**MOFs by Transformation of 1D-Coordination Polymers II:
The Homoleptic Divalent Rare Earth 3D-Benzotriazolate
 $^3_{\infty}[\text{Eu}(\text{Btz})_2]$ Initiating from $^1_{\infty}[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$**

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The Homoleptic Divalent Rare Earth 3D-Benzotriazolate ${}^3[\text{Eu}(\text{Btz})_2]$ Initiating from ${}^1[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$

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Dedicated to Professor Bernd Harbrecht on the Occasion of his 60th Birthday

Received...

Abstract. The solvent free reaction route produces coordination polymers that have a dimensionality of the linkage which is increasing with the thermal energy. The synthesis of the 3D MOF structure ${}^3[\text{Eu}(\text{Btz})_2]$ marks the final thermal reaction step within the system europium/1*H*-1,2,3-benzotriazole. It can be obtained by a reaction of the metal with a melt of benzotriazole above 230 °C or from thermal treatment of the 1D coordination polymer ${}^1[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$, $\text{Btz}^- = 1,2,3\text{-benzotriazolate anion}$, $\text{C}_6\text{H}_4\text{N}_3^-$, $\text{BtzH} = 1H\text{-}1,2,3\text{-benzotriazole}$, $\text{C}_6\text{H}_5\text{N}_3$, which is formed first at about 100 °C from the same reagents. In addition to the trivalent rare earth ions it can thus be shown that also divalent Eu^{II} together with benzotriazole exhibits transformation of a 1D coordination polymer into a 3D MOF. The homoleptic framework ${}^3[\text{Eu}(\text{Btz})_2]$ exhibits a high thermal stability (525 °C) for an exothermically decomposing coordination compound. As ${}^3[\text{Eu}(\text{Btz})_2]$ is always obtained as a microcrystalline product, structure solution and refinement were achieved by X-ray powder techniques.

For further characterization ^{151}Eu -Mössbauer, IR and Raman spectroscopy as well as micro and thermal analysis were carried out.

Keywords: MOFs; Coordination Polymers; Lanthanides; Benzotriazoles; Crystal structure

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Introduction

The synthesis of oxygen-free lanthanide coordination compounds like amides and amine donor complexes can be achieved via the reaction of metals with a self-consuming melt of an amine under solvent free conditions [1 - 3]. The utilization of an organic melt replaces the solvent. We successfully elaborated this synthesis strategy for lanthanide metals and observed a general trend towards the formation of coordination polymers. Several exhibit a 1D chain-like linkage [4], including the benzotriazolate ligand [5]. Depending on the coordination modes of the ligands also 2D and 3D amide frameworks are observed [6 - 7]. Thus this synthesis strategy is also a suitable approach to the chemistry of MOFs (Metal Organic Frameworks) [8, 9]. Here the 4f elements can play an important role because of luminescence as an intrinsic property of the frameworks [10, 11]. Due to the oxophilicity of the rare earth elements oxygen-free MOFs are rarely found in the literature. As the ligand 1*H*-1,2,3-benzotriazole is commercially used as an UV absorber [12], we consider it interesting as linker in MOF frameworks. For the trivalent lanthanides we could show that strand-like coordination polymers of the formula $^1_\infty[\text{Ln}(\text{Btz})_3(\text{L})]$ [5], Ln = La - Yb, Btz⁻ = benzotriazolate

anion, $\text{C}_6\text{H}_4\text{N}_3^-$, $\text{L} = \text{NH}_3$, Py , BtzH , $\text{Ph}(\text{NH}_2)_2$, transform upon release of L into homoleptic 3D MOF structures of the formula ${}^3_\infty[\text{Ln}(\text{Btz})_3]$ [13]. Thus also 3D-frameworks are accessible from BtzH . We can now expand this on the divalent state, as europium shows transformation of the 1D polymer ${}^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ into the homoleptic framework ${}^3_\infty[\text{Eu}(\text{Btz})_2]$. It retains the divalent state and is not oxidized.

