7(3)
N1	Th1	N4	127.74(8)	C4	C3	C2	121.7(3)
N1	Th1	N2	61.26(8)	C38	C39	N3	126.8(3)
O2	Th1	O1	83.66(8)	C51	C50	C49	121.5(3)
O2	Th1	O3	134.37(8)	C7	C8	C9	121.4(3)
O2	Th1	O4	79.63(8)	C50	C49	C48	120.9(3)
O2	Th1	N3	158.17(8)	C55	C54	C53	122.2(3)
O2	Th1	N4	107.86(8)	C52	C51	C50	118.8(3)
O2	Th1	N2	67.47(8)	C19	C28	O2	122.7(3)
O2	Th1	N1	104.75(8)	C27	C28	O2	119.0(3)
C1	O1	Th1	145.0(2)	C27	C28	C19	118.2(3)
C29	O3	Th1	140.23(19)	C43	C44	C45	121.3(3)
C56	O4	Th1	144.0(2)	C19	C18	N2	128.7(3)
C40	N3	Th1	113.26(19)	C39	C38	C29	120.4(3)
C39	N3	Th1	128.5(2)	C37	C38	C29	119.9(3)
C39	N3	C40	118.1(3)	C37	C38	C39	119.3(3)
C45	N4	Th1	112.75(19)	C32	C37	C38	119.0(3)
C46	N4	Th1	130.0(2)	C36	C37	C38	123.9(3)
C46	N4	C45	117.2(3)	C36	C37	C32	117.1(3)
C17	N2	Th1	112.25(19)	C47	C46	N4	127.4(3)
C18	N2	Th1	130.3(2)	C14	C15	C16	120.6(3)
C18	N2	C17	117.4(3)	C37	C32	C31	118.8(3)
C12	N1	Th1	112.66(18)	C33	C32	C31	121.2(3)
C11	N1	Th1	129.4(2)	C33	C32	C37	120.0(4)
C11	N1	C12	117.9(3)	C51	C52	C53	121.3(3)
C28	O2	Th1	143.8(2)	C54	C55	C56	120.5(3)
C45	C40	N3	116.8(3)	C24	C25	C20	119.1(4)
C41	C40	N3	124.2(3)	C26	C25	C20	118.3(3)
C41	C40	C45	119.0(3)	C26	C25	C24	122.5(4)
C28	C19	C20	120.6(3)	C34	C35	C36	119.9(4)
C18	C19	C20	118.5(3)	C22	C21	C20	121.2(4)
C18	C19	C28	120.4(3)	C31	C30	C29	121.1(4)
C9	C10	C11	118.7(3)	C42	C43	C44	119.9(3)

C1	C10	C11	121.2(3)	C23	C24	C25	121.4(4)
C1	C10	C9	119.5(3)	C35	C36	C37	121.9(4)
C40	C45	N4	116.7(3)	C6	C5	C4	121.1(4)
C44	C45	N4	124.1(3)	C43	C42	C41	119.6(3)
C44	C45	C40	119.1(3)	C15	C14	C13	120.6(3)
C47	C48	C53	119.4(3)	C23	C22	C21	121.2(4)
C49	C48	C53	117.3(3)	C34	C33	C32	120.9(4)
C49	C48	C47	123.2(3)	C25	C26	C27	122.5(4)
C17	C12	N1	116.6(3)	C6	C7	C8	120.6(4)
C13	C12	N1	124.4(3)	C33	C34	C35	120.2(4)
C13	C12	C17	118.9(3)	C7	C6	C5	120.2(3)
C10	C11	N1	127.6(3)	C22	C23	C24	119.3(4)
C3	C2	C1	121.0(3)	C63S	C58S	C59S	116.7(4)
C4	C9	C10	118.9(3)	C57S	C58S	C59S	121.5(5)
C8	C9	C10	124.2(3)	C57S	C58S	C63S	121.8(4)
C8	C9	C4	116.8(3)	C60S	C59S	C58S	122.7(5)
C15	C16	C17	119.2(3)	C62S	C63S	C58S	121.6(4)
C3	C4	C9	119.2(3)	C61S	C62S	C63S	120.1(5)
C5	C4	C9	119.9(3)	C61S	C60S	C59S	119.4(5)
C5	C4	C3	120.9(3)	C60S	C61S	C62S	119.4(5)
C25	C20	C19	118.9(3)	C65S	C66S	C67S	122.3(7)
C21	C20	C19	123.4(3)	C65S[1]	C67S	C66S	119.3(7)
C21	C20	C25	117.7(3)	C64S	C65S	C66S	122.9(11)
C26	C27	C28	121.1(4)	C67S[1]	C65S	C66S	118.4(8)
C38	C29	O3	122.9(3)	C67S[1]	C65S	C64S	118.7(12)
C30	C29	O3	117.9(3)				

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

Table 6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ThL2_FINAL.

Atom	***x***	***y***	***z***	**U(eq)**
H11	-3340(3)	6285(2)	2538(2)	23.9(10)
H2	-396(3)	5838(2)	2(2)	29.6(10)
H16	-2350(3)	3997(3)	4690(2)	29.4(10)
H27	64(3)	1855(3)	601(2)	41.8(12)
H13	-3450(3)	6730(3)	3934(2)	32.2(10)
H31	-936(3)	7166(3)	6550(2)	38.1(12)
H41	47(3)	8500(3)	2347(2)	31.4(10)

H3	-1580(3)	6706(2)	-587(2)	33.6(11)
H39	171(3)	8264(3)	3563(2)	26.9(10)
H50	6578(3)	4695(2)	364(2)	30.8(10)
H8	-4218(3)	7231(2)	2121(2)	35.2(11)
H49	4799(3)	5224(2)	848(2)	28.3(10)
H54	4796(3)	2727(3)	2707(2)	37.2(11)
H51	7470(3)	3538(3)	879(2)	35.2(11)
H44	2692(3)	6537(3)	692(2)	31.5(10)
H18	-2285(3)	2971(3)	3406(2)	24.5(10)
H46	3491(3)	5897(2)	1570.9(19)	23.0(9)
H15	-3607(3)	5036(3)	5537(2)	40.7(11)
H52	6489(3)	2843(3)	1819(2)	34.8(11)
H55	2998(3)	3156(3)	3172(2)	33.6(11)
H35	-1770(3)	10401(3)	5330(3)	49.2(13)
H21	-2193(3)	1674(3)	3668(2)	41.7(12)
H30	-319(3)	5886(3)	5514(2)	32.7(11)
H43	2256(3)	7966(3)	393(2)	39.0(11)
H24	-1484(3)	-876(3)	1289(3)	49.1(13)
H36	-1029(3)	9167(3)	4276(2)	40.4(11)
H5	-3326(3)	7600(3)	-563(2)	40.6(12)
H42	911(3)	8945(3)	1214(2)	36.7(11)
H14	-4181(3)	6371(3)	5147(2)	40.5(11)
H22	-2690(3)	84(3)	3648(3)	52.5(13)
H33	-1556(3)	8830(3)	7019(2)	48.3(13)
H26	-549(3)	305(3)	588(2)	47.8(12)
H7	-5405(3)	8039(3)	1442(3)	42.7(12)
H34	-2001(3)	10238(3)	6714(3)	54.5(14)
H6	-4979(3)	8187(3)	85(3)	45.0(12)
H23	-2386(3)	-1192(3)	2452(3)	53.5(13)
H59S	3503(4)	7333(3)	5118(3)	78.3(17)
H63S	5935(4)	9212(4)	4615(3)	77.4(17)
H62S	5091(5)	8947(4)	3262(3)	88.4(19)
H57a	4760(14)	8250(20)	6261(7)	122(3)
H57b	6044(16)	8230(20)	5892(4)	122(3)
H57c	5430(30)	9232(4)	6172(9)	122(3)
H60S	2695(4)	7023(4)	3770(4)	100(2)
H61S	3460(5)	7870(4)	2835(3)	92.7(19)
H66S	-6994(6)	9749(5)	-50(7)	126(3)

