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[Tb₄(OH)₄]-Cuboid Complex Dianion Stabilized with Six Carboxylate Bridges and Four Diketonate Caps

Yoshiki Yamaguchi and Takayuki Ishida * 

Department of Engineering Science, The University of Electro-Communications, Chofu, Tokyo 182-8585, Japan; yamaguchi@ttf.pc.uec.ac.jp

* Correspondence: takayuki.ishida@uec.ac.jp

Abstract: A cubane-like complex dianion [Tb₄(OH)₄(tfa)₆(hfac)₄]^{2−} was synthesized, accompanied by two counter cations of [Ni(hfac)(2pyIN)₂]⁺, where Htfa, Hhfac, and 2pyIN stand for trifluoroacetic acid, 1,1,1,5,5,5-hexafluoropentane-2,4-dione, and 4,4,5,5-tetramethyl-2-pyridylimidazolin-1-oxyl, respectively. In the complex anion, each Tb ion was capped with hfac, and each Tb⋯Tb diagonal was bridged with tfa, thus forming an approximate *Td* symmetry, though the whole molecular formula was crystallographically independent in an orthorhombic *Pbca* space group. The ionic charge was −2 in total. The magnetic study revealed that the complex ions were magnetically isolated from each other. Practically no 4f–4f superexchange interaction was operative, while the 2p–3d ferromagnetic coupling seemed to be appreciable, as anticipated from the proposed magnetostructural relationship.

Keywords: rare earth metal; lanthanide; lanthanoid; molecular magnetism; magnetic properties; ferromagnetic coupling



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1. Introduction

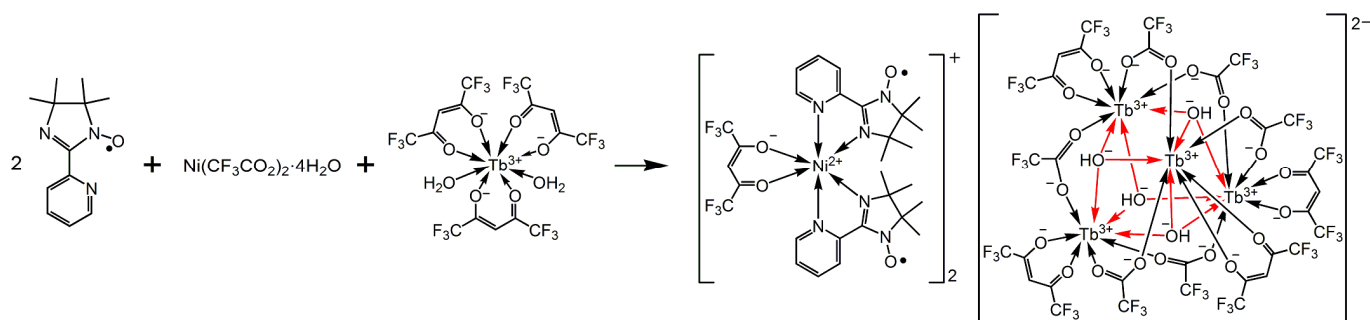
Heterospin magnetic materials are fascinating to researchers because of the wide variety of symmetries and energy levels of the paramagnetic centers available from the viewpoint of frontier-orbital engineering [1–12]. Lanthanide ions, as a 4f spin source, have a large magnetic moment and strong magnetic anisotropy, and become indispensable in the development of conventional bulk magnets as well as recently exploited single-molecule magnets (SMMs) [4]. As a working hypothesis to construct exchange-coupled clusters and networks, plausible magneto-structure correlations have been proposed for 2p–3d [5–7], 3d–4f [8,9], and 2p–4f [10–12] heterospin systems. There are an increasing number of reports describing 2p–3d–4f triad systems [13–17]. Hopefully, these paramagnetic centers would be better strongly exchange-coupled, because the resultant large total spin quantum number is favorable for SMM performance.