Experimental

All manipulations were carried out under inert atmospheric conditions using glove-box, ampoule as well as vacuum line techniques. The IR spectra were recorded using a BRUKER FTIR-IS66V-S spectrometer, the Raman spectra using a BRUKER FRA 106-S spectrometer. For the IR investigations KBr pellets were used under vacuum. The thermal properties were studied using multiple simultaneous DTA/TG experiments (SETARAM TG-DTA 92-16): on the reaction of europium metal with benzotriazole, on single crystalline ${}^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ and on ${}^3_\infty[\text{Eu}(\text{Btz})_2]$. All samples were heated from 20 °C up to 1000 °C in a constant He flow of 50 ml/min. 3.7 mg Eu and 15.3 mg BtzH were treated at a heating rate of 5 °C/min, 17.1 mg of crystalline ${}^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ as well as 17.2 mg ${}^3_\infty[\text{Eu}(\text{Btz})_2]$ were treated at a heating rate of 10 K/min. The micro analysis was carried out on a ELEMENTAR Vario El analyser.

Synthesis of ${}^3_\infty[\text{Eu}(\text{Btz})_2]$ (I)

a) ${}^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ (248 mg = $4.0 \cdot 10^{-4}$ mol) was sealed in an evacuated two-chamber DURAN glass ampoule and the substance chamber heated within 3 h to 350 °C in a tube oven. The other chamber was positioned outside the oven so that the temperature gradient to room temperature led to condensation of the released ligand in the second chamber. The temperature was held for 72 h and then cooled to room temperature within 3 h. The reaction gave 153

mg (0.39 mmol, 98 %) of a yellow-orange powder product of **1**. The reaction product showed a very small amount of black impurities most probably originating from decomposition of the released BtzH molecules.

b) Europium (76 mg = $5 \cdot 10^{-4}$ mol), 1H-benzotriazole (BtzH, $C_6H_5N_3$; 179 mg = $1.5 \cdot 10^{-3}$ mol), and Hg (20 mg) were sealed in an evacuated DURAN glass ampoule. The reaction mixture was heated within 23 h to 230 °C. The temperature was held for 120 h. The melt was cooled to 80 °C within 150 h and to room temperature in another 24 h. The reaction gave 178 mg (0.46 mmol, 92 %) of a yellow-orange powdery product of **1** with a small amount of a black decomposition product.

Anal. calc. $C_{12}H_8EuN_6$ ($M = 388.20 \text{ g mol}^{-1}$) C, 37.13 %; H, 2.08. Found: C, 37.5; H, 2.1.

MIR (KBr): (3061.6 w, 2258.2 vw, 1611.3 w, 1573.8 w, 1483.9 m, 1447.1 m, 1392.6 w, 1282.4 m, 1260.3 m, 1163.1 m, 144.0 vs, 1124.0 s, 993.2 w, 984.7 w, 912.4 m, 778.9 s, 744.3 vs, 694.0 m, 632.2 m, 546.7 m, 477.8 vw, 438.1 w, 418.5 w) cm^{-1} .

RAMAN: (3063.0 w, 1572.3 w, 1448.6 vw, 1393.1 w, 1283.6 vw, 1165.4 vw, 1138.9 vw, 1029.2 w, 780.8 w, 633.9 vw) cm^{-1} .

*Synthesis of ${}^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ (**2**)*

The synthesis of ${}^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ was carried out according to [5c]. Anal. calc. $C_{24}H_{18}N_{12}Eu$ ($M = 626.45 \text{ g mol}^{-1}$) C, 46.02; N, 26.83; H, 2.90. Found: C, 45.8; N, 26.9; H, 3.0. For **MIR** spectroscopy see also [5c].