H64a	-6840(60)	10850(70)	1510(30)	204(10)
H64b	-6540(80)	9823(10)	1640(40)	204(10)
H64c	-5660(20)	10770(70)	2019(11)	204(10)
H67S	-5963(9)	9348(5)	-1331(6)	133(3)

Table 7 Atomic Occupancy for ThL2_FINAL.

Atom ***Occupancy***	**Atom** ***Occupancy***	**Atom** ***Occupancy***
C64S 0.500000	H64a 0.500000	H64b 0.500000
H64c 0.500000		

Refinement model description

Number of restraints - 3, number of constraints - 94.

Details:

```
1. Others
 Fixed Sof: C64S(0.5) H64a(0.5) H64b(0.5) H64c(0.5)
```

Emily091116_0m – CeL2

Table 8 Crystal data and structure refinement for **CeL2**

Identification code	Emily091116_0m
Empirical formula	$C_{59}H_{36}CeN_4O_5$
Formula weight	1021.08
Temperature/K	180.45
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.0103(8)
b/Å	13.9521(8)
c/Å	26.1970(15)
α/°	90
β/°	99.6888(12)
γ/°	90
Volume/Å^3	4687.5(5)
Z	4
ρ_{calc}mg/mm^3	1.4468
m/mm^{-1}	1.028
F(000)	2064.4
Crystal size/mm^3	0.45 × 0.15 × 0.02
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	3.16 to 53.46°
Index ranges	$-16 \leq h \leq 15$, $-17 \leq k \leq 17$, $-33 \leq l \leq 32$
Reflections collected	61172
Independent reflections	9966 [R_{int} = 0.0428, R_{sigma} = 0.0340]
Data/restraints/parameters	9966/0/621
Goodness-of-fit on F^2	1.068
Final R indexes [I>=2σ (I)]	R_1 = 0.0292, wR_2 = 0.0699
Final R indexes [all data]	R_1 = 0.0442, wR_2 = 0.0769
Largest diff. peak/hole / e Å^{-3}	0.78/-0.60

Table 9 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for **CeL2**. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
Ce1	1318.5(1)	924.77(10)	1757.27(5)	16.96(5)
O1	2153.0(13)	1636.4(12)	2452.6(6)	20.5(4)
O2	218.8(13)	2157.9(13)	1776.9(7)	22.6(4)
N4	472.8(16)	112.9(14)	2439.2(8)	19.3(4)
C39	2988.5(19)	-1063.5(17)	2130.4(10)	19.4(5)
O4	-210.9(14)	285.7(13)	1391.0(7)	25.3(4)
N1	2969.9(16)	1761.5(15)	1562.4(8)	19.7(5)
N2	1130.1(16)	1872.6(15)	927.5(8)	19.3(4)
O3	1949.3(14)	-80.5(12)	1234.8(7)	22.9(4)
N3	2356.2(16)	-437.6(15)	2274.5(8)	18.7(4)
C46	-520.0(19)	3.7(18)	2434.2(10)	21.0(5)
C9	4885(2)	2432.3(17)	2724.8(10)	21.6(5)
C11	3738.4(19)	2143.0(18)	1878.7(10)	21.4(5)
C19	-626(2)	2491.1(18)	912.6(10)	21.4(5)
C53	-3244(2)	260.7(19)	1688.0(12)	29.4(6)
C29	2767(2)	-616.6(18)	1203.3(10)	20.6(5)
C8	5785(2)	2590.0(18)	2500.9(11)	26.0(6)
C20	-1563(2)	2823.2(19)	578.0(11)	25.6(6)
C37	4149.1(19)	-1752.9(17)	1555.7(10)	20.0(5)
C12	2995(2)	1815.7(19)	1021.7(10)	22.2(6)
C40	2174(2)	-483.5(18)	2794.6(10)	20.3(5)
C10	3890.0(19)	2133.1(17)	2432.7(9)	19.0(5)
C45	1183.8(19)	-187.4(18)	2881.2(10)	20.6(5)
C56	-1155(2)	301.1(18)	1506.0(11)	24.7(6)
C47	-1348.4(19)	231.7(18)	2015.1(10)	21.7(5)
C17	2031(2)	1838.1(18)	685.4(10)	21.8(6)
C35	5527(2)	-2890(2)	1874.3(11)	27.7(6)
C42	2694(2)	-761(2)	3709.7(11)	30.6(7)
C18	300.1(19)	2305.4(18)	696.2(10)	21.7(5)
C38	3300.9(19)	-1118.8(17)	1628.3(10)	18.7(5)
C16	1999(2)	1792(2)	151.9(10)	28.5(6)
C32	4439(2)	-1827.3(19)	1058.2(10)	25.4(6)
C52	-4287(2)	219(2)	1780.9(14)	36.5(7)