Lanthanide ions usually behave as a hard acid compared with transition-metal ions, which exhibit a soft nature [18]. Upon such selectivity, a simple synthesis has widely been applied, where the 2p, 3d, and 4f spin sources are mixed in a one-pot manner [13–17]. During our development on 2p–3d–4f heterospin magnets, we have found a cubane-like complex dianion [Tb₄(OH)₄(tfa)₆(hfac)₄]^{2−}, accompanied by two counter cations of [Ni(hfac)(2pyIN)₂]⁺ in a crystal lattice. Here, Htfa and Hhfac stand for trifluoroacetic acid and 1,1,1,5,5,5-hexafluoropentane-2,4-dione, respectively. Carbonyl compounds are often available as an antenna in luminescent materials [19,20]. The 2pyIN radical (4,4,5,5-tetramethyl-2-pyridylimidazolin-1-oxyl or 2-pyridyl iminonitroxide) [21] is popular in the metal-radical approach. We will describe the molecular/crystal structure and magnetic properties of the product. The formation of cubane-like clusters is not so astonishing since various oxo- and hydroxo-bridged metal clusters have been developed, but a highly symmetric architecture and dianionic valence is rare in the lanthanide cubane-like chemistry, to our knowledge.

2. Materials and Methods

2.1. Preparation

The complex formation was conducted according to the method for the known lanthanide–nitroxide complexes [22,23] with a slight modification. A heptane solution (20 mL) including $[\text{Tb}(\text{hfac})_3(\text{H}_2\text{O})_2]$ [24,25] (40.3 mg; 0.049 mmol) was refluxed and concentrated to ca. 2 mL. Similarly, another heptane suspension (20 mL) including $\text{Ni}(\text{CF}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}$ (Wako, 19.3 mg; 0.054 mmol) was refluxed and concentrated to ca. 2 mL. The above solution and suspension were cooled to ca. 40 °C and poured into a dichloromethane solution (1.5 mL) including 2pyIN [19] (21.7 mg; 0.10 mmol). Immediately, the combined solution was filtered, and the filtrate was allowed to stand in a freezer (−22 °C). After 3 days, $[\text{Ni}(\text{hfac})(2\text{pyIN})_2]_2[\text{Tb}_4(\text{OH})_4(\text{tfa})_6(\text{hfac})_4](\text{C}_7\text{H}_{16})_x$ (abbreviated as **1** hereafter) as orange polycrystalline precipitates were separated on a filter, washed with heptane, and air-dried (Scheme 1). The yield was 18.1 mg (40%). Mp 148–150 °C. Anal. (PerkinElmer 2400 II, PerkinElmer Inc., Waltham, MA, USA). Calcd. for $\text{C}_{97}\text{H}_{90}\text{F}_{54}\text{N}_{12}\text{Ni}_2\text{O}_{32}\text{Tb}_4$ ($x = 1$): C, 31.36%; H, 2.44%; N, 4.52%. Found: C, 31.42%; H, 1.25%; N, 4.72%. IR (neat, attenuated total reflection (Nicolet FT-IR 6700, Thermo Scientific, Waltham, MA, USA)) 3578, 1688, 1652, 1555, 1497, 1347, 1253, 1200, 1138, 1098, 794, 662, 583 cm^{-1} .



Scheme 1. Synthesis of **1**. Red arrows depict the coordination bonds in the cubane-like skeleton.

2.2. Structural Analysis

X-Ray diffraction data of a single crystal of **1** were collected on a Saturn 70 hybrid pixel array detector (Rigaku, Tokyo, Japan) with graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by a heavy-atom method and expanded using Fourier techniques in the Olex2 program [26]. The parameters were refined on Shelxl [27]. The thermal displacement parameters of non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and treated as “riding”. A disorder model was applied to four trifluoromethyl groups. Considerable residual electron densities were found in a void space, and solvent heptane molecules could not be placed, possibly owing to severe disorder. A “squeeze” treatment [28] was applied to 183 residual electrons in a void space of 1016 Å³ per asymmetric cell, corresponding to three heptane molecules as a solvent mask. Selected data are as follows: $\text{C}_{111}\text{H}_{122}\text{F}_{54}\text{N}_{12}\text{Ni}_2\text{O}_{32}\text{Tb}_4$, orthorhombic $Pbca$, $a = 32.1908(6)$, $b = 29.0734(5)$, $c = 32.2901(6)$ Å, $V = 30220.1(9)$ Å³, $Z = 8$, $d = 1.721$ g cm^{−3}, $\mu(\text{MoK}\alpha) = 2.228$ mm^{−1}, $R(F)$ ($I > 2\sigma(I)$) = 0.0526, $wR(F^2)$ (all reflections) = 0.1185, goodness-of-fit parameter = 0.976, $T = 96$ K for 41279 reflections. For experimental details and geometrical parameter tables, see CCDC reference number 2153576.

