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Journal:	*Dalton Transactions*
Manuscript ID	DT-ART-06-2018-002543.R2
Article Type:	Paper
Date Submitted by the Author:	19-Sep-2018
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Monomeric Thorium Chalcogenolates with Bipyridine and Terpyridine Ligands[a]

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Abstract

Thorium chalcogenolates $Th(ER)_4$ react with 2,2'-bipyridine (bipy) to form complexes with the stoichiometry $(bipy)_2Th(ER)_4$ (E = S, Se; R = Ph, C_6F_5). All four compounds have been isolated and characterized by spectroscopic methods and low-temperature single crystal x-ray diffraction. Two of the products, $(bipy)_2Th(SC_6F_5)_4$ and $(bipy)_2Th(SeC_6F_5)_4$, crystallize with lattice solvent, $(bipy)_2Th(SPh)_4$ crystallizes with no lattice solvent, and the selenolate $(bipy)_2Th(SePh)_4$ crystallizes in two phases, with and without lattice solvent. In all four compounds the available volume for coordination bounded by the two bipy ligands is large enough to allow significant conformational flexibility of thiolate or selenolate ligands. ^{77}Se NMR confirms that the structures of the selenolate products are the same in pyridine solution and in the solid state. Attempts to prepare analogous derivatives with 2,2′,6′,2″-terpyridine (terpy) were successful only in the isolation of $(terpy)(py)Th(SPh)_4$, the first terpy compound of thorium. These materials are thermochroic, with color attributed to ligand-to-ligand charge transfer excitations.

Introduction

The actinide elements continue to represent one of the great challenges in inorganic chemistry because of the complicated nature of the valence 5f orbitals and the variable influence of covalent/ionic bonding in actinide systems. Interest in probing the importance of covalent bonding has inspired recent efforts to develop the chemistry of actinides with relatively electropositive chalcogen based anions (i.e. ER^-, E^{2-}: E = S, Se, Te; R = organic) because of the greater propensity of these ligands form covalent bonds with metals.[1] A firm understanding of the fundamental chemical and physical properties of molecules with actinide-chalcogen bonds is also important because it provides the necessary foundation for understanding size dependent chemical and physical properties of actinide systems.

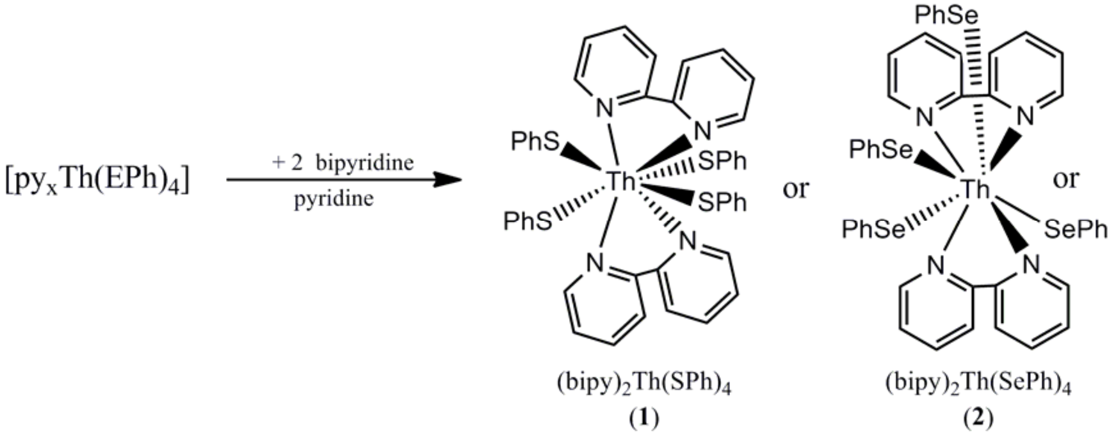
2,2'-Bipyridine (bipy) has been used extensively in actinide chemistry,[2] because chelating ligands impart thermal stability, and because the extended π^* orbitals are a potential reservoir for electrons in transition states[3] or in ground states, as a bipy radical anion.[4] Compounds of uranium with bipyridine dominate the actinide literature, with an extensive array of halide[3a,4a-d,5] and carboxylates derivatives,[6] but less conventional compounds such as the remarkable uranium imido bipy complexes also exist.[4a,b,5c-f,7] Products in which bipy is anionic are also well established, i.e. $U(bipy)_4$[4j] and a series of actinide metallocenes.[4d,8]

Thorium compounds are potential sources of insight into the electronic properties of actinide compounds because the electronically silent nature of the Th(IV) ion (no $f^n \rightarrow f^{n-1}d^1$ promotion, LM or ML charge transfer) simplifies the assignment of ligand based electronic transitions. While there are a number of Th compounds with bipy ligands[4d-g,5n,8a,b] and a number of instances where pairs of bidentate ligands have been used to give stable 8 coordinate bis-chelate ligand compounds,[4a,4h,5c,5j-m,8c,9] there are no examples of thorium compounds with two bipy ligands.

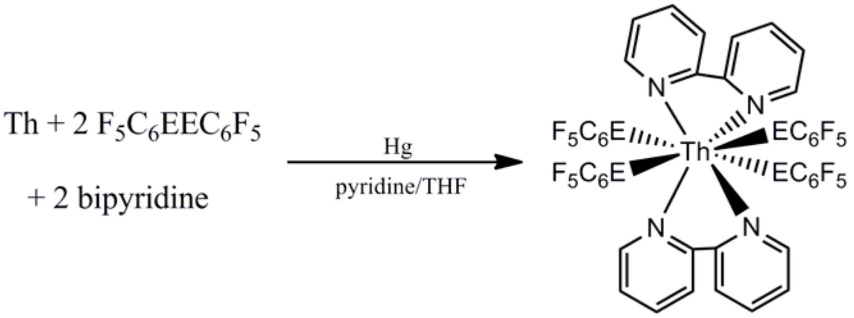
This work outlines the synthesis and characterization of bipyridine complexes of thorium chalcogenolates $Th(ER)_4$. In order to probe the origin of the color in these compounds, analogous chemistry with 2,2′,6′,2″-terpyridine (terpy) was also explored.

Results and Discussion

Thorium metal reacts with RE-ER (E = S, Se; R = Ph, C_6F_5) to reductively cleave the E-E bond and form Th(IV) chalcogenolates that react with bipy to form bis-bipy chelate compounds $(bipy)_2Th(EPh)_4$ (Scheme 1) and $(bipy)_2Th(EC_6F_5)_4$ (Scheme 2). This is an attractive synthetic approach due to the minimal number of reagents involved, the relatively high yields, and the ease with which intended products can be isolated, because there are no solid-state byproducts. Addition of catalytic mercury is not required, but reduces the amount of time required for all the Th metal to be consumed.



Scheme 1. Synthesis of bis-bipyridine thorium(IV) chalogenolate complexes by displacement of pyridine with bipy.