Crystal Structure Determination

A powder sample of ${}^3_\infty[\text{Eu}(\text{Btz})_2]$ (**1**) was prepared for X-ray powder diffraction analysis under glove-box conditions and sealed in a glass capillary of 0.3 mm diameter. The data

collection was carried out on a STOE STADI P X-Ray diffractometer (Mo $K_{\alpha 1}$ radiation 70.93171(4) pm, Ge-111 monochromator, Debye-Scherrer geometry) at 297 K. The structure was determined with the program package TOPAS ACADEMIC 4.1 [14] using the charge flipping algorithm of *Sütő* and *Oszlányi* [15] after intensity extraction with the Pawley-method [16]. Rietveld refinements for compound **1** were done with the TOPAS package, using the fundamental parameters approach for reflection profiles (convolution of appropriate source emission profiles with axial instrument contributions as well as crystallite microstructure effects). Preferred orientation of the crystallites was described with a spherical harmonics function of 8th order. ${}^3[\text{Eu}(\text{Btz})_2]$ crystallises in the cubic space group $Fd\bar{3}m$. The integrity of symmetry and geometry were checked using the program PLATON [17] that resulted in the addressed space group subsequent to an initial solution in the space group $Fd\bar{3}$. The diffractograms were checked for crystal systems of lower symmetry on a possible splitting of reflections and half widths of the reflections counter checked with the fit of the structure refinement, both giving no sign on a different crystal system. The Eu atoms were refined isotropically. Displacement parameters for the C and N atoms were refined isotropically using a constraint for all atoms of one element, thus refining one parameter for the displacement parameters of each element. H atoms have not been put into consideration in this structure refinement. The results from the powder diffraction data in their present state give a complete description of the crystal structure of ${}^3[\text{Eu}(\text{Btz})_2]$, however crystallinity of the product does not yet allow a refinement of final contentment regarding the weighted Durbin-Watson figure of merit and a less constraint refinement of displacement parameters. Crystallographic data are summarised in Table 1, Figure 1 shows measured and calculated diffractograms of **1**, as well as their difference plot. The crystal structure of **2** was already determined on single crystals [5c]. The chain structure crystallizes in the monoclinic space group $C2/c$. Further information was deposited at the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cam-

bridge CB2 1EZ, UK (fax: +44 1223336033 or e-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposition number CCDC-xxxx, the names of the authors and the literature citation.

Mössbauer spectroscopy

The 21.53 keV transition of ^{151}Eu with an activity of 130 MBq (2 % of the total activity of a $^{151}\text{Sm}:\text{EuF}_3$ source) was used for the Mössbauer spectroscopic experiment, which was conducted in the usual transmission geometry. The measurement was performed with a commercial helium-bath cryostat. The temperature of the absorber was kept at 77 K, while the source was kept at room temperature. The temperature was controlled by a resistance thermometer (± 0.5 K accuracy). The sample was enclosed in a small glass container at a thickness corresponding to about 15 mg of the Mössbauer active element/cm². 62.5 mg of **1** were used for the Mössbauer spectroscopic experiments equalling about 25 mg of Eu.

Discussion

Synthesis and Thermal Properties

The solvent free melt synthesis utilizing metals is a redox reaction that also produces hydrogen gas [3]. The metals are oxidized by the amine melt giving amides [1 - 4]. In order to keep the reaction temperatures in the range of the stability region of organic materials, amalgam activation is mostly suitable [1 - 7, 18]. If the thermal stabilities of the amine ligands is not sufficient, several other activation methods like the use of electrides [19] or microwaves [2e] can also be applied.

As we have previously shown that benzotriazoles of the lanthanides obtained from reactions of the metals with a self-consuming melt of the ligand constitute of one-dimensional coordina-

