Crystal structure of $[\text{Th}_3(\text{Cp}^*)_3(\text{O})(\text{OH})_3]_2\text{Cl}_2(\text{N}_3)_6$: a discrete molecular capsule built from multinuclear organothorium cluster cations

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An unusually large and structurally complex charge-neutral polynuclear cluster, hexa-$\mu_2$-azido-di-$\mu_3$-chlorido-hexa-$\mu_3$-hydroxido-di-$\mu_3$-oxido-hexakis(pentamethyloclopentadienyl)hexathorium–diethyl ether–tetrahydrofuran (1/0.56/1.44), $[\text{Th}_3(\text{C}_{10}\text{H}_{15})_6\text{Cl}_3(\text{N}_3)_6(\text{OH})_6\text{O}_2]0.56\text{C}_2\text{H}_4\text{O}0.56\text{C}_4\text{H}_{10}\text{O}$ or $[\text{Th}_3(\text{Cp}^*)_3(\text{O})(\text{OH})_3]_2\text{Cl}_2(\text{N}_3)_60.56\text{C}_2\text{H}_4\text{O}0.56\text{C}_4\text{H}_{10}\text{O}$ ($\text{Cp}^* = \text{[pentamethyloclopentadienyl]}^{2-}$), has been crystallized as a mixed tetrahydrofuran/diethyl ether solvate and structurally characterized. The molecule contains a number of unusual features, the most notable being a finite yet exceptionally long cyclic metal-azido chain. These rare features are the consequence of both sterically protecting Cp* ligands and highly bridging oxide and hydroxide ligands in the same system and illustrate the interesting new possibilities that can arise from combining organometallic and solvothermal $f$-block element chemistry.

1. Chemical context

Pentamethyloclopentadienyl ($\text{Cp}^*$) ligands have become almost ubiquitous in the organometallic chemistry of the $f$-block elements (Evans & Davis, 2002). These ligands protect the reactive metal center and allow the solubilization and recrystallization of metal complexes in non-coordinating organic solvents. The actinides in particular have unique chemical properties owing to the participation of $f$-orbital electrons in chemical bonding (Neidig et al., 2013) and the breakdown of periodic trends in the elements due to relativistic electron motion (Cary et al., 2015), making organoactinide chemistry an important frontier in fundamental chemistry. However, the general instability of $f$-element organometallic complexes towards air, moisture, and protic solvents has prevented them from being applied in other areas where $f$-elements have been successfully applied, such as the formation of unique extended structures driven by their unusual coordination polyhedra (Burns & Nyman, 2018; Li et al., 2017; Rocha et al., 2011).

Compared to uranium and the lanthanides, the coordination chemistry of thorium has been surprisingly under-investigated. Of the 55,423 entries in the Cambridge Structural Database [Version 2020.3.0 (November 2020); Groom et al., 2016] containing an $f$-element, only 1,241 contain thorium, and over two-thirds of these have only been reported since 2010. The increased number of Th-containing structures coincides with a renewed interest in actinide chemistry in general, and these
studies have revealed interesting structural features unique to Th-containing compounds such as a strong tendency of Th$^{4+}$ to form high-nuclearity yet discrete molecular complexes and ions (Wilson et al., 2007; Knope et al., 2011; Wacker et al., 2019.)

The title compound of this study was isolated during research using {Th(Cp*)$_2$}-based complexes to study novel organic transformations (Tarlton et al., 2020; Tarlton, Fajen et al., 2021) and actinide–main-group bonding involving Th$^{4+}$ (Tarlton, Yang et al. 2021; Runghanaphatsophon et al., 2018; Vilanova et al., 2017). It represents an unprecedented case of overlap between organothorium chemistry and the formation of polynuclear oxo-bridged clusters. Spontaneous cluster formation in other, oxygen-free complexes of Th$^{4+}$ with tetrel group elements is explored in a second publication as part of this joint special issue (Kelley et al., 2021).

2. Structural commentary

The molecule is a charge-neutral polynuclear metal complex of unusual size and complexity. It can be conceived as being built from two polyatomic cations with the formula [Th$_3$(Cp*)$_3$(O)(OH)$_3$]$^{4+}$, each of which is sandwiched between two terminal Cl$^-$ ions at either end of the molecule and a ring of 6 N$_3$$^-$ anions in the center (Fig. 1). The structure crystallizes in the monoclinic space group $C2/m$ with $Z = 2$. The molecule resides on a crystallographic mirror plane perpendicular to $b$, a crystallographic twofold proper axis parallel to $b$, and the inversion center where the axis and plane coincide, giving the entire molecule exact $C_{2h}$ symmetry. All Th$^{4+}$ centers in the structure are chemically equivalent, and the [[Th$_3$(Cp*)$_3$(O)(OH)$_3$]$^4+$ units have approximate $C_{3v}$ symmetry. The symmetry of the overall molecule is lowered by the arrangements of the N$_3$$^-$ ions, which tilt to differing degrees relative to the twofold axis.

There are no published structures containing a moiety exactly analogous to the [Th$_3$(Cp*)$_3$(O)(OH)$_3$]$^{6+}$ cluster, and published Th–O distances vary extremely widely due to the highly variable coordination geometry of Th$^{4+}$. Another neutral hexanuclear Th$^{4+}$ complex with the formula Th$_4$(O)$_2$(OH)$_2$(CHO$_2$)$_2$(OH$_2$)$_2$ has been reported and shows comparable Th–O$^{2-}$ distances, although the OH$^-$ ligands in this structure bridge three metal centers and have significantly longer bond distances (Takao et al., 2009). A polyatomic anion with the formula [Th$_3$Cl$_{10}$(OH)$_5$(OH$_2$)$_2$]$^{3-}$ is reported, which has the same six-membered cycle of Th$^{4+}$ and μ$^2$-OH$^-$ ligands (but no O$^{2-}$ ligands), and the Th–O distances for these ligands are very similar to those in [Th$_3$(Cp*)$_3$(O)(OH)$_3$]$^{4+}$ (Wacker et al., 2019).