C43	1721(2)	-462(2)	3797.7(11)	31.4(7)
C34	5788(2)	-2974(2)	1379.2(11)	29.3(6)
C4	4988(2)	2541.8(19)	3272.3(11)	24.6(6)
C1	3072.5(19)	1889.4(17)	2700(1)	19.3(5)
C31	3890(2)	-1274(2)	646.2(11)	32.8(7)
C44	976(2)	-169.2(19)	3387.6(10)	26.5(6)
C36	4729(2)	-2299.6(19)	1959.7(11)	24.4(6)
C48	-2409(2)	231.1(18)	2112.9(11)	25.0(6)
C21	-1670(2)	2843(2)	33.5(11)	34.2(7)
C25	-2421(2)	3140(2)	806.4(12)	32.1(7)
C6	6792(2)	3009(2)	3329.1(12)	32.7(7)
C5	5945(2)	2847(2)	3559.7(11)	31.1(6)
C30	3090(2)	-690(2)	712.2(11)	30.3(7)
C28	-597(2)	2460.2(18)	1452(1)	21.9(6)
C33	5257(2)	-2450(2)	984.5(12)	31.2(7)
C14	3874(2)	1757(2)	282.8(12)	39.6(8)
C27	-1472(2)	2805(2)	1661.4(11)	32.1(7)
C41	2920(2)	-764.7(19)	3211.9(11)	26.4(6)
C54	-3012(2)	320(2)	1178.8(12)	35.0(7)
C3	4123(2)	2301(2)	3516.9(11)	28.8(6)
C51	-4502(2)	171(2)	2272.5(14)	39.6(8)
C15	2917(2)	1754(2)	-46.9(11)	36.6(7)
C7	6715(2)	2858(2)	2797.4(12)	30.1(6)
C50	-3690(2)	174(2)	2691.6(13)	35.6(7)
C23	-3382(3)	3541(3)	-40.3(14)	48.5(9)
C26	-2341(2)	3119(2)	1349.2(12)	37.1(7)
C55	-2020(2)	344(2)	1086.9(12)	32.4(7)
C13	3911(2)	1774(2)	814.6(11)	30.9(7)
C49	-2668(2)	203(2)	2615.4(12)	30.0(6)
C22	-2555(3)	3205(3)	-264.5(13)	45.6(8)
C24	-3325(2)	3495(2)	483.3(14)	42.5(8)
C2	3217(2)	1968.1(19)	3246.4(10)	24.6(6)
O5s	-207(2)	742(2)	-412.4(11)	76.0(9)
C59s	5082(7)	60(5)	4725(3)	164(6)
C58s	6109(7)	503(6)	4711(4)	164(4)
C57s	6480(10)	598(6)	4228(3)	209(6)

Table 10 Anisotropic Displacement Parameters ($Å^2×10^3$) for **CeL2**. 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_{12}	U_{13}	U_{23}
Ce1	17.85(8)	19.76(8)	13.02(8)	-0.55(6)	1.86(5)	1.49(6)
O1	19.6(9)	24.5(9)	17.9(9)	-3.0(7)	4.6(7)	-1.2(7)
O2	23.4(9)	27.8(9)	15.6(9)	4.6(8)	0.9(7)	-0.2(8)
N4	21.8(11)	20.3(11)	15.3(11)	-0.6(9)	1.9(9)	2.0(9)
C39	19.0(12)	20.3(13)	18.1(13)	-1.4(10)	1.2(10)	3.4(10)
O4	24.6(10)	30.5(10)	19.8(10)	-5.6(8)	1.0(8)	1.3(8)
N1	20.0(11)	25.3(11)	13.8(11)	1.8(9)	3.1(9)	2.1(9)
N2	20.6(11)	22.5(11)	14.7(11)	-2.4(9)	3.0(9)	1.5(9)
O3	26.0(9)	25.3(9)	17.0(9)	4.6(8)	2.2(8)	0.1(8)
N3	20.1(10)	22.8(11)	13.3(11)	-1.1(9)	2.6(9)	1.0(9)
C46	23.8(13)	20.5(13)	19.3(14)	-1.9(10)	5.9(11)	0.1(10)
C9	22.1(13)	16.9(12)	24.5(14)	2.8(10)	0.1(11)	-0.7(10)
C11	20.6(13)	22.6(13)	21.4(14)	0.6(11)	5.1(11)	2.7(11)
C19	22.1(13)	20.7(13)	20.0(14)	-0.1(10)	-0.4(11)	1.7(10)
C53	23.7(14)	20.2(13)	41.8(18)	-2.1(11)	-2.0(13)	0.1(12)
C29	22.5(13)	20.1(12)	19.3(14)	-3.2(10)	3.9(11)	-0.4(10)
C8	25.6(14)	24.3(14)	27.8(16)	-2.3(11)	3.7(12)	-2.0(12)
C20	23.7(13)	24.0(13)	26.7(15)	-4.7(11)	-2.7(11)	3.0(12)
C37	19.2(12)	20.4(12)	20.6(14)	-4.8(10)	3.5(11)	1.7(11)
C12	24.0(13)	28.3(14)	15.0(13)	-2.0(11)	5.3(11)	3.9(11)
C40	23.7(13)	20.9(13)	15.7(13)	-0.7(10)	2.1(11)	1.4(10)
C10	20.7(12)	19.2(12)	16.4(13)	1.7(10)	1.2(10)	-1.6(10)
C45	22.5(13)	20.3(12)	18.6(14)	-1.2(10)	2.1(11)	2.7(10)
C56	22.4(13)	21.5(13)	28.2(15)	-5.5(11)	-1.2(11)	1.3(11)
C47	20.9(13)	18.1(12)	24.9(15)	-4.1(10)	0.3(11)	-0.2(11)
C17	26.2(14)	23.6(13)	16.5(13)	-1.3(11)	6.0(11)	3.8(11)
C35	22.2(13)	28.7(14)	31.4(16)	1.3(11)	2.4(12)	4.9(12)
C42	37.6(16)	35.7(16)	15.5(14)	6.4(13)	-4.3(12)	1.6(12)
C18	25.7(13)	22.9(13)	15.6(13)	-3.1(11)	1.4(11)	3.4(11)
C38	19.6(12)	17.6(12)	19.0(13)	-2.9(10)	3.6(10)	0.2(10)
C16	30.1(15)	37.6(16)	17.1(14)	-0.5(12)	2.2(12)	3.0(12)
C32	26.5(14)	28.3(14)	23.0(15)	-0.5(11)	8.9(12)	2.0(12)
C52	22.4(14)	24.4(14)	59(2)	-2.3(12)	-2.2(14)	-1.0(14)
C43	42.1(17)	37.2(16)	15.5(14)	5.4(14)	6.4(13)	3.2(12)
C34	23.1(14)	30.3(15)	36.5(17)	4.1(12)	11.3(13)	1.7(13)