tion polymers [5]. We elaborated that the thermal treatment can also lead to partial decomposition of the benzotriazole ring system, so that next to 1*H*-benzotriazole molecules products from the melt decomposition like NH₃ and Ph(NH₂)₂ are formed and incorporated into the coordination sphere of the rare earth ions as co-ligands L in $^1_\infty[\text{Ln}(\text{Btz})_3(\text{L})]$ [5]. The possible exchange of these neutral ligands vs. other amine bases such as pyridine [5b] as well as the thermal plateau subsequent to the release of the coordinating ligands BtzH = L in the thermal investigation of $^1_\infty[\text{Ce}(\text{Btz})_3(\text{BtzH})]$ [5a] gave rise to the question, what happens to the strand structures upon removal of the non-backbone ligands. The answer is the formation of framework structures for both trivalent [13] and divalent lanthanides, presented here. Though endothermic, the benzotriazole release is too rapid to grow single crystals of $^3_\infty[\text{Ln}(\text{Btz})_{2-3}]$ by heating, also if carried out with low heating rates. For the trivalent strands $^1_\infty[\text{Ln}(\text{Btz})_3(\text{BtzH})]$ reactions in solvothermal pyrrole conformed the thermal formation of $^3_\infty[\text{Ln}(\text{Btz})_3]$ [13] as they yield single crystalline material. The simulated powder patterns are identical to the decomposition products of $^1_\infty[\text{Ln}(\text{Btz})_3(\text{BtzH})]$. However, for divalent $^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ this treatment does not give crystals of suitable size. Accordingly, only microcrystalline material of the product of the benzotriazole release is available. Due to advances in the structure solution and refinement from powders, it is possible to present a structure solution here that corroborates the results of the other analysis methods and the formula $^3_\infty[\text{Eu}(\text{Btz})_2]$, and that also contains divalent europium. The formation of homoleptic $^3_\infty[\text{Eu}(\text{Btz})_2]$ (**1**) from $^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ (**2**) can be described as a condensation reaction under release of coordinating 1*H*-BtzH ligands as neutral N donor molecules.

>200 °C

From the thermal investigations that utilize simultaneous DTA/TG an identification of the signals is possible by comparison of investigations on the reaction of europium metal with benzotriazole, on single crystalline ${}^1_{\infty}[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ (**2**) and on the MOF ${}^3_{\infty}[\text{Eu}(\text{Btz})_2]$ (**1**). Figure 2 displays the results of simultaneous DTA/TG on the respective samples.

In the thermal investigation of the reaction itself signal (1) indicates the melting point of the ligand benzotriazole (96 °C; expected mp. 97 - 99 °C). Signal (2) starts directly afterwards and addresses to the endothermic reaction of BtzH and Eu, followed by signal (3) that indicates evaporation of excess BtzH. Signals (4) and (5) at 230 °C and 255 °C can be identified with the transformation of ${}^1_{\infty}[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ into ${}^3_{\infty}[\text{Eu}(\text{Btz})_2]$ under release of two equivalents of BtzH. Signal (6) indicates exothermic decomposition of the ${}^3_{\infty}[\text{Eu}(\text{Btz})_2]$ framework under release of N₂ at 525 °C.

The thermal investigation on ${}^1_{\infty}[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ (**2**) consequently shows only the signals (4 – 6) starting with the two step release of benzotriazole, the temperatures matching with the reaction DTA/TG. The mass loss in the TG experiment is 36.5 % equalling two BtzH equivalents (expected 37.7 %). Finally, the thermal investigation on ${}^3_{\infty}[\text{Eu}(\text{Btz})_2]$ (**1**) only exhibits the final exothermic decomposition step (6).

Thereby thermal formation of ${}^3_{\infty}[\text{Eu}(\text{Btz})_2]$ from ${}^1_{\infty}[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ also matches with the formation of ${}^3_{\infty}[\text{Ln}(\text{Btz})_3]$ from ${}^1_{\infty}[\text{Ln}(\text{Btz})_3(\text{L})]$, if the different valence is taken into account. The thermal stability of ${}^3_{\infty}[\text{Ln}(\text{Btz})_3]$ is 465 °C for La and 470 °C for Ce, and thus lower than of ${}^3_{\infty}[\text{Eu}(\text{Btz})_2]$, their decomposition also being exothermic due to the release of N₂ [13].

Crystal Structure

In contrast to the chain structure of $^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ (**2**, see description in [5c]) the crystal structure of $^3_\infty[\text{Eu}(\text{Btz})_2]$ (**1**) is a three-dimensional homoleptic framework structure (see Figure 3). The structure contains two crystallographically independent Eu atoms. Both are octahedrally coordinated by N atoms of six benzotriazolate anions each. The orientations of the six ligands vary for the two Eu sites (see Figure 4). A distinct difference is found for the linkages to other europium atoms. Eu1 is linked to four Eu2 atoms via face connections of four alternating triangular faces of the coordination octahedron giving a tetrahedral arrangement of Eu2 around Eu1. Eu2 is linking to only two Eu1 atoms via the antiprismatic triangular faces of the coordination octahedron resulting in a 180° linkage (see Figures 2 and 4).