The six Th$^{4+}$ atoms and six azido ligands are bridged into what is essentially a linear chain that has cyclized to form a 24-membered ring, which is the longest non-polymeric metal–azido chain reported. However, cycles with three or four repeat units are quite common, and one example is known for Th$^{4+}$ and has Th–N and azide N–N distances that overlap with those in this structure (Du et al. 2019). It is clear that while most of the individual building blocks within this structure have been observed previously, the unusual features arise from the termination of growth of a Th$^{4+}$ cluster ion by Cp* ligands, leading to very intricate interconnectivity between the metal centers.
3. Supramolecular features

The molecules pack through a herringbone arrangement of the \( \text{Cp}^* \) ligands so that the methyl groups of one \( \text{Cp}^* \) point towards the aromatic ring plane of the neighboring molecules, leading to infinite two-dimensional layers parallel to the \( ab \) face (Fig. 2, left). These layers stack along \( c \) such that the molecules in each layer reside over holes in the neighboring layer, analogous to cubic close packing of spheres (Fig. 2, right); this arrangement most likely reduces repulsion between the like-charged anionic groups at either end of the molecule.

For each molecule of the main moiety there are two solvent molecules of crystallization, which are located in the holes in each layer on the crystallographic mirror planes. These solvent molecules were found to be either tetrahydrofuran (THF) or diethyl ether (Et\(_2\)O) and are substitutionally disordered across the same site; their relative occupancies refined to 72%:28% THF:Et\(_2\)O. Both molecules are positioned such that the ether oxygen atom accepts a hydrogen bond from one of the bridging OH\(^-\) ions (Table 1, Fig. 1).

4. Synthesis and crystallization

The title compound was the byproduct of the reaction of \( (\text{C}_5\text{Me}_5)_2\text{Th}(\text{CH}_3)(\text{Cl}) \), Mes = 2,4,6-Me\(_3\)C\(_6\)H\(_2\), (Rungthanaphatsophon et al., 2018) with two equivalents of Me\(_3\)SiN\(_3\) in dimethoxyethane (DME) at room temperature. After stirring overnight, the resulting solution was allowed to crystallize inside an N\(_2\)-filled glove box at ambient temperature (~3 days). Crystals suitable for SCXRD were obtained by recrystallization of these solids from diethyl ether/tetrahydrofuran. The chloride is presumably due to the starting material, \( (\text{C}_5\text{Me}_5)_2\text{Th}(\text{CH}_3)(\text{Cl}) \), which is used to make \( (\text{C}_5\text{Me}_5)_2\text{Th}(\text{CH}_3)[\text{P}(\text{Mes})(\text{SiMe}_3)] \), while the oxo- and hydroxide ligands are due to an adventitious source of oxygen present in the solvent or glove box.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. The crystal structure was solved by an iterative dual space approach as implemented in SHELXT (Sheldrick, 2015a). All atoms could be refined anisotropically. The residual difference map contained large, chemically unreasonable peaks near the Th atoms which could not be modeled but could be reduced by truncating some of the high-angle data during reduction. The disordered THF and Et\(_2\)O molecules were located from the difference map. For the THF molecule, the oxygen atom and carbon atom C1\(_S\) had their \( y \) coordinates fixed to reside on the crystallographic mirror plane; the other atoms were refined as additionally disordered across both positions related by the mirror plane. All non-hydrogen atoms of the Et\(_2\)O molecule had their \( y \) coordinates fixed to lie on the mirror plane. The chemical occupancy of the THF molecule was fixed to a free variable, which refined to

![Figure 2](image-url)  
*Left:* Packing diagram showing a single two-dimensional layer of molecules, elements are color coded as in Fig. 1. *Right:* Packing diagram showing the CCP-like arrangement of one molecule (red) over the hole formed by four neighboring molecules in the adjacent layer (yellow/blue, all atoms drawn as spheres of vDW radii).
Table 2
Experimental details.

| Parameter                          | Value                        |
|------------------------------------|------------------------------|
| Crystal data                       |                              |
| Chemical formula                   | [Th$_6$(C$_{10}$H$_{15}$)$_6$Cl$_2$(N$_3$)$_6$(OH)$_6$O$_2$]$\cdot$0.56C$_4$H$_8$O$\cdot$1.44C$_4$H$_8$O |
| $M_r$                              | 2804.00                      |
| Crystal system, space group        | Monoclinic, $C2/m$            |
| Temperature (K)                    | 100                          |
| $a$, $b$, $c$ (Å)                  | 7.2587 (14), 7.2647 (14),    |
|                                    | 16.383 (2)                   |
| $\beta$ (°)                        | 121.876 (3)                  |
| $V$ (Å$^3$)                        | 4246.6 (7)                   |
| $Z$                                | 2                            |
| Radiation type                     | Mo K                         |
| $\mu$ (mm$^{-1}$)                  | 10.59                        |
| Crystal size (mm)                  | 0.17 × 0.13 × 0.04           |

Data collection

| Description                          | Details                        |
|--------------------------------------|--------------------------------|
| Diffractometer                      | Bruker VENTURE CMOS area detector |
| Absorption correction               | Multi-scan (AXSPro; Bruker, 2017) |
| $T_{min}$, $T_{max}$                 | 0.233, 0.431                   |
| No. of measured, independent and observed reflections | 46422, 5050, 4393 |
| $R_{int}$                            | 0.071                         |
| $(\sin \theta/\lambda)_{max}$ (Å$^{-1}$) | 0.650                        |

Refinement

| Description                          | Details                        |
|--------------------------------------|--------------------------------|
| $R(F^2 > 2\sigma(F^2))$, $wR(F^2)$, $S$ | 0.027, 0.056, 1.03             |
| No. of reflections                   | 5050                          |
| No. of parameters                    | 307                           |
| No. of restraints                    | 155                           |
| H-atom treatment                    | H atoms treated by a mixture of independent and constrained refinement |

$\Delta \rho_{max}$, $\Delta \rho_{min}$ (e Å$^{-3}$)

3.14, −0.91

Computer programs: APEX3 and SAINT (Bruker, 2017), SHELXT (Sheldrick, 2015a), SHELXL (Sheldrick, 2015b), and OLEX2 (Dolomanov et al., 2009).