C4	24.0(13)	24.7(14)	22.9(15)	3.5(11)	-2.1(11)	-1.5(11)
C1	21.0(13)	17.3(12)	18.6(13)	2.2(10)	0.4(10)	-0.6(10)
C31	38.7(17)	41.9(16)	20.4(15)	6.8(14)	13.1(13)	4.6(13)
C44	29.5(15)	31.3(15)	19.9(14)	3.3(12)	7.7(12)	1.7(12)
C36	22.1(13)	28.6(14)	23.1(15)	0.1(11)	5.5(11)	1.3(12)
C48	20.9(13)	17.3(12)	35.7(16)	-4.7(10)	1.5(12)	0.4(11)
C21	32.5(16)	39.5(17)	28.1(16)	-3.8(13)	-2.2(13)	4.9(14)
C25	27.1(15)	32.1(15)	35.2(18)	2.8(12)	-0.4(13)	3.1(13)
C6	23.9(14)	27.2(15)	41.6(19)	-0.7(12)	-10.3(13)	-2.9(13)
C5	30.0(15)	32.4(15)	26.6(16)	0.4(12)	-7.2(12)	-3.0(13)
C30	39.3(17)	33.9(15)	18.5(15)	6.5(13)	7.0(13)	7.5(12)
C28	23.5(13)	20.7(13)	20.8(14)	1(1)	1.6(11)	1.0(11)
C33	29.8(15)	38.1(16)	29.2(16)	2.5(13)	15.0(13)	1.0(13)
C14	31.2(16)	65(2)	25.7(16)	4.6(15)	14.2(13)	11.5(15)
C27	31.9(15)	39.7(16)	25.5(16)	8.9(13)	6.9(13)	0.4(13)
C41	26.6(14)	30.1(15)	21.2(15)	4.7(11)	0.9(12)	1.2(11)
C54	26.0(15)	32.6(16)	40.7(19)	-4.9(12)	-11.4(13)	3.5(14)
C3	32.8(15)	36.7(16)	15.9(14)	4.1(13)	1.3(12)	-0.0(12)
C51	22.6(15)	29.0(16)	69(2)	-3.8(12)	12.5(16)	-6.5(16)
C15	39.1(17)	58(2)	15.1(15)	3.0(15)	10.2(13)	4.8(14)
C7	22.2(14)	27.8(14)	39.5(18)	-1.2(12)	3.3(13)	-1.9(13)
C50	30.0(16)	28.8(15)	51(2)	-1.9(13)	16.0(15)	-3.3(14)
C23	33.6(18)	58(2)	46(2)	7.3(16)	-16.1(16)	11.5(18)
C26	28.0(15)	43.4(18)	40.6(19)	12.2(13)	8.4(14)	-0.1(15)
C55	33.2(16)	34.5(16)	26.3(16)	-7.5(13)	-4.4(13)	4.7(13)
C13	26.0(15)	45.2(17)	21.9(15)	1.2(13)	4.8(12)	5.1(13)
C49	25.1(14)	27.4(15)	37.5(18)	-3.3(12)	5.2(13)	-2.3(13)
C22	40.5(19)	60(2)	31.2(19)	0.7(16)	-10.1(15)	10.3(16)
C24	26.4(16)	48(2)	50(2)	9.8(14)	-2.4(15)	5.6(17)
C2	24.3(13)	30.9(15)	18.8(14)	1.8(12)	4.4(11)	1.1(11)
O5s	51.6(16)	114(3)	55.2(18)	-22.1(16)	-12.2(14)	2.7(17)
C59s	118(5)	76(4)	260(13)	55(4)	-82(8)	-97(8)
C58s	134(6)	108(6)	225(10)	50(5)	-43(7)	-74(7)
C57s	421(18)	101(5)	94(5)	148(8)	8(8)	9(4)

Table 11 Bond Lengths for **CeL2**.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Ce1	O1	2.1948(17)	C12	C13	1.391(4)
Ce1	O2	2.2437(17)	C40	C45	1.407(3)
Ce1	N4	2.519(2)	C40	C41	1.391(4)
Ce1	O4	2.2433(17)	C10	C1	1.410(3)
Ce1	N1	2.571(2)	C45	C44	1.398(4)
Ce1	N2	2.521(2)	C56	C47	1.402(4)
Ce1	O3	2.2117(17)	C56	C55	1.435(4)
Ce1	N3	2.580(2)	C47	C48	1.446(3)
Ce1	C56	3.291(3)	C17	C16	1.393(4)
Ce1	C28	3.281(3)	C35	C34	1.400(4)
O1	C1	1.309(3)	C35	C36	1.374(4)
O2	C28	1.313(3)	C42	C43	1.388(4)
N4	C46	1.299(3)	C42	C41	1.384(4)
N4	C45	1.418(3)	C16	C15	1.381(4)
C39	N3	1.299(3)	C32	C31	1.418(4)
C39	C38	1.443(3)	C32	C33	1.413(4)
O4	C56	1.313(3)	C52	C51	1.365(5)
N1	C11	1.300(3)	C43	C44	1.383(4)
N1	C12	1.424(3)	C34	C33	1.356(4)
N2	C17	1.424(3)	C4	C5	1.408(4)
N2	C18	1.295(3)	C4	C3	1.426(4)
O3	C29	1.315(3)	C1	C2	1.416(4)
N3	C40	1.423(3)	C31	C30	1.355(4)
C46	C47	1.439(4)	C48	C49	1.413(4)
C9	C8	1.413(4)	C21	C22	1.374(4)
C9	C10	1.450(3)	C25	C26	1.409(4)
C9	C4	1.426(4)	C25	C24	1.418(4)
C11	C10	1.431(3)	C6	C5	1.362(4)
C19	C20	1.452(4)	C6	C7	1.396(4)
C19	C18	1.439(4)	C28	C27	1.428(4)
C19	C28	1.408(4)	C14	C15	1.391(4)
C53	C52	1.418(4)	C14	C13	1.386(4)
C53	C48	1.419(4)	C27	C26	1.352(4)
C53	C54	1.419(4)	C54	C55	1.353(4)
C29	C38	1.397(4)	C3	C2	1.351(4)
C29	C30	1.423(4)	C51	C50	1.390(4)

C8	C7	1.374(4)	C50	C49	1.378(4)
C20	C21	1.410(4)	C23	C22	1.391(5)
C20	C25	1.423(4)	C23	C24	1.363(5)
C37	C38	1.452(3)	C59s	C59s[1]	1.503(19)
C37	C32	1.420(4)	C59s	C58s	1.479(14)
C37	C36	1.415(4)	C58s	C57s	1.435(13)
C12	C17	1.407(4)			