2.3. Magnetic Measurements

Direct and alternating current (dc and ac, respectively) magnetic susceptibilities of **1** were measured on MPMS-XL7 and MPMS3 SQUID magnetometers (Quantum Design Inc., San Diego, CA, USA). For the dc measurements, the magnetic responses were corrected with diamagnetic blank data of the sample holder measured separately, and further diamagnetic contribution was estimated from Pascal’s constants [29].

3. Results and Discussion

Compound **1** was prepared from the starting materials $[\text{Tb}(\text{hfac})_3(\text{H}_2\text{O})_2]$, $\text{Ni}(\text{CF}_3\text{CO}_2)_2$, and 2pyIN in a one-pot manner. The product was stable under ambient conditions, but the crystal solvent molecules incorporated escaped easily from the crystal lattice. The composition was confirmed to be $[\text{Ni}(\text{hfac})(2\text{pyIN})_2]_2[\text{Tb}_4(\text{OH})_4(\text{tfa})_6(\text{hfac})_4]$ by means of spectroscopic, analytic, and X-ray diffraction analyses. The single-crystal X-ray diffraction study clarified that the space group was orthorhombic *Pbca* with a whole formula unit crystallographically independent (Figure 1a). Considerable residual electron densities were found in a void space in a lattice, being ascribable to heptane. The complex cations and anions were discrete and accordingly seem to be magnetically isolated from each other. On the other hand, the Ni^{2+} ion and 2pyIN ligands must be magnetically correlated because of the direct metal–radical coordination bonds (see below).

As Figure 1b shows, the anionic portion has a tetranuclear Tb^{3+} cage cluster in **1**. Each Tb^{3+} ion is coordinated with three OH^- ions, and each OH^- ion plays the role of a tripodal bridge, forming a cube-like structure. The intra-cuboid $\text{Tb}-\text{O}$ bond lengths varied from 2.329(3) to 2.429(3) Å, the $\text{Tb}-\text{O}-\text{Tb}$ angles from 105.06(11) to 108.67(11)°, and the $\text{O}-\text{Tb}-\text{O}$ angles from 69.04(10) to 71.47(10)°. Thus, the cubane-like cluster was considerably distorted with the wider $\text{Tb}-\text{O}-\text{Tb}$ angles and narrower $\text{O}-\text{Tb}-\text{O}$ angles, compared to 90°. The peripheral ligands were characterized as follows: each Tb^{3+} ion was capped with an hfac anion, and every $\text{Tb}\cdots\text{Tb}$ diagonal was bridged with a tfa anion. Several tfa-bridged lanthanide complexes are known in the literature [30]. Thus, the tetra(μ_3 -hydroxo)- and hexa($\mu\text{-}\eta^2(\text{O},\text{O}')\text{-tfa}$)-bridged structure in **1** can be regarded as an approximate *Td* symmetry. The Tb^{3+} ions are eight-coordinate, and the SHAPE analysis [31] indicates that the TbO_8 coordination spheres are best described as a triangular dodecahedron (TDD-8). Hydrogen bonds were found between the anion and cation moieties; the $\text{O}\cdots\text{O}$ distances were 2.991(5) and 2.918(4) Å for $\text{O2}-\text{H2}\cdots\text{O25}$ and $\text{O4}-\text{H4}\cdots\text{O29}$, respectively. Such interactions brought about an L-shaped cation–dianion–cation arrangement, and the resultant bulkiness seems to afford a void space in a crystal lattice, where the crystal solvent molecules were incorporated.