Regarding the topology of the framework structure [20] that is depicted in Figure 5, a complicated topology of a 12,12 net results. However it can be described in a simplified way as it originates from the diamond structure of Eu1 atoms as connectivity points. In-between all Eu1 connectivity centres the Eu2 have to be considered as additional connectivity centres. This equals a diamond structure that would have an interstitial atom on each bond. It can also be described in comparison with β -cristobalite with Eu1 taking the positions of the silicon atoms and Eu2 the positions of the oxygen atoms. Therefore a simplified topology symbol is not 6,4 but 12,4 constituted of large twelve-membered rings to three other rings. For a complete consideration of the topology the face connections of the polyhedra can accordingly be addressed as “triple-bridges” [21]. This would enlarge the overall topology to a 12,12 net.

The Eu – N distances are 269.5(11) and 277.4(22) pm which indicates divalent Europium. Eu^{II} – N distances [22] of comparable compounds are e.g. ranging from 260.1(5) to 287.3(6) pm in $^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ [5c]. They can spread over a wide range and cover C.N. of Eu between 6 and 12, Eu^{II} – N being 252 – 268 pm in $^1_\infty[\text{Eu}(\text{Cbz})_2]$ [4a], 255 – 257 pm for $[\text{Eu}(\text{Cbz})_2(\text{thf})_4]$

[23], 258 –311 pm for ${}^3[\text{Eu}(\text{Tzpy})_2]$ [7e]. Completed coordination spheres for the europium atoms are depicted in Figure 6.

¹⁵¹Mössbauer Spectroscopy

The Mössbauer spectrum of compound **1** taken at 77 K is presented in Figure 7 together with transmission integral fits. The corresponding fitting parameters for the main component of the spectrum are an isomer shift $\delta = -12.44(3)$ mm/s, an experimental line width $\Gamma = 4.0(2)$ mm/s, and a quadrupole splitting parameter $\Delta E_Q = 3.4(6)$ mm/s. This signal clearly reflects divalent europium. The isomer shift of -12.44 mm/s lies in the range of divalent europium and is comparable to other europium containing metal organic frameworks [7e]. An additional spectral component is detected near 0.8 mm/s, indicating the presence of some Eu^{3+} , most likely due to partial hydrolyses of the sample, leading to europium (III) oxide or hydroxide. This signal was included as a simple Lorentzian in the fit. The resulting ratio of $\text{Eu}^{2+} / \text{Eu}^{3+}$ is 83 : 17, respectively.

The experimental line width of 4.0 mm/s of the Eu(II) signal is somewhat high. The broadening results from the two crystallographically independent europium sites confirmed by the crystal data. It was not possible to differentiate between these two sites due to their similarity. Summing up, the Mössbauer spectroscopic investigation validates the divalent character of both europium sites.

Conclusions

Conversion of a 1D-coordination polymer into a 3D-linked MOF is shown by the transformation of ${}^1[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ into ${}^3[\text{Eu}(\text{Btz})_2]$. It is the first example for a divalent rare earth ion to show this conversion. The divalence of europium is proven by ¹⁵¹Mössbauer spectroscopy. The homoleptic framework ${}^3[\text{Eu}(\text{Btz})_2]$ exhibits an exceptionally high thermal stability for an exothermically decomposing coordination compound and MOF structure.

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Legends for Figures

Figure 1 X-ray powder diffraction diffractogram of **1**. Experimental data are displayed in black, calculated in grey. Difference plot and reflex position markers are displayed below.

Figure 2 Simultaneous DTA/TG investigation of the reaction of Eu with BtzH (top), of $^1\text{Eu}(\text{Btz})_2(\text{BtzH})_2$ (middle) and of $^3\text{Eu}(\text{Btz})_2$ (bottom). Signal (1) indicates the melting point of BtzH, signal (2) belongs to the endothermic reaction of BtzH and Eu, (3) indicates

evaporation of excess BtzH, signals (4) and (5) can be identified with the transformation of $^1_\infty[\text{Eu}(\text{Btz})_2(\text{BtzH})_2]$ into $^3_\infty[\text{Eu}(\text{Btz})_2]$ under release of two equivalents of BtzH. Signal (6) indicates exothermic decomposition of the $^3_\infty[\text{Eu}(\text{Btz})_2]$ framework under release of N_2 .