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

Table 12 Bond Angles for **CeL2**.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O2	Ce1	O1	82.09(6)	C36	C37	C32	117.2(2)
N4	Ce1	O1	80.15(6)	C17	C12	N1	117.2(2)
N4	Ce1	O2	88.41(6)	C13	C12	N1	123.4(2)
O4	Ce1	O1	144.50(6)	C13	C12	C17	119.3(2)
O4	Ce1	O2	77.96(7)	C45	C40	N3	116.5(2)
O4	Ce1	N4	70.29(6)	C41	C40	N3	123.9(2)
N1	Ce1	O1	69.28(6)	C41	C40	C45	119.5(2)
N1	Ce1	O2	102.34(6)	C11	C10	C9	119.4(2)
N1	Ce1	N4	145.52(7)	C1	C10	C9	119.2(2)
N1	Ce1	O4	143.74(6)	C1	C10	C11	121.3(2)
N2	Ce1	O1	116.18(6)	C40	C45	N4	116.3(2)
N2	Ce1	O2	69.37(6)	C44	C45	N4	124.4(2)
N2	Ce1	N4	148.94(7)	C44	C45	C40	119.2(2)
N2	Ce1	O4	83.64(6)	O4	C56	Ce1	29.48(11)
N2	Ce1	N1	63.50(6)	C47	C56	Ce1	98.86(16)
O3	Ce1	O1	128.11(6)	C47	C56	O4	122.8(2)
O3	Ce1	O2	143.59(6)	C55	C56	Ce1	139.15(19)
O3	Ce1	N4	113.92(7)	C55	C56	O4	117.9(2)
O3	Ce1	O4	83.00(7)	C55	C56	C47	119.2(2)
O3	Ce1	N1	75.85(7)	C56	C47	C46	120.7(2)
O3	Ce1	N2	77.96(7)	C48	C47	C46	118.7(2)
N3	Ce1	O1	75.83(6)	C48	C47	C56	119.9(2)
N3	Ce1	O2	146.33(6)	C12	C17	N2	115.8(2)
N3	Ce1	N4	63.17(6)	C16	C17	N2	124.2(2)
N3	Ce1	O4	106.25(6)	C16	C17	C12	120.0(2)
N3	Ce1	N1	93.32(6)	C36	C35	C34	120.6(3)

N3	Ce1	N2	143.68(6)	C41	C42	C43	120.1(3)
N3	Ce1	O3	69.02(6)	C19	C18	N2	125.9(2)
C56	Ce1	O1	128.03(6)	C29	C38	C39	121.4(2)
C56	Ce1	O2	66.52(6)	C37	C38	C39	119.3(2)
C56	Ce1	N4	59.60(7)	C37	C38	C29	119.2(2)
C56	Ce1	O4	16.74(7)	C15	C16	C17	119.9(3)
C56	Ce1	N1	154.42(7)	C31	C32	C37	118.8(2)
C56	Ce1	N2	90.93(7)	C33	C32	C37	119.5(2)
C56	Ce1	O3	99.25(7)	C33	C32	C31	121.7(2)
C56	Ce1	N3	108.54(6)	C51	C52	C53	121.2(3)
C28	Ce1	O1	98.99(6)	C44	C43	C42	120.0(3)
C28	Ce1	O2	17.06(6)	C33	C34	C35	119.3(3)
C28	Ce1	N4	93.55(6)	C5	C4	C9	119.7(2)
C28	Ce1	O4	64.70(6)	C3	C4	C9	118.6(2)
C28	Ce1	N1	106.32(6)	C3	C4	C5	121.7(3)
C28	Ce1	N2	59.18(6)	C10	C1	O1	121.5(2)
C28	Ce1	O3	127.50(6)	C2	C1	O1	118.4(2)
C28	Ce1	N3	156.60(6)	C2	C1	C10	120.0(2)
C28	Ce1	C56	56.43(6)	C30	C31	C32	121.9(3)
C1	O1	Ce1	144.66(16)	C43	C44	C45	120.6(2)
C28	O2	Ce1	132.87(15)	C35	C36	C37	121.6(3)
C46	N4	Ce1	126.73(17)	C47	C48	C53	119.3(3)
C45	N4	Ce1	114.15(15)	C49	C48	C53	117.4(2)
C45	N4	C46	119.0(2)	C49	C48	C47	123.3(2)
C38	C39	N3	126.2(2)	C22	C21	C20	120.9(3)
C56	O4	Ce1	133.78(17)	C26	C25	C20	119.2(3)
C11	N1	Ce1	129.64(16)	C24	C25	C20	119.2(3)
C12	N1	Ce1	112.42(15)	C24	C25	C26	121.5(3)
C12	N1	C11	117.9(2)	C7	C6	C5	119.3(3)
C17	N2	Ce1	113.49(15)	C6	C5	C4	121.5(3)
C18	N2	Ce1	126.90(16)	C31	C30	C29	120.6(3)
C18	N2	C17	119.4(2)	O2	C28	Ce1	30.07(11)
C29	O3	Ce1	142.02(16)	C19	C28	Ce1	98.96(16)
C39	N3	Ce1	130.07(17)	C19	C28	O2	122.9(2)
C40	N3	Ce1	112.28(15)	C27	C28	Ce1	138.44(18)
C40	N3	C39	117.6(2)	C27	C28	O2	118.0(2)
C47	C46	N4	126.7(2)	C27	C28	C19	119.1(2)
C10	C9	C8	123.7(2)	C34	C33	C32	121.8(3)

C4	C9	C8	117.2(2)	C13	C14	C15	120.0(3)
C4	C9	C10	119.1(2)	C26	C27	C28	121.1(3)
C10	C11	N1	127.0(2)	C42	C41	C40	120.5(3)
C18	C19	C20	119.5(2)	C55	C54	C53	122.0(3)
C28	C19	C20	119.6(2)	C2	C3	C4	122.0(2)
C28	C19	C18	120.5(2)	C50	C51	C52	119.7(3)
C48	C53	C52	119.5(3)	C14	C15	C16	120.4(3)
C54	C53	C52	121.7(3)	C6	C7	C8	120.9(3)
C54	C53	C48	118.9(3)	C49	C50	C51	120.6(3)
C38	C29	O3	122.3(2)	C24	C23	C22	119.6(3)
C30	C29	O3	117.6(2)	C27	C26	C25	122.0(3)
C30	C29	C38	120.1(2)	C54	C55	C56	120.8(3)
C7	C8	C9	121.3(3)	C14	C13	C12	120.4(3)
C21	C20	C19	123.2(3)	C50	C49	C48	121.5(3)
C25	C20	C19	118.9(2)	C23	C22	C21	121.2(3)
C25	C20	C21	117.9(3)	C23	C24	C25	121.1(3)
C32	C37	C38	119.3(2)	C3	C2	C1	120.8(2)
C36	C37	C38	123.5(2)	C57s	C58s	C59s	120.0(9)

Table 13 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for **CeL2**.