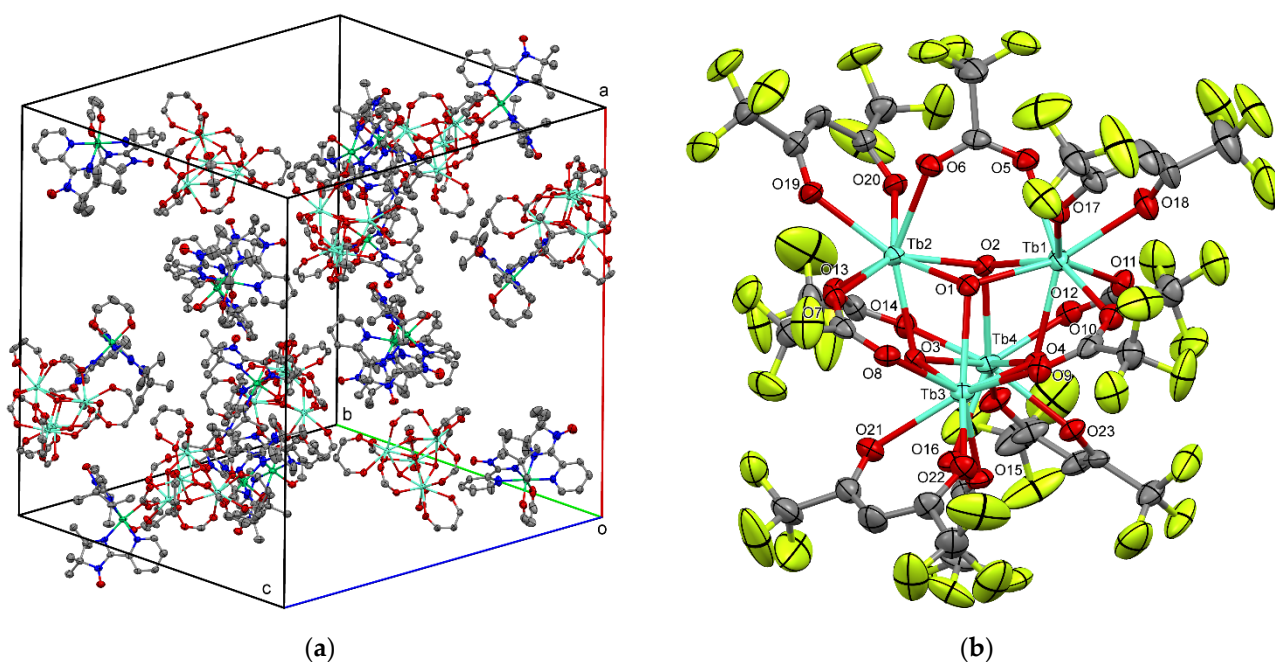


Figure 1. Cont.