Figure 3 Crystal structure of $^3_\infty[\text{Eu}(\text{Btz})_2]$ as a depiction of the coordination polyhedra with a view along [110] (top) and [001] (bottom). Eu atoms are displayed in grey, N atoms in dark and C atoms in light grey. Edges of the polyhedra do not represent bonds.

Figure 4 The coordination spheres of the atoms Eu1 and Eu2 in $^3_\infty[\text{Eu}(\text{Btz})_2]$ as a depiction of the coordination polyhedra.

Figure 5 Schematic drawing of the network topology of $^3_\infty[\text{Eu}(\text{Btz})_2]$ (**1**).

Figure 6 The complete coordination spheres and linkage of Eu1 and Eu2 in **1**. Symmetry Operations: I: $x, \frac{3}{4} - y, \frac{3}{4} - z$; II: $\frac{3}{4} - y, z, \frac{3}{4} - x$; III: $y, \frac{3}{4} - z, \frac{3}{4} - x$; IV: $z, \frac{3}{4} - x, \frac{3}{4} - y$; V: $\frac{3}{4} - z, \frac{3}{4} - x, y$; VI: $\frac{3}{4} - x, \frac{3}{4} - y, z$; VII: $\frac{3}{4} - x, y, \frac{3}{4} - z$; VIII: y, z, x ; IX: $\frac{3}{4} - y, \frac{3}{4} - z, x$; X: $-x, -z, -y$; XI: $-x, \frac{1}{4} + z, \frac{1}{4} + y$; XII: $-y, -x, -z$; XIII: $\frac{1}{4} + y, -x, \frac{1}{4} + z$; XIV: z, x, y ; XV: $\frac{3}{4} - z, x, \frac{3}{4} - y$; XVI: $\frac{1}{4} + z, \frac{1}{4} + y, -x$; XVII: $-z, -y, -x$.

Figure 7 Experimental and simulated ^{151}Eu Mössbauer spectrum of **1** at 77 K.

Table 1. Crystallographic data for ${}^3\infty[\text{Eu}(\text{Btz})_2]$ (**1**). Standard deviations are given in parentheses.

Formula	$\text{C}_{12}\text{H}_8\text{EuN}_6$
Formula weight [g/mol]	388.20
Crystal system, space group	cubic, $Fd\bar{3}m$
Lattice parameter [pm]	$a = 1994.3(1)$
Cell volume [nm^3]	7931(1)
Z	24
Density [g/cm^3]	1.91
μ [cm^{-1}]	51.9
X-ray radiation	Mo- $\text{K}_{\alpha 1}$, $\lambda = 70.93171(4)$ pm
Diffractometer	STOE STADI P
d range	1.27670 – 11.51392
Data Points	3000
Reflections	123
Refined parameters	38
R_p	0.0703
wR_p	0.0933
R_{bragg}	0.0442
χ^2	1.915
Wght. Durbin-Watson	0.435

Table 2. Selected interatomic distances (in pm) and angles between atoms of ${}^3[\text{Eu}(\text{Btz})_2]$ (1).

Standard deviations are given in parentheses. Symmetry Operations: II: $\frac{3}{4} - y, z, \frac{3}{4} - x$; IV: $z, \frac{3}{4} - x, \frac{3}{4} - y$; VI: $\frac{3}{4} - x, \frac{3}{4} - y, z$; VIII: y, z, x ; X: $-x, -z, -y$; XII: $-y, -x, -z$; XIV: z, x, y ; XVII: $-z, -y, -x$.

Eu1–N1	277.4(22)	N1–Eu1–N1 ^{II/IV/VIII/XIV}	90
Eu2–N2	269.5(11)	N1–Eu1–N1 ^{VI}	180
Eu1–Eu2	431.0(1)	N2–Eu2–N2 ^X	180
		N2–Eu2–N2 ^{XIV/XVII}	85.7(6)
		N2–Eu2–N2 ^{VIII/XII}	94.3(6)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7