Atom	***x***	***y***	***z***	**U(eq)**
H39	3272.5(19)	-1529.1(17)	2379.3(10)	23.2(6)
H46	-720.0(19)	-253.2(18)	2738.7(10)	25.2(6)
H11	4255.1(19)	2462.9(18)	1725.6(10)	25.6(7)
H8	5748(2)	2509.1(18)	2138.2(11)	31.2(7)
H35	5906(2)	-3245(2)	2153.8(11)	33.2(7)
H42	3205(2)	-964(2)	3991.6(11)	36.7(8)
H18	303.0(19)	2519.8(18)	352.3(10)	26.0(7)
H16	1348(2)	1787(2)	-75.1(10)	34.2(7)
H52	-4845(2)	225(2)	1495.9(14)	43.8(9)
H43	1568(2)	-459(2)	4139.7(11)	37.7(8)
H34	6331(2)	-3393(2)	1320.2(11)	35.1(8)
H31	4089(2)	-1314(2)	314.1(11)	39.3(8)
H44	316(2)	46.6(19)	3450.5(10)	31.8(7)
H36	4561(2)	-2257.2(19)	2298.2(11)	29.3(7)
H21	-1123(2)	2604(2)	-129.4(11)	41.1(8)

H6	7429(2)	3222(2)	3528.3(12)	39.2(8)
H5	6001(2)	2942(2)	3922.4(11)	37.3(8)
H30	2742(2)	-328(2)	428.1(11)	36.4(8)
H33	5441(2)	-2504(2)	649.7(12)	37.4(8)
H14	4502(2)	1746(2)	143.5(12)	47.5(9)
H27	-1443(2)	2814(2)	2026.2(11)	38.6(8)
H41	3591(2)	-960.8(19)	3154.9(11)	31.6(7)
H54	-3570(2)	344(2)	894.0(12)	42.1(8)
H3	4185(2)	2378(2)	3881.2(11)	34.5(7)
H51	-5204(2)	135(2)	2327.9(14)	47.5(9)
H15	2894(2)	1726(2)	-411.0(11)	43.9(9)
H7	7313(2)	2942(2)	2638.1(12)	36.1(8)
H50	-3841(2)	155(2)	3033.9(13)	42.8(9)
H23	-3983(3)	3800(3)	-251.0(14)	58.2(11)
H26	-2914(2)	3333(2)	1500.6(12)	44.5(9)
H55	-1894(2)	390(2)	740.9(12)	38.9(8)
H13	4565(2)	1758(2)	1038.9(11)	37.1(8)
H49	-2125(2)	204(2)	2907.4(12)	36.0(8)
H22	-2603(3)	3226(3)	-630.3(13)	54.8(10)
H24	-3901(2)	3705(2)	634.3(14)	51(1)
H2	2670(2)	1784.3(19)	3425(1)	29.5(7)

Refinement model description

Number of restraints - 0, number of constraints - 72.

Details:

```
1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups
2.a Aromatic/amide H refined with riding coordinates:
 C39(H39), C46(H46), C11(H11), C8(H8), C35(H35), C42(H42), C18(H18),
C16(H16),
 C52(H52), C43(H43), C34(H34), C31(H31), C44(H44), C36(H36), C21(H21),
C6(H6),
 C5(H5), C30(H30), C33(H33), C14(H14), C27(H27), C41(H41), C54(H54), C3(H3),
 C51(H51), C15(H15), C7(H7), C50(H50), C23(H23), C26(H26), C55(H55),
C13(H13),
 C49(H49), C22(H22), C24(H24), C2(H2)
```

Computational Details

The B3LYP functional was chosen combined with the correlation consistent cc-pVDZ basis set for C, N, H, and O atoms. For Ce and Th, the Stuttgart relativistic small-core effective core potentials (RSC-ECP) and their companion basis sets were used.[4,5] The inner 27 and 80 electrons are represented by the RSC-ECP for Ce and Th, respectively. A set of 5s5p4d3f/Ce and 8s7p6d4f/Th Gaussian basis functions were employed for the rest of the electrons.

The experimental geometries were used as initial structures to optimize the geometry at the B3LYP level. The Gaussian16 package was invoked for this reason. No other low-lying structures (isomers) were located. The TD-DFT calculations for the excited states were done with NWChem. The vertical excitation energies and transition dipole moments were obtain with TD-DFT.

DFT optimized structures

The B3LYP/cc-pVDZ optimized geometries are

Th-complex

Th 0.0300000000 0.0000000000 0.0000000000
O -1.1690000000 0.6880000000 1.8330000000
O -1.1700000000 -0.6860000000 -1.8320000000
O 1.8210000000 -1.1130000000 -0.9600000000
N -1.6550000000 -2.0370000000 0.5030000000
N 0.8520000000 -2.0610000000 1.4450000000
N 0.8530000000 2.0620000000 -1.4450000000
N -1.6540000000 2.0390000000 -0.5030000000
O 1.8220000000 1.1120000000 0.9600000000
C -1.4840000000 -2.4930000000 1.8320000000
C 3.1080000000 2.4620000000 -0.5430000000
C -2.8880000000 2.3340000000 1.6120000000
C -0.1580000000 -2.5010000000 2.3350000000
C 4.3790000000 -3.1180000000 0.8080000000
C -1.4820000000 2.4950000000 -1.8320000000
C -2.5440000000 2.6350000000 0.2490000000
H -3.0700000000 3.4880000000 -0.1970000000
C -2.4840000000 1.1290000000 3.7280000000
H -1.8940000000 0.3790000000 4.2570000000
C -3.9690000000 3.0640000000 2.2610000000
C 0.0780000000 2.8960000000 -3.6600000000
H 1.0930000000 2.8590000000 -4.0580000000
C -4.2620000000 2.7990000000 3.6380000000
C 4.3810000000 3.1170000000 -0.8070000000
C 3.9900000000 1.7150000000 1.6360000000
H 3.8070000000 1.1670000000 2.5610000000
C -2.1540000000 -1.3650000000 -2.3540000000
C -0.1560000000 2.5020000000 -2.3340000000
C 2.9290000000 -1.7320000000 -0.6680000000
C -2.5370000000 2.8810000000 -2.6730000000
H -3.5630000000 2.8260000000 -2.3040000000
C -3.4880000000 -1.8220000000 -4.3410000000
H -3.7220000000 -1.6330000000 -5.3920000000
C -2.1550000000 1.3650000000 2.3530000000
C 5.4120000000 -3.0680000000 -0.1820000000
C -2.5400000000 -2.8780000000 2.6730000000
H -3.5650000000 -2.8230000000 2.3040000000
C 3.1070000000 -2.4630000000 0.5440000000
C -3.4920000000 1.8200000000 4.3390000000
H -3.7280000000 1.6290000000 5.3890000000
C -2.5440000000 -2.6340000000 -0.2490000000
H -3.0710000000 -3.4860000000 0.1970000000
C 5.9000000000 -4.4140000000 2.2250000000
H 6.0900000000 -4.9260000000 3.1720000000
C -4.7790000000 4.0330000000 1.6070000000
H -4.6210000000 4.2670000000 0.5550000000
C 4.6780000000 -3.7960000000 2.0210000000
H 3.9460000000 -3.8230000000 2.8280000000
C 5.1720000000 -2.3590000000 -1.4010000000
H 5.9670000000 -2.3320000000 -2.1510000000
C 6.9030000000 -4.3790000000 1.2340000000
H 7.8640000000 -4.8670000000 1.4060000000
C 2.9300000000 1.7310000000 0.6680000000
C 0.0750000000 -2.8950000000 3.6610000000