72 (1)%, and the chemical occupancies of the THF and Et$_2$O molecules were constrained to sum to 100%. The fractional occupancies of all atoms in both solvent molecules were set to 50% of the chemical occupancies due to their residence on or disorder across a crystallographic mirror plane. Both solvent molecules were also refined with C–C distances restrained to 1.54 (2) Å, C–O distances restrained to 1.41 (2) Å, and all anisotropic displacement parameters among bonded atoms restrained to be equal within an e.s.d. of 0.01 Å$^2$. A hydrogen atom was located from the difference map for the non-hydrogen bonding –OH group, and its coordinates were refined with the O–H distance restrained to 0.84 (2) Å. For the –OH group engaged in the strong hydrogen bond with THF, a hydrogen atom was placed along the ideal O–H...O hydrogen bond vector and restrained to a distance of 0.84 Å from the covalently bonded O atom. The identities of the –OH groups are established on the basis of charge-balance considerations and consistency with Th–O distances in the literature for –OH vs O$^2$– ligands, rather than the location of H atoms from the difference map. All other hydrogen atoms were placed in calculated positions, and were constrained to ride on their carrier atoms. Methyl group hydrogen atoms were refined with a riding-rotating model (except for disordered Et$_2$O methyl groups which were fixed in idealized staggered geometries). For all H atoms, displacement parameters were constrained to be multiples of U$_{eq}$ for the bonded non-hydrogen atom.
Crystal structure of [Th₃(Cp*)₃(O)(OH)₃]₂Cl₂(N₃)₆: a discrete molecular capsule built from multinuclear organothorium cluster cations

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Computing details
Data collection: APEX3 (Bruker, 2017); cell refinement: APEX3 and SAINT (Bruker, 2017); data reduction: APEX3 and SAINT (Bruker, 2017); program(s) used to refine structure: SHELXL (Sheldrick, 2015b); molecular graphics: OLEX2 (Dolomanov et al., 2009); software used to prepare material for publication: OLEX2 (Dolomanov et al., 2009).

Hexa-μ₂-azido-di-μ₃-chlorido-hexa-μ₃-hydroxido-di-μ₃-oxido-hexakis(pentamethylcyclopentadienyl)hexathorium–diethyl ether–tetrahydrofuran (1/0.56/1.44)

Crystal data

| Parameter                                              | Value                                      |
|--------------------------------------------------------|--------------------------------------------|
| [Th₆(C₁₀H₁₅)₆Cl₂(N₃)₆(OH)₆O₂]·0.56C₄H₁₀O·1.44C₄H₈O |                                           |
| M_r = 2804.00                                           |                                            |
| Monoclinic, C2/m                                       |                                            |
| a = 17.6783 (14) Å                                      |                                            |
| b = 17.2647 (14) Å                                     |                                            |
| c = 16.383 (2) Å                                       |                                            |
| β = 121.867 (3)°                                       |                                            |
| V = 4246.6 (7) Å³                                      |                                            |
| Z = 2                                                  |                                            |

Data collection

| Parameter                                              | Value                                      |
|--------------------------------------------------------|--------------------------------------------|
| Bruker VENTURE CMOS area detector diffractometer       |                                            |
| Radiation source: Incoatec IMuS microfocus Mo tube     |                                            |
| shutterless ω and phi scans                            |                                            |
| (AXScale; Bruker, 2017)                                |                                            |
| T_min = 0.333, T_max = 0.431                           |                                            |

Refinement

| Parameter                                              | Value                                      |
|--------------------------------------------------------|--------------------------------------------|
| Refinement on F²                                        |                                            |
| Least-squares matrix: full                             |                                            |
| R[F² > 2σ(F²)] = 0.027                                  |                                            |
| wR(F²) = 0.056                                         |                                            |
| S = 1.03                                               |                                            |
| 5050 reflections                                       |                                            |
| 307 parameters                                         |                                            |
| 155 restraints                                         |                                            |
| Primary atom site location: dual                       |                                            |

Secondary atom site location: difference Fourier map
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement

Hydrogen site location: mixed

| Parameter                                              | Value                                      |
|--------------------------------------------------------|--------------------------------------------|
| w = 1/[σ²(Fo)² + (0.0229P)² + 34.2882P]                 |                                            |
| (Δρ)max = 3.14 e Å⁻³                                   |                                            |
| Δρmin = −0.90 e Å⁻³                                    |                                            |
Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

**Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)**

|  | x     | y     | z     | U(eq)  | Occ. (<1) |
|---|-------|-------|-------|--------|-----------|
| Th1 | 0.68056 (2) | 0.60822 (2) | 0.69358 (2) | 0.01292 (5) |          |
| Th2 | 0.53556 (2) | 0.500000 | 0.75710 (2) | 0.01168 (6) |          |
| Cl1 | 0.73648 (11) | 0.500000 | 0.86411 (11) | 0.0174 (3) |          |
| O1  | 0.5917 (3) | 0.500000 | 0.6566 (3) | 0.0147 (9) |          |
| O2  | 0.7638 (3) | 0.500000 | 0.6957 (3) | 0.0169 (10) |          |
| H2  | 0.809 (3) | 0.500000 | 0.691 (6) | 0.025* |          |
| O3  | 0.5971 (2) | 0.62494 (18) | 0.7689 (2) | 0.0168 (7) |          |
| H3  | 0.563 (6) | 0.663 (4) | 0.748 (7) | 0.025* | 0.5 |
| N1  | 0.4076 (3) | 0.5858 (3) | 0.6357 (3) | 0.0233 (9) |          |
| N2  | 0.3749 (3) | 0.5981 (2) | 0.5529 (3) | 0.0153 (8) |          |
| N3  | 0.3402 (3) | 0.6128 (2) | 0.4715 (3) | 0.0228 (9) |          |
| N4  | 0.5440 (3) | 0.6925 (2) | 0.5842 (3) | 0.0198 (9) |          |
| N5  | 0.500000 | 0.6919 (3) | 0.500000 | 0.0168 (12) |          |
| C1  | 0.8493 (3) | 0.6738 (3) | 0.8077 (4) | 0.0204 (10) |          |
| C2  | 0.8168 (3) | 0.7073 (3) | 0.7160 (3) | 0.0211 (11) |          |
| C3  | 0.7461 (4) | 0.7577 (3) | 0.6962 (4) | 0.0236 (11) |          |
| C4  | 0.7349 (3) | 0.7564 (3) | 0.7756 (3) | 0.0208 (10) |          |
| C5  | 0.7987 (3) | 0.7044 (3) | 0.8442 (3) | 0.0187 (10) |          |
| C6  | 0.9278 (4) | 0.6209 (3) | 0.8601 (4) | 0.0307 (13) |          |
| H6A | 0.918535 | 0.585471 | 0.900768 | 0.046* |          |
| H6B | 0.981731 | 0.651592 | 0.900265 | 0.046* |          |
| H6C | 0.934610 | 0.590903 | 0.813530 | 0.046* |          |
| C7  | 0.8561 (4) | 0.6980 (4) | 0.6544 (4) | 0.0332 (14) |          |
| H7A | 0.884053 | 0.646886 | 0.665711 | 0.050* |          |
| H7B | 0.901031 | 0.738296 | 0.670865 | 0.050* |          |
| H7C | 0.808905 | 0.702819 | 0.586503 | 0.050* |          |
| C8  | 0.6968 (4) | 0.8088 (3) | 0.6087 (4) | 0.0314 (13) |          |
| H8A | 0.675395 | 0.777497 | 0.550602 | 0.047* |          |
| H8B | 0.736905 | 0.849200 | 0.611231 | 0.047* |          |
| H8C | 0.645907 | 0.832931 | 0.607281 | 0.047* |          |
| C9  | 0.6695 (4) | 0.8042 (3) | 0.7866 (4) | 0.0276 (12) |          |
| H9A | 0.611609 | 0.803876 | 0.726080 | 0.041* |          |
| H9B | 0.691318 | 0.857577 | 0.803166 | 0.041* |          |
| H9C | 0.663160 | 0.782241 | 0.837851 | 0.041* |          |
| C10 | 0.8162 (4) | 0.6901 (3) | 0.9437 (4) | 0.0260 (12) |          |
| H10A| 0.762198 | 0.701260 | 0.944310 | 0.039* |          |
| H10B| 0.864643 | 0.723791 | 0.989868 | 0.039* |          |
| H10C| 0.833217 | 0.635783 | 0.961429 | 0.039* |          |
| C11 | 0.4835 (3) | 0.4335 (3) | 0.8752 (3) | 0.0154 (9) |          |
|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| C12 | 0.4289 (4) | 0.500000 | 0.8363 (5) | 0.0171 (14) |   |   |
| C13 | 0.5718 (3) | 0.4589 (3) | 0.9384 (3) | 0.0154 (9) |   |   |
| C14 | 0.4549 (4) | 0.3503 (3) | 0.8574 (4) | 0.0260 (12) |   |   |
| H14A | 0.395664 | 0.346319 | 0.798828 | 0.039* |   |   |
| H14B | 0.452683 | 0.330173 | 0.912070 | 0.039* |   |   |
| H14C | 0.497535 | 0.319910 | 0.849670 | 0.039* |   |   |
| C15 | 0.3290 (5) | 0.500000 | 0.7689 (5) | 0.0279 (17) |   |   |
| H15A | 0.312567 | 0.464474 | 0.715426 | 0.042* | 0.5 |   |
| H15B | 0.308772 | 0.552425 | 0.743913 | 0.042* | 0.5 |   |
| H15C | 0.300794 | 0.483101 | 0.803799 | 0.042* | 0.5 |   |
| C16 | 0.6503 (4) | 0.4080 (3) | 0.9991 (3) | 0.0222 (11) |   |   |
| H16A | 0.705180 | 0.436174 | 1.017657 | 0.033* |   |   |
| H16B | 0.646369 | 0.361634 | 0.962550 | 0.033* |   |   |
| H16C | 0.650705 | 0.392683 | 1.056974 | 0.033* |   |   |
| O2S | 0.962 (2) | 0.500000 | 0.674 (2) | 0.061 (4) | 0.280 (11) |   |
| C5S | 1.055 (2) | 0.500000 | 0.720 (2) | 0.065 (5) | 0.280 (11) |   |
| H5SA | 1.075920 | 0.546619 | 0.701666 | 0.078* | 0.140 (5) |   |
| H5SB | 1.075920 | 0.453381 | 0.701666 | 0.078* | 0.140 (5) |   |
| C6S | 1.091 (3) | 0.500000 | 0.828 (3) | 0.064 (6) | 0.280 (11) |   |
| H6SA | 1.156583 | 0.500000 | 0.864533 | 0.097* | 0.280 (11) |   |
| H6SB | 1.070092 | 0.546347 | 0.844821 | 0.097* | 0.140 (5) |   |
| H6SC | 1.070092 | 0.453653 | 0.844821 | 0.097* | 0.140 (5) |   |
| C7S | 0.923 (2) | 0.500000 | 0.573 (2) | 0.058 (4) | 0.280 (11) |   |
| H7SA | 0.942803 | 0.453573 | 0.554259 | 0.069* | 0.140 (5) |   |
| H7SB | 0.942803 | 0.546427 | 0.554259 | 0.069* | 0.140 (5) |   |
| C8S | 0.822 (2) | 0.500000 | 0.522 (3) | 0.054 (4) | 0.280 (11) |   |
| H8SA | 0.795779 | 0.500000 | 0.452448 | 0.081* | 0.280 (11) |   |
| H8SB | 0.802133 | 0.453653 | 0.540462 | 0.081* | 0.140 (5) |   |
| H8SC | 0.802133 | 0.546347 | 0.540462 | 0.081* | 0.140 (5) |   |
| O1S | 0.8969 (7) | 0.500000 | 0.6553 (7) | 0.050 (2) | 0.360 (5) |   |
| C1S | 0.8526 (10) | 0.500000 | 0.5515 (11) | 0.055 (3) | 0.360 (5) |   |
| H1SA | 0.805267 | 0.539887 | 0.523128 | 0.066* | 0.360 (5) |   |
| H1SB | 0.825386 | 0.448814 | 0.525057 | 0.066* | 0.360 (5) |   |
| C2S | 0.9243 (12) | 0.5179 (12) | 0.5292 (15) | 0.066 (4) | 0.360 (5) |   |
| H2SA | 0.934339 | 0.574303 | 0.528668 | 0.079* | 0.360 (5) |   |
| H2SB | 0.910796 | 0.494664 | 0.467676 | 0.079* | 0.360 (5) |   |
| C3S | 1.0042 (13) | 0.4768 (12) | 0.6179 (14) | 0.067 (4) | 0.360 (5) |   |
| H3SA | 0.998454 | 0.419714 | 0.613336 | 0.080* | 0.360 (5) |   |
| H3SB | 1.062238 | 0.492263 | 0.627273 | 0.080* | 0.360 (5) |   |
| C4S | 0.9910 (10) | 0.510 (2) | 0.6976 (15) | 0.061 (3) | 0.360 (5) |   |
| H4SA | 1.025462 | 0.480111 | 0.758113 | 0.073* | 0.360 (5) |   |
| H4SB | 1.008272 | 0.565129 | 0.710357 | 0.073* | 0.360 (5) |   |