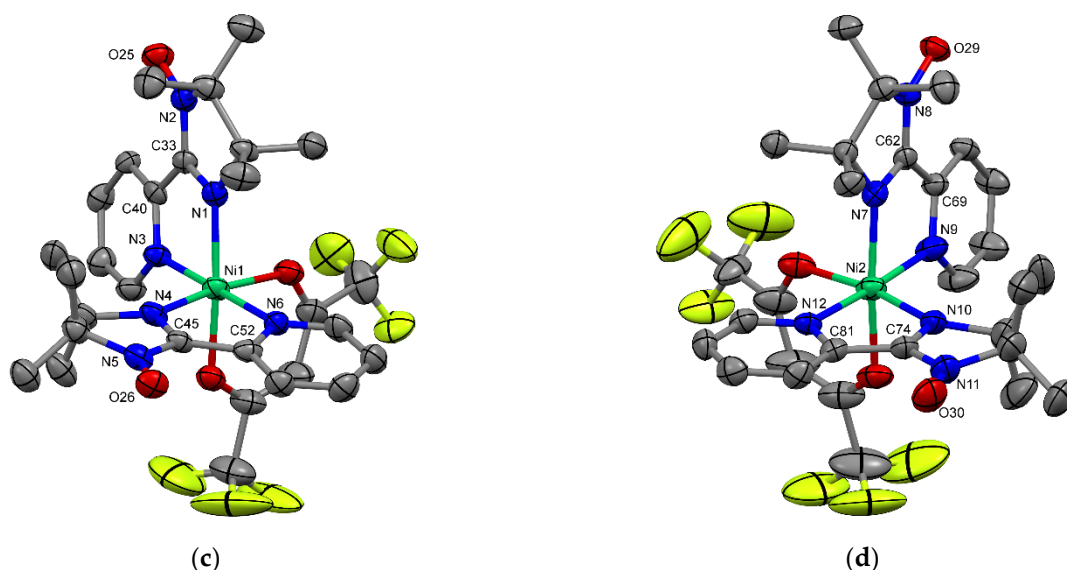


Figure 1. (a) X-ray crystal structure of **1**. Trifluoromethyl groups, hydrogen atoms, and disordered solvent molecules are omitted for the sake of clarity. (b) The dianionic $[\text{Tb}_4(\text{OH})_4(\text{tfa})_6(\text{hfac})_4]^{2-}$ portion and (c,d) two cationic $[\text{Ni}(\text{hfac})(2\text{pyIN})_2]^+$ portions in the crystal of **1**. Only a major conformer is drawn for disordered trifluoromethyl groups, and hydrogen atoms are omitted for clarity in (b–d). The thermal ellipsoids are drawn at the 50% probability level. The atomic color codes are: C, black; O, red; N, blue; F, yellow; Tb, turquoise; Ni, green.

The $[\text{Tb}_4(\text{OH})_4]^{8+}$ core in **1** was similar to that of the known lanthanide cuboids [32–35]. A possible formation mechanism has already been discussed elsewhere [35]. In comparison with the known compounds, it should be noted that the present complex had peripheral ligands located in a highly symmetrical manner. Furthermore, a dianionic valence of the cuboidal complex ion is rather rare.

As for the cation moiety of **1** (Figure 1c,d), we can find two 2pyIN chelate rings around the Ni^{2+} ($3d^8$) ion. The $\text{C}_{2\text{py}}\text{--}\text{C}_{2\text{im}}\text{--}\text{N}\text{--}\text{Ni}$ torsion angle, ϕ , is proposed to be a convenient metric to assess magnetostructural relationship. The torsion angles were $1.1(6)$, $1.7(6)$, $-2.5(6)$, and $0.7(5)^\circ$ around the $\text{C}40\text{--}\text{C}33\text{--}\text{N}1\text{--}\text{Ni}1$, $\text{C}52\text{--}\text{C}45\text{--}\text{N}4\text{--}\text{Ni}1$, $\text{C}69\text{--}\text{C}62\text{--}\text{N}7\text{--}\text{Ni}2$, and $\text{C}74\text{--}\text{C}81\text{--}\text{N}12\text{--}\text{Ni}2$ bonds, respectively. These small torsions guarantee the absence of $d_{z^2}/d_{x^2-y^2}\text{--}\pi^*$ orbital overlap. A closely related $2p/3d = 1/1$ complex $[\text{Ni}(\text{hfac})_2(2\text{pyIN})]$ was reported to display orthogonal $d\text{--}\pi^*$ orbital arrangement and ferromagnetic coupling [36]. According to the magnetostructural relationship, the critical $|\phi_C|$, where the exchange coupling alters from ferro- to antiferromagnetic, was reported to be $12.8(8)^\circ$ for the Cu^{2+} and Ni^{2+} compounds [7] and $21(1)$ or $26(3)^\circ$ for the Ni^{2+} compounds [37]. We can safely predict that the $[\text{Ni}(\text{hfac})(2\text{pyIN})_2]^+$ portions in **1** should behave as a ground quintet species.

Figure 2a displays the dc magnetic susceptibility result on **1**. A relatively temperature-insensitive character appeared, indicating that each complex ion was magnetically isolated from each other. This finding also implies that the Tb–O–Tb superexchange coupling was negligible. At 300 K, the $\chi_m T$ value was $50.5 \text{ cm}^3 \text{ K mol}^{-1}$, in good agreement with the theoretical value $50.7 \text{ cm}^3 \text{ K mol}^{-1}$ expected from the sum of four Tb^{3+} ions ($11.81 \text{ cm}^3 \text{ K mol}^{-1}$ each with the angular moment $J = L + S = 6$ and the Landé factor $g_J = 3/2$), two Ni^{2+} ions ($1.00 \text{ cm}^3 \text{ K mol}^{-1}$ each), and four radicals ($0.375 \text{ cm}^3 \text{ K mol}^{-1}$ each). On cooling, the $\chi_m T$ value gradually decreased and reached $45.6 \text{ cm}^3 \text{ K mol}^{-1}$ at 1.8 K, and this profile can partly be explained in terms of depopulation effect regarding the J^z sublevels in the Tb^{3+} ion. Such a lanthanide single-ion property sometimes disturbs exchange coupling analysis. In the present case, the $2p\text{--}3d$ interaction in the cation portions could not be evaluated.