H 1.0910000000 -2.8580000000 4.0590000000
C 2.0050000000 2.6820000000 -1.4360000000
H 2.1270000000 3.5130000000 -2.1440000000
C -2.8880000000 -2.3330000000 -1.6120000000
C -3.9680000000 -3.0640000000 -2.2620000000
C 2.0030000000 -2.6820000000 1.4370000000
H 2.1250000000 -3.5120000000 2.1460000000
C -0.9810000000 3.2940000000 -4.4800000000
H -0.7850000000 3.5860000000 -5.5140000000
C -4.2590000000 -2.8010000000 -3.6410000000
C 6.6550000000 -3.7070000000 0.0530000000
H 7.4230000000 -3.6530000000 -0.7240000000
C 3.9890000000 -1.7170000000 -1.6350000000
H 3.8060000000 -1.1690000000 -2.5600000000
C 5.4140000000 3.0670000000 0.1830000000
C -5.7890000000 -4.7050000000 -2.2740000000
H -6.3860000000 -5.4430000000 -1.7330000000
C 4.6800000000 3.7960000000 -2.0190000000
H 3.9480000000 3.8230000000 -2.8270000000
C -2.4810000000 -1.1300000000 -3.7290000000
H -1.8910000000 -0.3800000000 -4.2580000000
C -0.9830000000 -3.2910000000 4.4800000000
H -0.7880000000 -3.5830000000 5.5150000000
C 6.6570000000 3.7050000000 -0.0510000000
H 7.4240000000 3.6510000000 0.7260000000
C -4.7780000000 -4.0340000000 -1.6090000000
H -4.6210000000 -4.2660000000 -0.5560000000
C -5.3060000000 3.4990000000 4.2950000000
H -5.5000000000 3.2730000000 5.3470000000
C -2.2920000000 -3.2830000000 3.9860000000
H -3.1250000000 -3.5670000000 4.6310000000
C -2.2890000000 3.2870000000 -3.9860000000
H -3.1220000000 3.5710000000 -4.6310000000
C 5.9020000000 4.4140000000 -2.2230000000
H 6.0920000000 4.9260000000 -3.1700000000
C -5.3010000000 -3.5020000000 -4.2980000000
H -5.4940000000 -3.2770000000 -5.3500000000
C 5.1730000000 2.3570000000 1.4020000000
H 5.9690000000 2.3290000000 2.1520000000
C -5.7920000000 4.7040000000 2.2720000000
H -6.3880000000 5.4420000000 1.7310000000
C -6.0600000000 -4.4450000000 -3.6340000000
H -6.8600000000 -4.9800000000 -4.1490000000
C -6.0640000000 4.4420000000 3.6310000000
H -6.8650000000 4.9770000000 4.1450000000
C 6.9050000000 4.3780000000 -1.2320000000
H 7.8670000000 4.8660000000 -1.4030000000

Ce-complex

Ce -0.0180000000 0.0000000000 0.0000000000
O 1.1290000000 -0.6880000000 1.7990000000
O -1.7550000000 -1.0800000000 0.9490000000
N -0.8420000000 1.9890000000 1.4700000000
N 1.6550000000 -1.9850000000 -0.5360000000
N -0.8420000000 -1.9890000000 -1.4690000000
C 3.9560000000 -3.0270000000 2.2270000000
C 2.5450000000 -2.5880000000 0.2050000000
H 3.0820000000 -3.4280000000 -0.2530000000
C 4.7840000000 -3.9800000000 1.5710000000
H 4.6380000000 -4.2030000000 0.5150000000
C 1.4860000000 -2.4100000000 -1.8720000000
C 2.8750000000 -2.3040000000 1.5750000000

C 0.1600000000 -2.4080000000 -2.3720000000
C -1.9990000000 -2.5920000000 -1.4720000000
H -2.1400000000 -3.4060000000 -2.1970000000
C -0.0780000000 -2.7730000000 -3.7050000000
C 4.2310000000 -2.7740000000 3.6110000000
C 2.1180000000 -1.3540000000 2.3180000000
H -1.0930000000 2.7270000000 4.1010000000
C 6.0520000000 -4.3950000000 3.6040000000
H 6.8540000000 -4.9260000000 4.1210000000
C 5.2760000000 -3.4680000000 4.2710000000
H 5.4570000000 -3.2520000000 5.3270000000
C 2.2890000000 -3.1530000000 -4.0440000000
H 3.1220000000 -3.4220000000 -4.6980000000
C 3.4410000000 -1.8110000000 4.3140000000
H 3.6630000000 -1.6290000000 5.3690000000
C 5.7970000000 -4.6450000000 2.2390000000
H 6.4080000000 -5.3710000000 1.6970000000
C 2.5410000000 -2.7760000000 -2.7230000000
H 3.5680000000 -2.7280000000 -2.3550000000
C 2.4300000000 -1.1270000000 3.7000000000
H 1.8260000000 -0.3900000000 4.2300000000
H -1.0940000000 -2.7280000000 -4.1000000000
C 0.9800000000 -3.1510000000 -4.5360000000
H 0.7820000000 -3.4200000000 -5.5750000000
C 2.5450000000 2.5870000000 -0.2050000000
H 3.0830000000 3.4270000000 0.2530000000
O 1.1290000000 0.6870000000 -1.7980000000
N 1.6560000000 1.9840000000 0.5360000000
C 2.1180000000 1.3530000000 -2.3180000000
C 3.9550000000 3.0270000000 -2.2280000000
C 1.4870000000 2.4090000000 1.8730000000
C 0.1610000000 2.4070000000 2.3720000000
C 5.7960000000 4.6460000000 -2.2400000000
H 6.4070000000 5.3720000000 -1.6980000000
C 2.2900000000 3.1510000000 4.0440000000
H 3.1230000000 3.4200000000 4.6980000000
C 2.8740000000 2.3040000000 -1.5750000000
C 4.2300000000 2.7740000000 -3.6120000000
C 0.9810000000 3.1500000000 4.5360000000
H 0.7840000000 3.4190000000 5.5760000000
C 6.0500000000 4.3970000000 -3.6050000000
H 6.8520000000 4.9270000000 -4.1220000000
C 3.4390000000 1.8120000000 -4.3140000000
H 3.6610000000 1.6300000000 -5.3700000000
C -0.0770000000 2.7720000000 3.7060000000
C 4.7830000000 3.9800000000 -1.5720000000
H 4.6380000000 4.2030000000 -0.5160000000
C 2.4300000000 1.1270000000 -3.7000000000
H 1.8250000000 0.3900000000 -4.2310000000
C 5.2740000000 3.4690000000 -4.2720000000
H 5.4550000000 3.2540000000 -5.3280000000
C 2.5420000000 2.7750000000 2.7230000000
H 3.5680000000 2.7270000000 2.3550000000
O -1.7540000000 1.0810000000 -0.9490000000
C -1.9990000000 2.5920000000 1.4730000000
C -3.0920000000 -2.3670000000 -0.5660000000
C -5.4050000000 2.9180000000 -0.1730000000
C -4.3810000000 -2.9870000000 -0.8240000000
C -2.8820000000 1.6570000000 -0.6520000000
C -3.0910000000 2.3670000000 0.5660000000
C -6.6650000000 3.5240000000 0.0580000000
H -7.4260000000 3.4560000000 -0.7240000000
C -4.3800000000 2.9870000000 0.8250000000