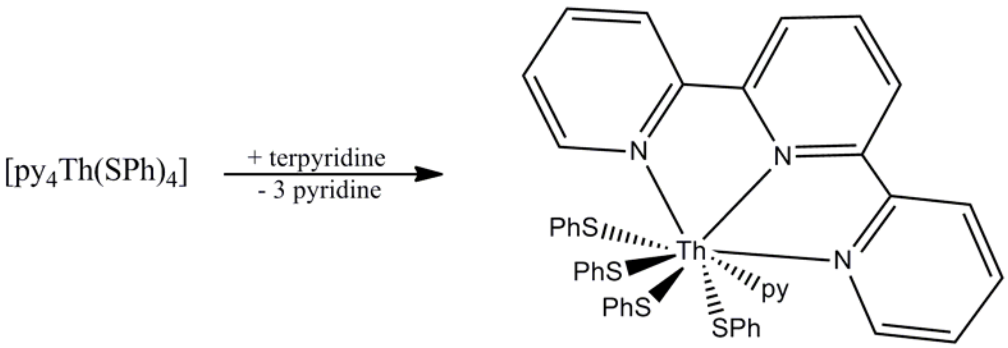
$(bipy)_2Th(EC_6F_5)_4$
E = S (**3**)
E = Se (**4**)

Scheme 2. Synthesis of bipyridine thorium monomers with fluorinated chalcogenido ligands.

All four bis-bipy products were isolated and characterized by conventional methods and low temperature single crystal x-ray diffraction. Because reliable elemental analyses are often difficult to obtain, due to the facile loss of lattice solvent at room temperature and the possibility that other phases may also precipitate from the same flask, all compounds were also characterized by powder x-ray diffraction. Observed diffraction profiles were compared with profiles calculated from respective single crystal results to determine the level of purity of the bulk isolated material.

All four bipy compounds are thermochromic in the solid state, reversibly becoming darker as the temperature increases. Thermochromic properties are rare in actinide systems, with a mere two reports outlining thermochroic behavior in uranyl systems.[10] Because the analogous pyridine derivatives are colorless at room and elevated temperatures, the most likely source of the color change for the bipy compounds may be a low energy ligand-to-ligand charge transfer (LLCT) process in which an electron on the relatively electropositive EPh anion is transferred to a delocalized π* orbital on the bipy.[11] We were unable to observe any well-defined absorption maxima that could be assigned to such an LLCT process, but the hypothesis can be tested by replacing bipy with terpy, where the more extended π* orbitals on the terpy ligand should lower the energy requirements of a LLCT process even more.[12] Addition of terpy to a solution of $Th(ER)_4$ led to the successful isolation and characterization of the thiolate product $(py)(terpy)Th(SPh)_4$, **5**, which was characterized by IR/UV/vis spectroscopic methods, PXRD, and low-temperature single crystal x-ray diffraction. Compound **5** is the first thorium compound containing terpy.

Although not quantitative because of variable crystal thicknesses, the yellow color of **5** appears darker to the naked eye than the colorless $(py)_4Th(SPh)_4$[13] and the light yellow $(bipy)_2Th(SPh)_4$, **1** implying that the electronic transition responsible for complex color is shifted increasingly into the visible spectrum as the extent of conjugation in the neutral donor is extended. This behavior is consistent with the above LLCT assignment. Unfortunately, there was no well-defined absorption maximum in the UV/vis spectrum of $(py)(terpy)Th(SPh)_4$.



$(py)(terpy)Th(SPh_2)_4$ (**5**)

Scheme 3. Synthesis of the monomeric terpyridine thorium thiolate.

Figures 1 - 5 show the thermal ellipsoid diagrams[14] for **1** - **5** respectively.

All five compounds are eight coordinate, with four chalcogenolate ligands and two neutral chelating ligands. These compounds crystallize in four structural types that differ greatly in overall conformation, but only slightly in the geometry of the ThE_4N_4 core coordination (see below). For **1 – 5**, this situation contrasts that for the 7-coordinate $(py)_3Th(ER)_4$ derivatives (ER = SePh, SC_6F_5).[13] Unexpectedly, for $(py)_3Th(SePh)_4$,[13] a seven coordinate structure is even maintained in pyridine solution, as determined by ^{77}Se NMR data and DFT calculations.[15]

In contrast to the relatively less crowded 7-coordinate Th compound $(py)_3Th(SC_6F_5)_4$,[18] eight -coordinate $(bipy)_2Th(SC_6F_5)_4$, **3**, contains no dative Th…F bonds, most likely due to space constraints when the two bidentate bipy ligands are present as in Fig. 3. This hypothesis is also supported by the absence of Th…F dative bonds in the 8-coordinate $(py)_4Th(SeC_6F_5)_4$.[18] Many dative actinide···F interactions are found in the Cambridge Structure Database (CSD),[16] but only seven were found to involve an F atom from a ligand containing a C_6F_5 moiety.[11,14] The three py in $(py)_3Th(SC_6F_5)_4$[13] are all located on one side of the molecule, so that the molecular dipole is very large, in contrast to all of the 8-coordinate molecules presented here, which have pairs of ER located on opposite (**1**, **3**, **4**) or on nearly opposite (**2**, **5**) sides of the molecule.

As shown in Fig. 6, the primary ThE_4N_4 coordination spheres in **1** - **5** can be viewed as having distorted square antiprism (SAP) symmetry.[17] However, based upon the ligand-Th-ligand bond angles (Tab. S4, S11, S18, S25, and S32 for **1** – **5**, respectively), a bicapped trigonal prism (BTP) coordination, with capping N atoms – one from each bipy, is a more accurate description. The coordination scheme for $(bipy)_2Th(SPh)_4$, $(bipy)_2Th(SC_6F_5)_4$, and $(bipy)_2Th(SeC_6F_5)_4$ is described by Kepert[18] as the *trans* configuration for two bidentate and four unidentate ligands, and contrasts the *cis* configuration of two bidentate ligands demonstrated by $(bipy)_2Th(SePh)_4$, and possibly $(py)(terpy)Th(SPh)_4$, if, for the sake of analysis, one considers N(2) and N(3) to belong to one bidentate ligand and N(1) and N(4) to belong to the other (see Fig. 5). For $(bipy)_2Th(SC_6F_5)_4$, as in Fig. 3(top), and $(bipy)_2Th(SeC_6F_5)_4$, as in and Fig. 4, all ER are positioned to provide two instances of double π…π (e.g., ER…bipy…ER) stacking within a single molecule. However, for $(bipy)_2Th(SPh)_4$, and $(bipy)_2Th(SePh)_4$, with a comparatively smaller and more electropositive ER ligand, the double π…π stacking motif, which may exist in solution, certainly is not observed in the solid state. For a fuller comparison of π…π interaction geometries, Table 1 includes the Th angles to the centroids of the neutral ligands as well as the coordination bond angles.

The Th-Se, Th-S, and Th-N bond geometries in **1** - **5** are consistent with prior literature,[16] and are summarized in Table 1. The twist (dihedral) angle between the pair of mean bipy planes, the distance and angles from Th to the bipy center-of-mass, and the acute E-Th-N angles are also in Table 1. Because of the geometry of pairs of ligands in an 8-coordinate environment for **1** - **5**, the E'-Th-E bond angles in Table 1 may be grouped into 3 ranges, namely *cis* at 66 – 85 ° (e.g., acute angles), *meta* at 90 – 131 °, and nearly *trans* at 142 -149 °. None of the conformations of **1** – **5** include truly *trans* (e.g., E'-Th-E of 180 °), and, further, all of the molecules have a substantial molecular dipole.