|   |   |   |   |   |   |   |
|---|---|---|---|---|---|---|
| U11 | 0.01355 (9) | 0.01211 (8) | 0.01065 (8) | −0.00232 (6) | 0.00472 (7) | −0.00054 (6) |
| U22 | 0.01279 (12) | 0.01143 (11) | 0.01021 (11) | 0.000 | 0.00567 (9) | 0.000 |

*Atomic displacement parameters (Å²)*

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**Acta Cryst. (2021). E77, 971-974**
|  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|
| Cl1 | 0.0168 (8) | 0.0177 (8) | 0.0122 (7) | 0.000 | 0.0039 (6) | 0.000 |
| O1 | 0.015 (2) | 0.014 (2) | 0.010 (2) | 0.000 | 0.0034 (19) | 0.000 |
| O2 | 0.014 (2) | 0.019 (2) | 0.017 (2) | 0.000 | 0.008 (2) | 0.000 |
| O3 | 0.0188 (18) | 0.0151 (16) | 0.0162 (17) | 0.0004 (13) | 0.0090 (15) | 0.0016 (13) |
| N1 | 0.021 (2) | 0.033 (2) | 0.015 (2) | 0.0002 (17) | 0.0074 (18) | 0.0004 (17) |
| N2 | 0.014 (2) | 0.0136 (18) | 0.017 (2) | 0.0002 (17) | 0.0022 (18) | 0.0013 (16) |
| N3 | 0.019 (2) | 0.021 (2) | 0.011 (2) | 0.0002 (17) | 0.0022 (18) | 0.0013 (16) |
| N4 | 0.018 (3) | 0.012 (3) | 0.019 (3) | 0.000 | 0.008 (3) | 0.000 |
| N5 | 0.019 (3) | 0.018 (2) | 0.022 (3) | −0.007 (2) | 0.009 (2) | −0.0013 (19) |
| C1 | 0.020 (3) | 0.037 (3) | 0.028 (3) | 0.002 (2) | 0.008 (2) | −0.005 (2) |
| C2 | 0.035 (3) | 0.040 (3) | 0.029 (3) | −0.017 (3) | 0.020 (3) | −0.013 (3) |
| C3 | 0.039 (3) | 0.025 (3) | 0.021 (3) | −0.010 (3) | 0.010 (3) | 0.003 (2) |
| C4 | 0.031 (3) | 0.019 (3) | 0.027 (3) | −0.003 (2) | 0.012 (3) | −0.008 (2) |
| C5 | 0.029 (3) | 0.026 (3) | 0.018 (3) | −0.006 (2) | 0.009 (2) | −0.002 (2) |
| C6 | 0.018 (2) | 0.019 (2) | 0.014 (2) | −0.010 (2) | 0.005 (2) | −0.0050 (19) |
| C7 | 0.019 (3) | 0.017 (2) | 0.022 (3) | −0.009 (2) | 0.010 (2) | −0.002 (2) |
| C8 | 0.022 (3) | 0.017 (2) | 0.017 (2) | −0.007 (2) | 0.007 (2) | −0.0037 (19) |
| C9 | 0.018 (2) | 0.019 (2) | 0.014 (2) | −0.010 (2) | 0.005 (2) | −0.0050 (19) |
| C10 | 0.019 (3) | 0.037 (3) | 0.028 (3) | 0.002 (2) | 0.008 (2) | −0.005 (2) |
| C12 | 0.020 (3) | 0.037 (3) | 0.028 (3) | 0.002 (2) | 0.008 (2) | −0.005 (2) |
| C13 | 0.035 (3) | 0.019 (3) | 0.027 (3) | −0.003 (2) | 0.012 (3) | −0.008 (2) |
| C14 | 0.018 (2) | 0.019 (2) | 0.014 (2) | −0.010 (2) | 0.005 (2) | −0.0050 (19) |
| C15 | 0.017 (4) | 0.045 (5) | 0.020 (4) | 0.000 | 0.008 (3) | 0.000 |
| C16 | 0.028 (3) | 0.021 (2) | 0.017 (2) | 0.006 (2) | 0.011 (2) | 0.007 (2) |
| C17 | 0.059 (6) | 0.055 (6) | 0.085 (6) | 0.000 | 0.050 (6) | 0.000 |
| C18 | 0.058 (7) | 0.057 (7) | 0.090 (7) | 0.000 | 0.046 (7) | 0.000 |
| C19 | 0.055 (9) | 0.058 (9) | 0.091 (9) | 0.000 | 0.046 (8) | 0.000 |
| C20 | 0.058 (6) | 0.055 (5) | 0.084 (6) | 0.000 | 0.053 (6) | 0.000 |
| C21 | 0.057 (7) | 0.051 (6) | 0.081 (7) | 0.000 | 0.054 (6) | 0.000 |
| C22 | 0.052 (5) | 0.049 (4) | 0.079 (5) | 0.001 (5) | 0.054 (5) | 0.000 |
| C23 | 0.058 (6) | 0.051 (5) | 0.083 (6) | 0.003 (5) | 0.054 (5) | 0.000 |
| C24 | 0.063 (6) | 0.059 (6) | 0.089 (7) | 0.012 (5) | 0.050 (6) | 0.006 (5) |
| C25 | 0.062 (6) | 0.062 (6) | 0.090 (7) | 0.010 (4) | 0.050 (6) | 0.009 (4) |