C -4.7030000000 -3.6510000000 -2.0390000000
C -5.4060000000 -2.9180000000 0.1730000000
C -2.8830000000 -1.6560000000 0.6520000000
C -3.9380000000 -1.6160000000 1.6260000000
H -3.7330000000 -1.0820000000 2.5550000000
C -5.1380000000 2.2240000000 -1.3950000000
H -5.9280000000 2.1810000000 -2.1500000000
C -6.9360000000 4.1820000000 1.2430000000
H -7.9110000000 4.6450000000 1.4110000000
C -5.9410000000 4.2370000000 2.2400000000
H -6.1490000000 4.7400000000 3.1880000000
C -5.1390000000 -2.2230000000 1.3950000000
H -5.9290000000 -2.1800000000 2.1500000000
C -3.9370000000 1.6170000000 -1.6260000000
H -3.7320000000 1.0830000000 -2.5550000000
C -4.7020000000 3.6520000000 2.0400000000
H -3.9750000000 3.6940000000 2.8510000000
C -6.6660000000 -3.5230000000 -0.0580000000
H -7.4270000000 -3.4550000000 0.7240000000
H -3.9760000000 -3.6940000000 -2.8510000000
C -6.9370000000 -4.1820000000 -1.2420000000
H -7.9120000000 -4.6450000000 -1.4100000000
C -5.9420000000 -4.2370000000 -2.2400000000
H -6.1500000000 -4.7400000000 -3.1870000000
H -2.1390000000 3.4050000000 2.1980000000

TD-DFT vertical excitation energies and transition dipole moments

The B3LYP/cc-pVDZ excitation energies (ΔE, eV) and transition dipole moments (μ, a.u.) are:

Th-complex

State	ΔE	μ	State	ΔE	μ
1	2.8762	0.9973	11	3.2317	0.1152
2	2.9569	0.2192	12	3.2872	0.3811
3	2.9826	0.6182	13	3.3320	0.0109
4	3.0605	0.3396	14	3.3424	0.2195
5	3.0739	0.8624	15	3.4006	0.5399
6	3.1143	0.3448	16	3.4341	2.4020
7	3.1536	0.2832	17	3.7866	1.2257
8	3.1814	0.9174	18	3.8019	1.3213
9	3.1978	0.7228	19	3.8290	0.8023
10	3.2259	1.8956	20	3.8574	0.3905

Ce-complex

State	ΔE	μ	State	ΔE	μ
1	1.4457	0.0658	51	2.8171	0.3512
2	1.4575	0.0742	52	2.8224	0.1011
3	1.4666	0.1857	53	2.8261	0.0589
4	1.5095	0.1259	54	2.8521	0.0446
5	1.6004	0.2492	55	2.8538	0.2077

6	1.6424	0.3959	56	2.8655	0.0629
7	1.6648	0.4375	57	2.8723	0.1719
8	1.6678	0.1473	58	2.8784	0.0205
9	1.6860	0.1904	59	2.8819	0.1107
10	1.7094	0.2121	60	2.8851	0.1173
11	1.7274	0.1059	61	2.8974	0.3176
12	1.7409	0.0808	62	2.9061	0.0654
13	1.7480	0.0720	63	2.9103	0.1531
14	1.7627	0.0637	64	2.9153	0.3690
15	1.7712	0.3851	65	2.9288	0.7331
16	1.7839	0.0242	66	2.9398	0.0703
17	1.7972	0.0704	67	2.9509	0.1850
18	1.7991	0.2164	68	2.9636	0.0633
19	1.8382	0.5862	69	2.9665	0.2949
20	1.8470	0.2913	70	2.9817	0.3608
21	1.8575	0.7558	71	2.9863	0.8221
22	1.9204	0.0826	72	2.9870	0.3263
23	1.9314	0.4908	73	2.9897	0.0047
24	1.9381	0.5508	74	2.9939	0.2088
25	1.9739	0.6781	75	3.0003	0.7108
26	2.0074	0.1961	76	3.0091	0.2130
27	2.0538	0.0156	77	3.0516	0.1760
28	2.0890	0.0007	78	3.0593	0.3072
29	2.5310	0.1365	79	3.0713	0.2209
30	2.5558	0.1102	80	3.0770	0.3154

31	2.5688	0.1984	81	3.0892	0.1523
32	2.5784	0.6090	82	3.0976	0.1434
33	2.6112	0.0272	83	3.1064	0.0450
34	2.6265	0.0589	84	3.1179	0.1905
35	2.6318	0.3687	85	3.1275	0.2305
36	2.6698	0.3002	86	3.1363	0.1977
37	2.6767	0.3787	87	3.1508	0.0801
38	2.6916	0.1605	88	3.1615	0.1949
39	2.6987	0.1204	89	3.1707	0.1137
40	2.7119	0.0972	90	3.1732	0.3995
41	2.7222	0.2511	91	3.1769	0.0496
42	2.7315	0.1578	92	3.1849	0.8908
43	2.7388	0.1976	93	3.2207	0.3660
44	2.7459	0.0126	94	3.2360	0.3065
45	2.7634	0.1408	95	3.2549	0.8574
46	2.7758	0.3104	96	3.2569	0.2383
47	2.7810	0.1238	97	3.2645	0.4785
48	2.7830	0.2414	98	3.2713	1.1708
49	2.7963	0.1910	99	3.2739	0.9560
50	2.8030	0.1075	100	3.2755	0.1479

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