By examination of Fig. 1 – 5, it is apparent that the torsion angles about the Th-E and E-C bonds are good measures of any conformational flexibility of ER ligands and the steric effects of nearest neighbor organic ligands. Interestingly, the Th-E-C-C' torsion angles have a narrow range, 82 – 85 ° for $(bipy)_2Th(SC_6F_5)_4$, and $(bipy)_2Th(SeC_6F_5)_4$, (Table 1), which may be due to a lower influence of packing interactions for their larger F-containing rings versus the smaller Ph rings of $(bipy)_2Th(SPh)_4$, and $(bipy)_2Th(SePh)_4$. The number and ranges for the weak intramolecular H bonding between the aromatic C-H donors and S or Se acceptors given in Table 1 indicate that more of these interactions are possible in the more "open" structures of **1** and **5** compared to the more compact structures of **3** and **4**. Compound **2**, with positions of one selenolate and one bipy switched with respect to those in **1** and **3**, has an intermediate number of H bonding interactions. With respect to close H…F contacts,[19] the values in Table 1 for **3** and **4** include one intra- and 2 inter-molecular H…F per EC_6F_5 for a total of 12 H…F per molecule. Because the E atoms are buried near the core of the molecule, there are no intermolecular H-bonding interactions to S or Se in **1** – **5**. Also, it is clear that there is little or no charge residing on the bipy ligands, as evidenced by the central C-C bond lengths here that range from 1.46 to 1.50 Å, an observation which is consistent with the descriptions of neutral bipy ligands [2c,2g,4e,5a,5i,5m,8a] of actinide compounds. The unit cell packing in each crystal structure of **1** – **5** is comprised of 2-dimensional sheets containing closely associated molecules but separated by more remote intermolecular H…H contacts of likely dispersive interactions. Non-typically and perhaps because of its larger terpy ligand, the intermolecular interactions in **5** more closely approximate H(Ar)…Ar type of crystal packing interaction.[20] Supplementary Fig.S22 – S26 show edge-on views of these

2-D sheets in the unit cell packing diagrams of **1 – 5**, respectively. The combination of the *trans* or near *trans* pair[21] of bipy ligands in **1 – 4** and the apparent requirement of bidirectional π…π interactions, likely creates the observed 2D sheet motif in all of these structures.

Solution structure

^{77}Se NMR data for **2** and **4** provide information about the solution structure of these molecules, much as this technique has been informative for establishing the solution structure of related thorium selenolates and selenido cluster compounds. The SePh and SeC_6F_5 compounds **2** and **4** have ^{77}Se NMR resonances with chemical shifts that indicate their eight coordinate solid-state structures are maintained in solution. Shifts for the SePh compound cannot be compared directly with the related pyridine derivative because the latter crystallized with three coordinated pyridines and had a ^{77}Se resonance at 659 ppm[22] while **2** is eight coordinate with four neutral nitrogen donors. Given this experimental value and DFT calculations of the ^{77}Se NMR chemical shifts for a hypothetical $(py)_4Th(SePh)_4$ (calculated 565 ppm)[15] and $(py)_3Th(SePh)_4$ (calculated 644 ppm[15] and experimental 659 ppm[22]), it is reasonable to conclude that the 586 ppm resonance found for $(bipy)_2Th(SePh)_4$ (**2**) is consistent with a solution structure in which all four nitrogen donors remain coordinated, and no additional pyridine is present in the primary coordination sphere.

The fluorinated selenolate compounds behave similarly. In this case, both $(py)_4Th(SeC_6F_5)_4$ (experimental 400 ppm)[22] and $(bipy)_2Th(SeC_6F_5)_4$ (**4**) (361 ppm) have ^{77}Se resonances in the range expected for eight coordinate structures, consistent with

DFT calculations for $(py)_4Th(SeC_6F_5)_4$ (402 ppm),[15] and in contrast with calculations that predict a significantly upfield shifted resonance for the hypothetical seven coordinate $(py)_3Th(SeC_6F_5)_4$ (490 ppm).[22]

Unfortunately thiolates do not have an equally informative sulfur isotope with which to probe solution conformation. Still, from ^1H NMR data it appears that complex **1** retains some form of asymmetry in solution, as judged by the inequivalence of the bipy and SPh resonances that are split into 8 and 6 distinct peaks respectively, with all resonances broadening and coalescing at elevated temperatures. A rigid eight coordinate Th coordination sphere was also noted in cubane clusters,[23] where exchange between bridging and terminal selenolate ligands was slow on the NMR timescale.

Conclusions

Bipyridine forms bis-chelate compounds with thorium chalcogenolates. Upon isolation, lattice solvent dissociates to leave thermally stable compounds. These compounds are all colored, most likely due to ligand to ligand (ER to bipy) charge transfer, consistent with intermolecular π… π stacking. All bipyridine complexes adopt similar eight coordinate structures, and both fluorinated compounds here exhibit π-π stacking interactions and no dative Th-F bonds. The single terpy product $(terpy)(py)Th(EPh)_4$ similarly forms an eight coordinate product with one py and one terpy coordinating to the Th(IV) center with the four N atoms positioned similar to those of the two bipy ligands in the other four compounds. From the ^{77}Se NMR chemical shifts it is clear that the eight coordinate structures of the Th(ER)$_4$ derivatives are maintained in solution.

Experimental Section

Thorium-232 is a strong alpha-emitter and potentially is a health hazard. Appropriate radioactive and personal safety trainings should be mandatory before reproducing this work.

General Methods. All syntheses were carried out under ultra-pure nitrogen (Welco Praxair), using conventional drybox or Schlenk techniques. Pyridine and tetrahydrofuran (THF) (Aldrich) were purified with a dual column Solv-Tek solvent purification system and collected immediately prior to use. $Se_2(C_6F_5)_2$ [24] and $S_2(C_6F_5)_2$[25] were prepared according to literature procedures. 2.2'-bipyridine (Sigma), terpyridine (Sigma), and PhSeSePh (Aldrich) were purchased and recrystallized from hexanes. PhSSPh (Acros), thorium chips (International Bio-analytical Industries Inc., 3495 North Dixie Hwy.Unit # 8, Boca Raton, FL 33431) and mercury (Strem Chemicals) were purchased and used as received. Melting points were recorded in sealed capillaries and are uncorrected. IR spectra were recorded on a Thermo Nicolet Avatar 360 FTIR spectrometer from 4000 to 450 cm^{-1} as Nujol mulls on CsI plates. UV-Vis absorption spectra were recorded on a Varian DMS 100S spectrometer with the samples dissolved in pyridine, placed in either a 1.0 mm x 1.0 cm Spectrosil quartz cell or a 1.0 cm^2 special optical glass cuvette, and scanned from 190–800 nm. ^{1}H and ^{19}F NMR spectra were obtained at 499.92 and 470.33 MHz, respectively, on a Varian VNMRS 500 spectrometer at 25°C with the compounds dissolved in pyridine-d_5 or toluene-d_8. All ligand peaks were integrated independently of the pyridine peaks at 8.70, 7.55, and 7.18 ppm. Powder X-ray diffraction (PXRD) data were obtained at 20ºC on a Bruker Vantec500 area detector using Rigaku Osmic mirror optics and Cu Kα radiation (λ = 1.5418 Å) from a Nonius 571 rotating-anode generator. The 2D PXRD data were integrated by use of Bruker program GADDS.[26] For the comparisons of experimental[26-27] to calculated[14] PXRD patterns (Fig. S1 – S5), MSI program JADE7[11b] and the wavelength of 1.525 Å were used, the latter to account for the 193 K temperature difference. To confirm that the single crystal sample is consistent with the respective bulk material for each compound, powder samples were isolated and immediately subjected to x-ray powder diffraction, with the PXRD profile then compared with the calculated[14] diffraction profile. Elemental analyses were performed by Quantitative Technologies, Inc. (Whitehouse, NJ). Because these compounds are prone to loss of lattice solvent and coordinated pyridine, elemental analyses are time dependent. Thorium-232 is a strong alpha-emitter and potentially is a health hazard. Appropriate radioactive and personal safety trainings should be mandatory before reproducing this work.