| C26 | 0.056 (6) | 0.057 (6) | 0.088 (6) | 0.001 (4) | 0.051 (6) | 0.002 (4) |

**Geometric parameters (Å, °)**

| Distances (Å) | Angles (°) |
|---|---|
| Th1—Cl1 | 3.0589 (12) |
| C10—H10A | 0.9800 |
| Th1—O1 | 2.307 (3) |
| C10—H10B | 0.9800 |
| Th1—O2 | 2.367 (3) |
| C10—H10C | 0.9800 |
| Th1—C1 | 2.791 (5) |
| Th1—N3i | 2.530 (4) |
| Th1—C12 | 1.417 (6) |
| Th1—C13 | 1.500 (7) |
| Th1—N1 | 2.567 (4) |
| Th1—C14 | 1.510 (10) |
| Th1—N2 | 2.816 (5) |
| Th1—C15 | 1.417 (9) |
| Th1—N3 | 2.820 (5) |
| Th1—C16 | 1.493 (7) |
| Th1—C4 | 2.813 (5) |
| Th1—C11 | 1.417 (9) |
| Th1—C17 | 1.500 (7) |
| Th1—C18 | 1.510 (10) |
| Th1—C19 | 1.417 (9) |
| Th1—C20 | 1.493 (7) |
| Th1—C21 | 2.813 (5) |
| Th1—C22 | 1.417 (9) |
| Th1—C23 | 1.493 (7) |
| Th1—C24 | 2.813 (5) |

*Acta Cryst. (2021). E77, 971-974*
| Bond          | Length (Å) | Bond          | Length (Å) |
|--------------|------------|--------------|------------|
| Th1—C5       | 2.787 (5)  | C14—H14B     | 0.9800     |
| Th2—Cl1      | 3.0190 (17)| C14—H14C     | 0.9800     |
| Th2—O1       | 2.329 (4)  | C15—H15A     | 0.9800     |
| Th2—O3       | 2.378 (3)  | C15—H15A     | 0.9800     |
| Th2—O3ii     | 2.378 (3)  | C15—H15B     | 0.9800     |
| Th2—N1       | 2.553 (4)  | C15—H15C     | 0.9800     |
| Th2—N1ii     | 2.553 (4)  | C15—H15C     | 0.9800     |
| Th2—C11      | 2.791 (4)  | C16—H16A     | 0.9800     |
| Th2—C11ii    | 2.791 (4)  | C16—H16B     | 0.9800     |
| Th2—C12      | 2.796 (6)  | C16—H16C     | 0.9800     |
| Th2—C13      | 2.780 (4)  | O2S—C5S      | 1.415 (19) |
| O2—H2        | 0.84 (2)   | O2S—C7S      | 1.411 (19) |
| O3—H3        | 0.84 (2)   | C5S—H5SA     | 0.9900     |
| N1—N2        | 1.180 (5)  | C5S—H5SB     | 0.9900     |
| N2—N3        | 1.165 (5)  | C5S—C6S      | 1.542 (19) |
| N4—N5        | 1.172 (4)  | C6S—H6SA     | 0.9800     |
| C1—C2        | 1.418 (7)  | C6S—H6SB     | 0.9800     |
| C1—C5        | 1.415 (7)  | C6S—H6SC     | 0.9800     |
| C2—C3        | 1.414 (8)  | C7S—H7A      | 0.9900     |
| C2—C7        | 1.505 (7)  | C7S—C8S      | 1.523 (19) |
| C3—C4        | 1.415 (7)  | C8S—H8SA     | 0.9800     |
| C3—C8        | 1.508 (7)  | C8S—H8SB     | 0.9800     |
| C4—C5        | 1.415 (7)  | C8S—H8SC     | 0.9800     |
| C4—C9        | 1.507 (7)  | O1S—C1S      | 1.448 (15) |
| C5—C10       | 1.511 (7)  | O1S—C4S      | 1.435 (15) |
| C6—H6A       | 0.9800     | C1S—H1SA     | 0.9900     |
| C6—H6B       | 0.9800     | C1S—H1SB     | 0.9900     |
| C6—H6C       | 0.9800     | C1S—C2S      | 1.525 (16) |
| C7—H7A       | 0.9800     | C2S—H2SA     | 0.9900     |
| C7—H7B       | 0.9800     | C2S—H2SB     | 0.9900     |
| C7—H7C       | 0.9800     | C2S—C3S      | 1.563 (17) |
| C8—H8A       | 0.9800     | C3S—H3SA     | 0.9900     |
| C8—H8B       | 0.9800     | C3S—H3SB     | 0.9900     |
| C8—H8C       | 0.9800     | C3S—C4S      | 1.551 (17) |
| C9—H9A       | 0.9800     | C4S—H4SA     | 0.9900     |
| C9—H9B       | 0.9800     | C4S—H4SB     | 0.9900     |