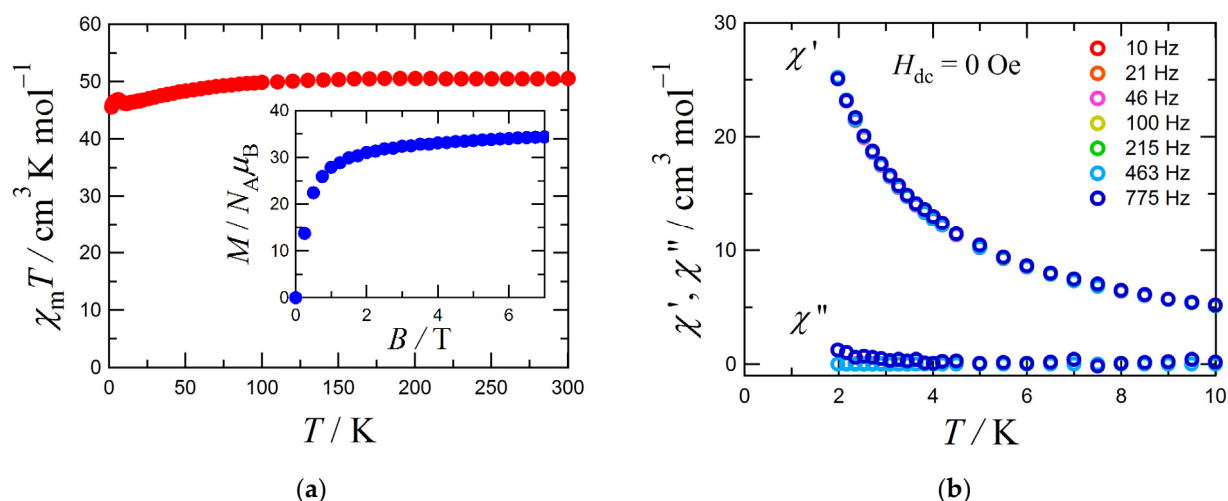


Figure 2. (a) The $\chi_m T(T)$ plot for **1**, measured at 500 Oe. The polycrystalline sample was fixed with a small amount of eicosane. Inset: the $M(H)$ plot for **1**, measured at 1.8 K. The sample was not fixed. (b) Ac magnetic susceptibilities for **1** without any applied dc field.

The $M-H$ curve (Figure 2a, inset) displays a positive slope even at 7 T, and the magnetization ($34.4 N_A \mu_B$ at 7 T and 1.8 K when the sample was unfixed) was lower than the theoretical maximum value $44 N_A \mu_B$, mainly because of the strong magnetic anisotropy of the Tb^{3+} moment.

Figure 2b shows the in-phase (χ') and out-of-phase parts (χ'') of the molar ac magnetic susceptibilities for **1**, measured in no dc bias field. In further experiments with applied fields of 1000 and 2000 Oe, no appreciable χ'' was recorded either. There have been several reports on Dy-based SMMs including $Dy_4(OH)_4$ cuboids [33]. The Kramers theorem suggests that Dy^{3+} ion has a double-well potential surface suitable for SMMs but Tb^{3+} ion does not [38,39]. After combining the results of the Tb_4 - and Dy_4 -based cuboids, the single-ion magnetic property of Tb^{3+} and Dy^{3+} seems to regulate the whole molecular magnetism. This conclusion is compatible with the negligible 4f–4f coupling in the cuboid.

4. Conclusions

A dianionic cuboidal complex ion $[Tb_4(OH)_4(tfa)_6(hfac)_4]^{2-}$ was synthesized, accompanied by two counter cations of $[Ni(hfac)(2pyIN)_2]^+$ in a crystal lattice. In the complex anion, each Tb ion is capped with hfac and bridged with tfa in a highly symmetrical manner. The magnetic study revealed that the complex ions were magnetically isolated and that the Tb–O–Tb superexchange coupling was negligible, although the 2p–3d–4f heterospin material was realized. Building upon the present architectural study, the use of a wide diversity of carboxylates and diketonates will be of interest to supramolecular chemistry involving a lanthanide cuboid building block.

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Data Availability Statement: CCDC reference number 2153576 contains the supplementary crystallographic data for **1**. These data are provided free of charge by the Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/structures (accessed on 21 February 2022).

Conflicts of Interest: The authors declare no conflict of interest.

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