Synthesis of (bipy)$_2$Th(SPh)$_4$ (1). Th (0.232 g, 1.00 mmol), Hg (0.018 g, 0.090 mmol), and PhSSPh (0.437 g, 2.00 mmol) were combined in 20 mL of pyridine (20 mL) and stirred at 25ºC for 3 days to form a white precipitate in a light green solution. The mixture was heated for one hour at 60ºC to dissolve the precipitate and then a pyridine solution of 2,2'-bipyridine (0.312 g, 2.00 mmol in 10 mL of pyridine) was added, resulting in an immediate change in solution color to deep orange. After 30 min the hot solution was filtered, cooled to 25ºC and layered with 20 mL of hexanes to form pale yellow crystals (0.41 g, 33%) that reversibly turn orange at 186°C, melt at 212°C and turn deep red, becoming black and condensing a colorless liquid at the top of the capillary at 319°C. Anal. Calcd for $C_{44}H_{36}N_4S_4Th$: C, 53.9; H, 3.70; N, 5.71. Found: C, 52.8; H, 3.89; N, 5.75. IR: 2926 (w), 1596 (s), 1573 (s), 1457 (w), 1376 (s), 1261 (m), 1240 (s), 1080 (s), 1012 (s), 764 (s), 731 (s), 699 (s), 690 (s) cm^{-1} ^{1}H NMR: 10.55 (d, 2H, J = 6 Hz, bipy), 10.38 (dd, 2H, J = 1, 5.5 Hz, bipy), 8.74 -8.68 (overlapping m, 5H, bipy and py), 7.95 (d, 5H, J = 8.5 Hz, bipy), 7.79-7.67 (overlapping m, 6H, bipy and SPh), 7.55 (m, 1H, py), 7.35-7.29 (m, 4H, bipy), 7.24-7.18 (overlapping m, 4H, bipy, SPh, py), 7.03 (t, 2H, J = 8.5 Hz, SPh), 6.90-6.68 (m, 3H, SPh). Crystallographic details for **1** (see Table S1 for combined details for **1-5**): M = 981.05, Monoclinic, Cc, *a* = 25.426(1)Å, *b* = 25.274(1)Å, *c* = 24.336(1) Å, β = 90.948(2)°, V = 15636.8(13)Å^3, Z = 16, D(calc) = 1.667 g cm^{-3}, T = 100(2)K, μ = 4.066 mm^{-1}, R(int) = 0.0879, N(unique) = 28537, R(F, $I > 2\sigma$) = 0.0522, wR(F^2, $I > 2\sigma$) = 0.1175, CCDC no. 1841858.

Synthesis of $(bipy)_2Th(SePh)_4 \cdot py$ (2). Th (0.232 g, 1.00 mmol), Hg (0.018 g, 0.090 mmol), and PhSeSePh (0.624 g, 2.00 mmol) were combined in pyridine (30 mL) and stirred at 25°C for 5 hours to form a yellow solution. 2,2'-bipyridine (0.312 g, 2.00 mmol) was added and the color changed immediately to deep red. The solution was stirred for an hour at 25°C, filtered and concentrated to 20 mL, layered with hexanes (20 mL), and left for one day to yield orange crystals (0.87 g, 70%) that melt at 186°C and decompose at 304°C. Anal. Calcd for $C_{49}H_{41}N_5Se_4Th$: C, 47.2; H, 3.31; N, 5.61 (lattice-desolvated $C_{44}H_{36}N_4Se_4Th$: C, 45.2; H, 3.10; N, 4.80). Found: C, 45.1; H, 3.43; N, 4.82. IR: 2922 (w), 1658 (s), 1562 (s), 1455 (w), 1377 (m), 1154 (m), 1067 (m), 1013 (s), 755 (s), 723 (s), 691(m) cm^{-1}. ^{1}H NMR: 10.25 (d, 2H, J = 4 Hz, bipy), 8.71 (d, 2H, J = 4 Hz, py, solvent), 7.89 (d, 2H, J = 8 Hz, bipy), 7.78 (overlapping td, J = 1.5, 7.5 Hz, 2H, bipy), 7.74 (overlapping td, J = 2, 7.5 Hz, 2H, py), 7.55 (tt, J = 2, 7.5 Hz, 1H, py, solvent), 7.46 (d, J = 8.5 Hz, 1H, py), 7.34 (overlapping d, 2H, J = 7.5 Hz, SePh), 7.30 (overlapping t, 2H, J = 6.5 Hz, bipy), 7.2 (overlapping dd, 2H, J = 4.5, 7.5 Hz, py), 7.19 (overlapping m, 2H, py, solvent), 6.80 (t, H, J = 7 Hz, SePh), 6.70 (t, 2H, J = 7.5 Hz, SePh). ^{77}Se NMR: 568 (s). Crystallographic details for **2**: M = 1247.75, Monoclinic, P2$_1$/c, a = 20.895(2)Å, b = 9.473(1)Å, c = 22.825(3)Å, β=100.916(1)°, V=4434.5(9)Å^3, Z=4, D(calc)=1.869 g cm^{-3}, T=100(2)K, μ=6.686 mm^{-1}, R(int)= 0.0586, N(unique)=10170, R(F, I > 2σ)=0.0404, wR(F^2, I > 2σ)=0.0879, CCDC no. 1841859.