O1—Th1—Cl1 | 65.94 (10) | C8—C3—Th1 | 119.6 (3) |
O1—Th1—O2 | 72.32 (13) | C3—C4—Th1 | 75.7 (3)  |
O1—Th1—O3 | 73.33 (13) | C3—C4—C9  | 126.1 (5) |
O1—Th1—N3 | 92.85 (14) | C5—C4—Th1 | 74.3 (3)  |
O1—Th1—N4 | 90.95 (13) | C5—C4—C3  | 107.5 (4) |
O1—Th1—C1 | 147.52 (14)| C5—C4—C9  | 126.3 (5) |
O1—Th1—C2 | 160.60 (14)| C9—C4—Th1 | 117.7 (3) |
O1—Th1—C3 | 164.27 (14)| C1—C5—Th1 | 75.4 (3)  |
| Bond/Angle | Value (deg) |
|------------|------------|
| O1—Th1—C4 | 151.16 (15) |
| O1—Th1—C5 | 143.48 (14) |
| O2—Th1—Cl1 | 66.77 (11) |
| O2—Th1—O3 | 129.52 (12) |
| O2—Th1—N3i | 77.23 (15) |
| O2—Th1—N4 | 143.70 (14) |
| O2—Th1—C1 | 82.76 (14) |
| O2—Th1—C2 | 89.72 (14) |
| O2—Th1—C3 | 118.37 (14) |
| O2—Th1—C4 | 131.14 (14) |
| O2—Th1—C5 | 106.72 (15) |
| O3—Th1—Cl1 | 65.92 (8) |
| O3—Th1—N3i | 140.13 (13) |
| O3—Th1—N4 | 71.49 (12) |
| O3—Th1—C1 | 109.77 (13) |
| O3—Th1—C2 | 125.35 (13) |
| O3—Th1—C3 | 104.02 (14) |
| O3—Th1—C4 | 77.98 (13) |
| N3i—Th1—Cl1 | 142.14 (10) |
| N3i—Th1—C1 | 101.77 (14) |
| N3i—Th1—C2 | 75.63 (14) |
| N3i—Th1—C3 | 79.31 (14) |
| N3i—Th1—C4 | 107.60 (14) |
| N3i—Th1—C5 | 123.06 (14) |
| N4—Th1—Cl1 | 135.67 (10) |
| N4—Th1—C1 | 121.10 (14) |
| N4—Th1—C2 | 99.86 (15) |
| N4—Th1—C3 | 73.69 (14) |
| N4—Th1—C4 | 77.07 (14) |
| N4—Th1—C5 | 105.63 (14) |
| C1—Th1—Cl1 | 85.43 (10) |
| C1—Th1—C2 | 29.29 (14) |
| C1—Th1—C3 | 48.40 (15) |
| C2—Th1—Cl1 | 114.22 (11) |
| C2—Th1—C3 | 29.07 (15) |
| C3—Th1—Cl1 | 127.82 (11) |
| C4—Th1—Cl1 | 104.78 (10) |
| C4—Th1—C2 | 48.11 (15) |
| C5—Th1—Cl1 | 79.97 (10) |
| C5—Th1—C1 | 29.39 (15) |
| C5—Th1—C2 | 48.16 (14) |
| C5—Th1—C3 | 48.03 (14) |
| C5—Th1—C4 | 29.26 (14) |
| O1—Th2—Cl1 | 66.47 (11) |