Synthesis of (bipy)$_2$Th(SC$_6$F$_5$)$_4$· 2THF (3). Th (0.116 g, 0.50 mmol), (SC$_6$F$_5$)$_2$ (0.398 g, 1.00 mmol) and 2,2'-bipyridine (0.156 g, 1.00 mmol) were combined with Hg (0.010 g, 0.05 mmol) in THF (10 mL) and stirred for 24 h at 25°C. The solution was filtered to remove trace grey precipitate, concentrated to 3 mL, and cooled to -30°C to yield colorless crystals (0.31 g, 42%) that melt at 179°C and decompose at 318°C. Anal. Calcd for $C_{52}H_{32}F_{20}O_2N_4S_4Th$: C, 42.1; H, 2.17; N, 3.77 (lattice desolvated $C_{44}H_{16}F_{20}N_4S_4Th$: C, 39.4, H,1.20, N, 4.18). Found: C, 43.2; H, 2.68; N, 4.28. IR: 2924 (m), 2584 (w), 1599 (m), 1500 (w), 1458 (s), 1376 (s), 1162 (w), 1076 (m), 1012 (m), 969 (s), 862 (s), 766 (m), 734 (m), 646 (m), 628 (w) cm^{-1}. ^{1}H NMR (pyridine-d_5): 8.76 (d, 2H, J=5.0Hz, bipy), 8.71 (dt, 2H, J = 8.0, 1.2 Hz, bipy), 7.77 (td, 2H, J = 8.0, 1.5 Hz, bipy), 7.25 (ddd, 2H, J = 7.5, 4.8, 1.3 Hz, bipy), 3.67 (m, 3H, THF), 1.61 (m, 3H, THF). ^{19}F NMR (pyridine-d_5): -132 (m, 2F), -161 (s, 1F), -165 (m, 2F). Crystallographic details for **3**: M

= 1485.09, Monoclinic, C2/c, *a* = 26.247(1)Å, *b* = 12.598(1)Å, *c* = 17.213(1)Å, β=114.189(1)°, V = 5191.9(4)Å^3, Z=4, D(calc) = 1.900 g cm^{-3}, T = 100(2) K, μ=3.153 mm^{-1}, R(int)= 0.0412, N(unique) = 7926, R(F, I > 2σ) = 0.0290, wR(F^2, I > 2σ) = 0.0643, CCDC no. 1841860.

Synthesis of (bipy)$_2$Th(SeC$_6$F$_5$)$_4$ · 2THF (4). Th (0.116 g, 0.50 mmol) and (SeC$_6$F$_5$)$_2$ (0.492 g, 1.00 mmol) were combined with Hg (0.020 g, 0.10 mmol) in pyridine (11 mL). The solution was stirred for 24 h. The solvent was removed under vacuum, 2,2'-bipyridine (0.156 g, 1.00 mmol) and THF (14 mL) were added and the mixture was stirred for 24 h. The resulting red solution was filtered to remove trace greenish precipitate and layered with hexane (10 mL) to form pale yellow (0.77 g, 46%) crystals that turn brown-deep orange at 101°C, melt at 105°C and decompose at 173°C. Anal. Calcd for $C_{52}H_{32}F_{20}O_2N_4Se_4Th$: C, 37.3; H, 1.93; N, 3.35 (lattice desolvated $C_{44}H_{16}F_{20}N_4Se_4Th$: C, 34.6; H, 1.05; N, 3.67). Found: C, 36.7; H, 1.63; N, 3.36. UV-vis: This compound does not show an optical absorption maximum from 400 to 1000 nm. IR: 2957 (s), 2923 (s), 2853 (s), 2361 (w), 1598 (w), 1462 (m), 1376 (m), 1261 (m), 1153 (w), 1081 (m), 1013 (m), 967 (w), 800 (m), 722 (w) cm^{-1}. ^{1}H NMR (pyridine-*d*$_5$): 10.2 (d, 2H, J = 5.0Hz, bipy), 8.47 (dt, 2H, J = 8.5, 1.0 Hz, bipy), 8.21 (td, 2H, J = 7.7, 1.6 Hz, bipy), 7.73 (ddd, 2H, J = 7.5, 5.5, 1.1 Hz, bipy), 3.64 (m, 3H, THF), 1.61 (m, 3H, THF). ^{19}F NMR (pyridine-*d*$_5$): -124 (m, 2F), -161 (s, 1F), -163 (m, 2F). ^{77}Se NMR (pyridine-*d*$_5$): 361 (s). Crystallographic details for **4**: M = 1672.69 , Monoclinic, C2/c, *a* = 26.340(1) Å, *b* = 12.750(1) Å, *c* = 17.396(1) Å, β = 114.296(1)°, V = 5324.7(4) Å^3, Z = 4, D(calc) =

2.087 g cm^{-3}, T = 100(2) K, μ = 5.652 mm^{-1}, R(int) = 0.0357, N(unique) = 8110, R(F, I > 2σ) = 0.0271, wR(F^2, I > 2σ) = 0.0605, CCDC no. 1841861.

Synthesis of (py)(terpy)Th(SPh)$_4$ · 2py (5). Th (0.232 g, 1.00 mmol), and PhSSPh (0.437 g, 2.00 mmol) were combined with catalytic amount of Hg (0.018 g, 0.090 mmol) in pyridine (40 mL) and stirred for 3 days at 25ºC to give a pale yellow solution. 2,2:6,'2"-terpyridine (0.289 g, 1.24 mmol) was added and the color immediately turned to red orange. The solution was filtered to remove trace black powder and concentrated to 20 mL, then layered with 13 mL of hexanes and left for 1 day to yield orange crystals (1.41 g, 87%) that melt at 171°C and decompose at 390°C. Anal. Calcd for $C_{54}H_{46}N_6S_4$ Th: C, 56.9; H, 4.07; N, 7.38 (lattice-desolvated $C_{39}H_{31}N_3S_4Th$:C, 51.9; H, 3.46; N, 4.66). Found: C, 52.9; H, 3.83; N, 5.95. UV-vis: This compound does not show an optical absorption maximum from 400 to 1000 nm. IR: 2957 (w), 1463 (m), 1377 (s), 1260 (s), 1081 (m), 1021 (m), 799 (m), 722 (m) cm^{-1}. ^{1}H NMR (pyridine-*d*$_5$): 10.36 (d, 2H, J=4.5 Hz, terpy), 8.70 (m, 2H, py, solvent), 8.26 (d, 2H, J= 8.0 Hz, terpy), 8.14 (m, 3H, terpy), 7.88 (t, 2H, J = 15, 8 Hz, terpy), 7.56 (m, 1H, py, solvent), 7.36 (t, 2H, J= 6.5, 12 Hz, terpy), 7.26 (d, 2H, J= 7.5 Hz, SPh), 7.20 (m, 2H, py, solvent), 6.81 (t, 2H, J= 7.5, 15 Hz, SPh), 6.75 (m, 1H, SPh). Crystallographic details for **5**: M = 1139.25, Monoclinic, P2$_1$/n, *a* = 15.188(1) Å, *b* = 21.632(1) Å, c = 15.651(1) Å, β = 111.146(1)°, V = 4795.8(5)Å^3, Z = 4, D(calc)= 1.578 g cm^{-3}, T = 100(2)K, μ = 3.328 mm^{-1}, R(int) = 0.0398, N(unique) = 13310, R(F, I > 2σ) = 0.0371, wR(F^2, I > 2σ) = 0.0733, CCDC no. 1841862.

X-ray Structure Determination. Single crystal diffraction data for **1** – **5** were collected on a Bruker APEX CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at low temperatures (see Table S1) using Bruker program SMART.[27b] Crystals were immersed in Paratone oil and immediately placed in the low temperature nitrogen stream. The data were corrected for Lorenz effects and polarization, and absorption, the latter by a numerical method for **3** or by a multi-scan method for **1**, **2**, **4**, and **5** using Bruker program APEX3.[28] The structures were solved by the dual-space algorithm in SHELXT.[29] All non-hydrogen atoms were refined based upon F_{obs}^2 and all hydrogen atom coordinates were calculated with idealized geometries as in SHELXL.[30] Crystallographic data and final R indices for **1** - **5** are given in Table S1. Thermal ellipsoid diagrams for **1** - **5** are shown in Figures 1-5, respectively, and were drawn using CCDC program Mercury.[14] Complete crystallographic details are given in the Supporting Information.

ASSOCIATED CONTENT

Supporting information: X-Ray crystallographic files in CIF format for the crystal structures of **1** – **5**; calculated and observed PXRD profiles for **1-5**. This material is available free of charge via the Internet at www.rsc.org**.**

Conflicts of interest

There are no conflicts to declare.

Acknowledgements:

This material is based upon work supported by the National Science Foundation under CHE – 1464887.

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

Table 1 Selected Inter-atomic and Inter-ligand geometries for **1-5**

Length, Angle, or Torsion[a]	(bipy)$_2$Th(SPh)$_4$ E = S, R = Ph	(bipy)$_2$Th(SePh)$_4$·py E = Se, R = Ph	(bipy)$_2$Th(SC$_6$F$_5$)$_4$·2THF E = S, R = C$_6$F$_5$	(bipy)$_2$Th(SeC$_6$F$_5$)$_4$·2THF E = Se, R = C$_6$F$_5$	(py)(terpy)Th(SPh)$_4$·2py E = S, R = Ph
Th-N (Å)	2.606-2.691	2.620-2.653	2.628-2.631	2.613-2.618	2.598-2.734
Th-E (Å)	2.826- 2.867	2.954-3.015	2.843-2.873	2.970-3.016	2.828-2.848
E'-Th-E (°)	83.9-85.0, 89.2-120.4, 142.4-144.2	65.6-67.8, 98.0-105.5, 143.8-149.1	67.7-67.7, 114.9-128.8, 147.6-147.6	65.0-65.0, 117.7-130.8, 148.6-148.6	67.9-78.2, 91.4-105.6, 143.3-148.2
E-Th-N (°)[b]	10, 63.0 – 87.5	10, 64.7 – 84.9	12, 74.1 – 82.5	12, 74.1 – 82.8	10, 64.4 – 84.9
N'-Th-N (°)[c]	60.9 – 61.7, 106.2 – 108.8	61.4 – 61.8, 83.7	62.4 – 62.4, 115.5	62.7 – 62.7, 113.8	62.4 – 72.5, 62.8
Th-E-C1-C2 (°)[d]	63.0 – 70.0	67.4	84.6	83.2	77.9
	63.6 – 70.2	81.7	82.5	83.8	76.2
	77.9 – 86.2	28.9	84.6	83.2	84.1
	76.5 – 82.2	78.7	82.5	83.8	88.7
twist (°)[e]	40.3, 38.8, 40.7, 41.3	48.8	60.3	57.0	53.0
Th…com (Å)	3.44 – 3.45	3.16, 3.18	3.42, 3.42	3.41, 3.41	3.40, 3.32
com-Th-com (°)	164.5, 164.2, 163.1 164.3	133.2	170.0	170.2	120.0
#, C-H…E (Å)[f]	9-10, 2.70-3.00	6, 2.74 – 2.91	4, 2.77 – 2.78	4, 2.87 – 2.92	8, 2.74 – 2.99
#, C-H…F, N(py) (Å)	n/a	n/a	12, 2.40 – 2.61	12, 2.32 – 2.60	n/a
#, C'…C intra (Å)[g]	4, 3.30 – 3.44	3, 3.09 – 3.28	2, 3.12 – 3.14	2, 3.16 – 3.17	4, 3.11 – 3.26
#, C'…C inter (Å)	8, 3.13 – 3.32	1, 3.37	3.34	3.40	n/a
#, π dihedral intra (°)	4, 1.2 – 3.2	3, 7.6 – 27.1	2, 15.0 – 15.1	2, 7.2 – 8.9	4, 8.2 – 19.5
#, π dihedral inter (°)	8, 11.6 – 26.6	1, 25.7	0.00	0.00	n/a

[a] The ESD values for Th-E related bonds, angles, and torsions are approximately 0.001 Å, 0.02 °, and 0.05 °, respectively.

[b] The number () and values of E-Th-N angles reported here are only for the acute angles.

[c] The first two N-Th-N values are for N atoms in the same bipy ligand; the third is the smallest angle using one N atom from either bipy.

[d] For Th-E-C-C', the atom labeled C' is the closer to Th of the 2- or 6-position atom on the ring; absolute values are listed, and for each E in order

of label.

[e] The “twist” is the interplanar dihedral for the mean planes of the bipy ligands. Pseudo-atom center of mass “com” is the centroid of the bipy (for **5**, the centroid of the N3 and N2 rings and the centroid of the N1 and N4 rings were used).

[f] The number per molecule and range of H…E distances for intra-and inter-molecular H-bonding are for distances less than the corresponding van der Waals radii sum.[21]

[g] The “C’…C” distance is the shortest interatomic distance between pairs of 6-membered rings having a π…π interaction, and the “π,π dihedral” is the angle between those two rings.

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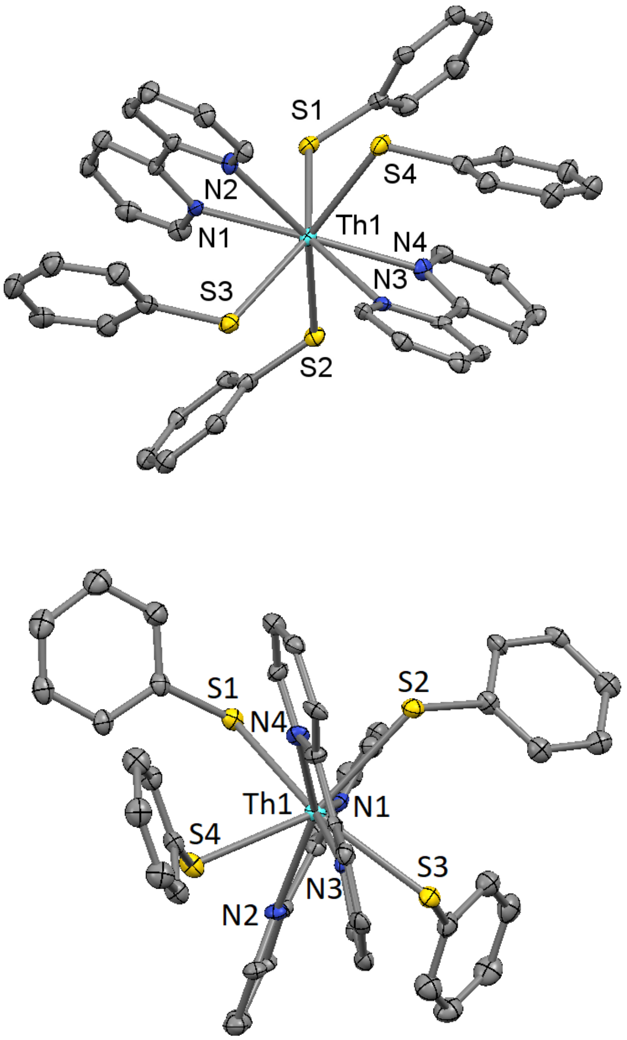


Fig. 1: Thermal ellipsoid diagram of $(bipy)_2Th(SPh)_4$, **1**, with the H atoms removed for clarity and ellipsoids at the 50% probability level. (TOP) View showing distorted square antiprismic coordination; (BOTTOM) view showing nearly regular bicapped trigonal prismic coordination with $\pi\ldots\pi$ interactions evident between the aromatic bipy and SPh groups comprising each trigonal face, namely, N1, N2, and S3 (below the viewing plane), or N3, N4, and S4 (above the viewing plane); capping ligands are the SPh with S1 and S2. Of the four unique molecules in **1**, two are nearly the same and the other two are nearly their inversion mates.