Note: All angles are given in degrees with standard deviations in parentheses.
| Bond                  | Distance (Å) | Bond                  | Distance (Å) |
|----------------------|--------------|----------------------|--------------|
| O1—Th2—O3           | 73.12 (9)    | C11—C13—C13"        | 108.1 (3)    |
| O1—Th2—O3"          | 73.12 (9)    | C11—C13—C16         | 125.7 (4)    |
| O1—Th2—N1           | 88.99 (13)   | C13—C13—Th2         | 75.23 (9)    |
| O1—Th2—N1"          | 88.99 (13)   | C13—C13—C16         | 126.1 (3)    |
| O1—Th2—C11          | 155.49 (10)  | C16—C13—Th2         | 118.1 (3)    |
| O1—Th2—C11"         | 155.49 (10)  | C11—C14—H14A        | 109.5        |
| O1—Th2—C12          | 166.28 (18)  | C11—C14—H14B        | 109.5        |
| O1—Th2—C13          | 144.28 (14)  | C11—C14—H14C        | 109.5        |
| O1—Th2—C13"         | 144.28 (14)  | H14A—C14—H14B       | 109.5        |
| O3—Th2—C11          | 66.73 (8)    | H14A—C14—H14C       | 109.5        |
| O3—Th2—C11"         | 66.73 (8)    | H14B—C14—H14C       | 109.5        |
| O3—Th2—O3           | 130.25 (16)  | C12—C15—H15A"      | 109.5 (13)   |
| O3—Th2—N1           | 73.53 (13)   | C12—C15—H15A        | 109.5        |
| O3—Th2—N1"          | 140.27 (13)  | C12—C15—H15B        | 109.5 (5)    |
| O3—Th2—C11          | 128.42 (12)  | C12—C15—H15C        | 109.5        |
| O3—Th2—C11"         | 82.80 (12)   | H15A—C15—H15A"     | 77.5         |
| O3—Th2—C11"         | 82.80 (12)   | H15A—C15—H15B       | 109.5        |
| O3—Th2—C12          | 110.75 (9)   | H15A—C15—H15C       | 109.5        |
| O3—Th2—C12"         | 110.75 (9)   | H15B—C15—H15A"     | 34.6         |
| O3—Th2—C13          | 107.88 (12)  | H15B—C15—H15B       | 109.5        |
| O3—Th2—C13"         | 107.88 (12)  | H15B—C15—H15C"     | 109.5        |
| O3—Th2—C13"         | 81.05 (12)   | H15A—C15—H15C"     | 134.9        |
| O3—Th2—C13"         | 81.05 (12)   | H15B—C15—H15A"     | 34.6         |
| O3—Th2—C13"         | 107.88 (12)  | H15B—C15—H15B"     | 134.9        |
| N1—Th2—C11          | 137.70 (10)  | H15B—C15—H15C"     | 109.5        |
| N1—Th2—C11"         | 137.70 (10)  | H15B—C15—H15C"     | 109.5        |
| N1—Th2—N1           | 70.9 (2)     | H15B—C15—H15C"     | 77.5         |
| N1—Th2—C11          | 107.32 (14)  | H15C—C15—H15A"     | 134.9        |
| N1—Th2—C11"         | 107.32 (14)  | H15C—C15—H15B"     | 77.5         |
| N1—Th2—C11"         | 79.65 (13)   | H15C—C15—H15C"     | 34.6         |
| N1—Th2—C11"         | 79.65 (13)   | C13—C16—H16A        | 109.5        |
| N1—Th2—C12          | 79.86 (15)   | C13—C16—H16B        | 109.5        |
| N1—Th2—C12"         | 79.86 (15)   | C13—C16—H16C        | 109.5        |
| N1—Th2—C13          | 107.11 (14)  | H16A—C16—H16B       | 109.5        |
| N1—Th2—C13"         | 126.15 (13)  | H16A—C16—H16C       | 109.5        |
| N1—Th2—C13"         | 126.15 (13)  | H16B—C16—H16C       | 109.5        |
| N1—Th2—C13"         | 107.11 (13)  | C7S—O2S—C5S         | 109 (3)      |
| C11—Th2—C11         | 108.35 (10)  | O2S—C5S—H5SA        | 110.7        |
| C11—Th2—C11"        | 108.35 (10)  | O2S—C5S—H5SB        | 110.7        |
| C11—Th2—C11"        | 48.60 (19)   | O2S—C5S—C6S         | 105 (3)      |
| C11—Th2—C12         | 29.38 (12)   | H5SA—C5S—H5SB       | 108.8        |
| C11—Th2—C12"        | 29.38 (12)   | C6S—C5S—H5SA        | 110.7        |
| C12—Th2—C11         | 127.25 (14)  | C6S—C5S—H5SB        | 110.7        |
| C12—Th2—C11"        | 80.94 (10)   | C5S—C6S—H6SA        | 109.5        |
| C13—Th2—C11         | 80.94 (10)   | C5S—C6S—H6SB        | 109.5        |
| C13—Th2—C11"        | 29.39 (13)   | C5S—C6S—H6SC        | 109.5        |
C13—Th2—C11ii 48.59 (13) H6SA—C6S—H6SB 109.5
C13ii—Th2—C11 48.59 (13) H6SA—C6S—H6SC 109.5
C13ii—Th2—C11ii 29.39 (13) H6SB—C6S—H6SC 109.5
C13—Th2—C12 48.39 (16) O2S—C7S—H7SA 109.6
C13—Th2—C12 48.39 (16) O2S—C7S—H7SB 109.6
C13iii—Th2—C13 29.54 (18) O2S—C7S—C8S 110 (3)
Th1—C11—Th1 75.30 (4) H7SA—C7S—H7SB 108.1
Th2—C11—Th1 75.86 (3) C8S—C7S—H7SA 109.6
Th2—C11—Th1ii 108.19 (18) C7S—C8S—H7SA 109.5
Th1—O1—Th1ii 107.42 (12) C7S—C8S—H7SB 109.5
Th1—O1—Th2 107.42 (12) C7S—C8S—H8SC 109.5
Th1—O1—Th2 107.42 (12) C7S—C8S—H8SC 109.5

Hydrogen-bond geometry (Å, °)

| D—H⋯A       | D—H  | H⋯A  | D⋯A     | D—H⋯A   |
|-------------|------|------|---------|---------|
| O2—H2⋯O1S   | 0.84 (2) | 1.93 (3) | 2.762 (10) | 170 (8) |

Symmetry codes: (i) −x+1, y, −z+1; (ii) x, −y+1, z.