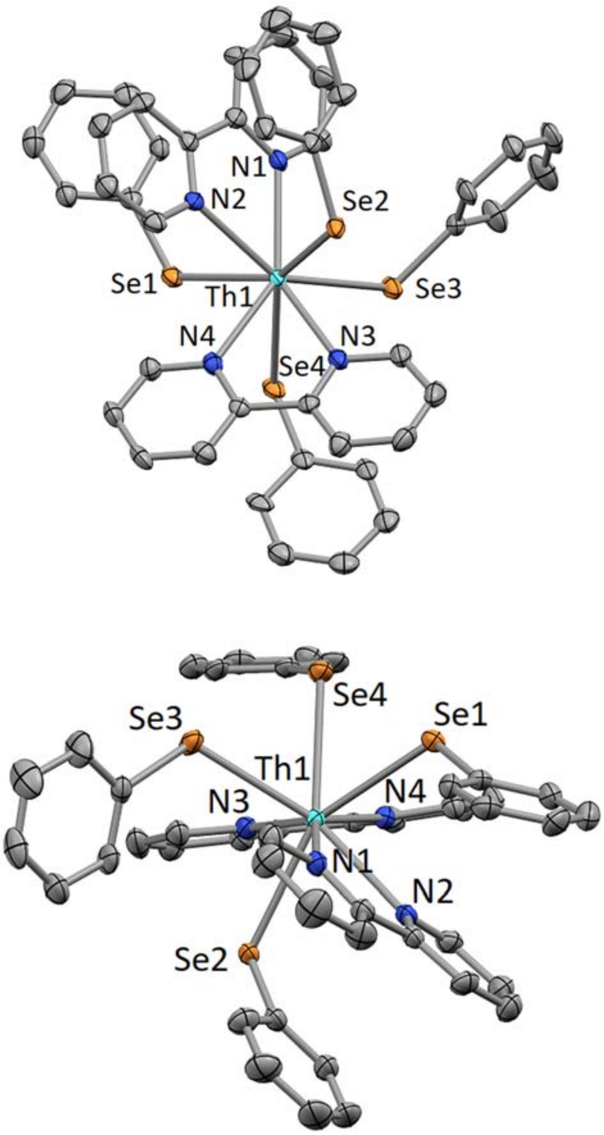


Fig. 2: Thermal ellipsoid diagram of (bipy)$_2$Th(SePh)$_4$, **2**, with the H atoms removed for clarity and ellipsoids at the 50% probability level. (TOP) View showing distorted square antiprismic coordination; (BOTTOM) view showing distorted bicapped trigonal prismic coordination with different connectivity than in **1**; The distortion and connectivity in **2** allow π…π interactions between the aromatic bipy and SePh groups comprising the trigonal faces, namely, N3, N4, and Se4 (below the viewing plane), and N1, N2, and Se2 (above the viewing plane); capping ligands are the SePh with Se3 and Se1, with the latter SePh rotated to provide additional π…π interaction to bipy containing N1 and N2.

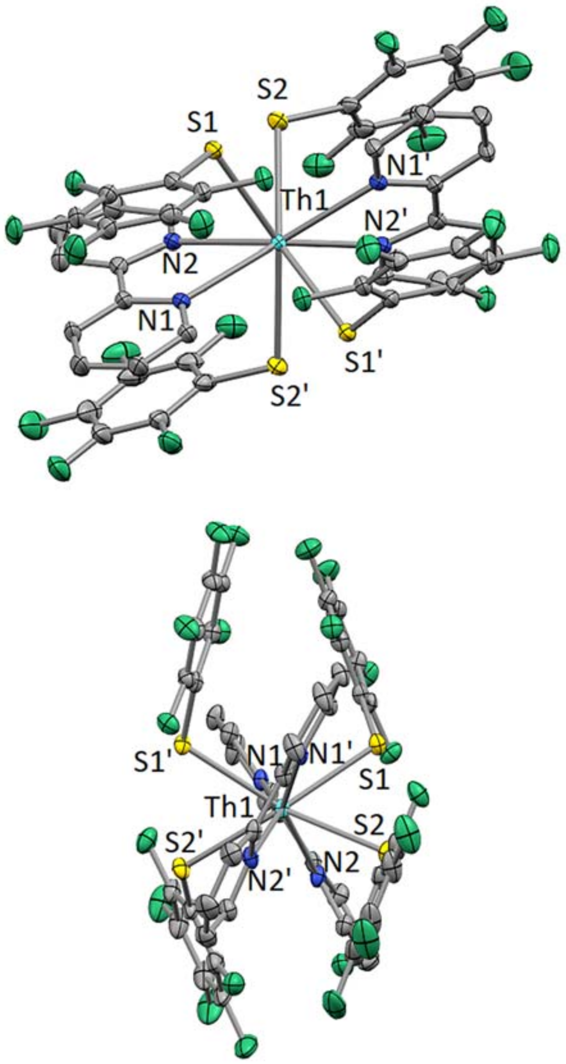


Fig. 3: Thermal ellipsoid diagram of $(py)_3Th(SC_6F_5)_4$, **3**, with the H atoms removed for clarity and ellipsoids at the 50% probability level. Symmetry transformation *-x, y, 1/2-z* used to generate equivalent atoms (primed labels). (TOP) View showing distorted square antiprismic coordination; (BOTTOM) view showing nearly regular bicapped trigonal prismic coordination with more symmetrical connectivity than in **1** due to the crystallographic C_2 site symmetry. The π…π interactions are between the aromatic bipy and SC_6F_5 groups comprising each trigonal face, namely, N1, N2, and S1 (below the viewing plane), or N1', N2', and S1' (above the viewing plane); capping ligands are the SC_6F_5 with S2 and S2', and their aromatic rings are considerably rotated with respect to analogous Ph rings in **1** to yield the maximum number of intramolecular π…π interactions for **3** and **4**.

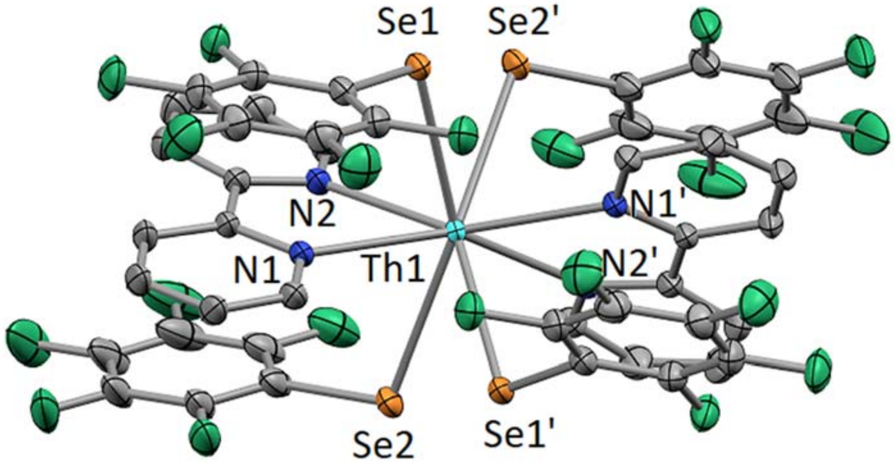


Fig. 4. Thermal ellipsoid diagram of $(py)_4Th(SeC_6F_5)_4$, **4**, with the H atoms removed for clarity and ellipsoids at the 50% probability level. Compound **4** is isomorphous to **3**, with very similar coordination angles, e.g., Se-Th-Se and Se-Th-N, and intramolecular π…π interaction geometries, despite the 0.15 A longer Th-Se bond *versus* Th-S bond, on average.

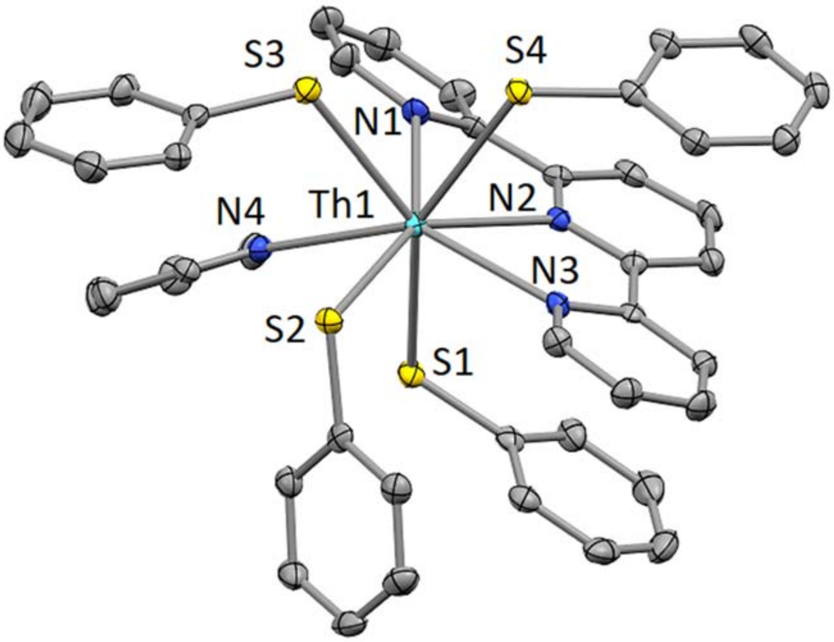


Fig. 5. Thermal ellipsoid diagram of (py)(terpy)Th(SPh_2)$_4$, **5**, with the H atoms removed for clarity and ellipsoids at the 50% probability level. With two narrow adjacent N-Th-N angles, a distorted square antiprism description for **5** appears to be better suited than a bicapped trigonal prism one. Only two intramolecular π…π interactions are found in **5**, involving both sides of the terpy ligand and thiolates with S1 and S4, unlike **1-4**, are located on only one side of the molecule. The rotationally flexible thiolate ligands with S2 and S3 and the py ligand are all available for intermolecular π…π interactions, but only the py ligand appears to have a π…π interaction, and only with a py of solvation (see text).

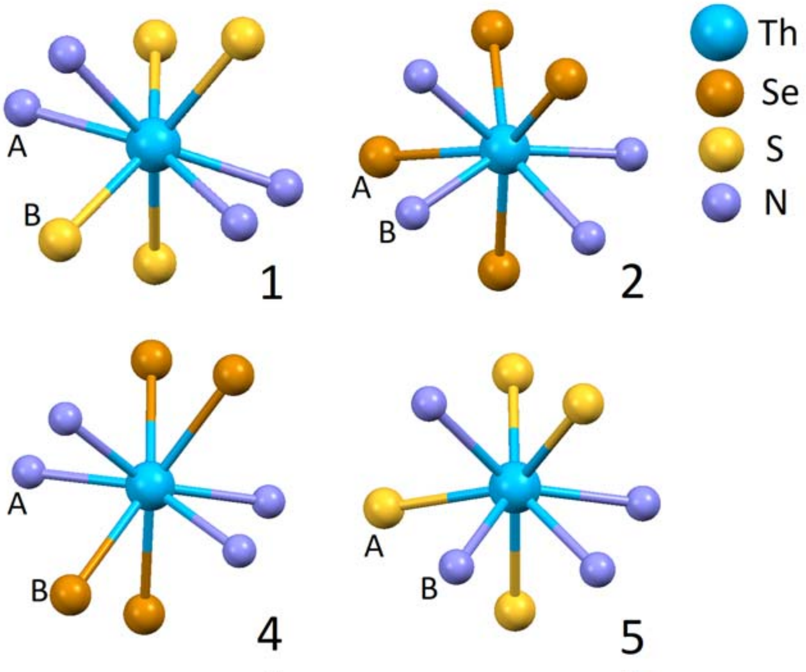
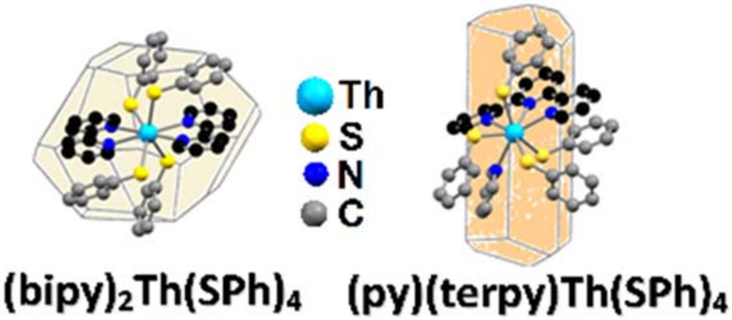


Fig. 6. Ball and stick diagrams of the atoms in the coordination sphere of the title compounds. Compound **3** (not shown) is the S-containing isomorphous analog of **4**. The coordination motifs are very similar in that six of the eight E or N relative positions are essentially the same and the other two, labeled A and B here, are switched in **2** and **5**, with respect to **1** and **4**. This switching has significant consequences for the intra- and intermolecular interactions of the aromatic ring portions of the ligands (see text).

TOC:

Thorium chalcogenolates react with bipyridine or terpyridine to form a series of chelate stabilized Th(ER)$_4$ compounds (E = S, Se; R = Ph, C_6F_5). ^{77}Se NMR shows that the eight coordinate structures are maintained in solution. These compounds are thermochroic, with color originating from a visible ligand to ligand charge transfer excitation.



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