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A First and Homoleptic Rare Earth 3D-Bipyrazolate MOF: $3\infty[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$

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A First and Homoleptic Rare Earth 3D-Bipyrazolate MOF:
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Keywords:	Metal Organic Frameworks, Lanthanides, Europium, Coordination polymers, Twinning



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3 **A First and Homoleptic Rare Earth 3D-Bipyrazolate MOF:**
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5 $\infty^3[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$
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18 Received...

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22 *Dedicated to Professor Martin Jansen on the Occasion of his 65th Birthday.*
23

24
25 **Abstract.** The homoleptic framework $\infty^3[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$, $\text{Me}_4\text{BpzH}^- = 3,3',5,5'$ -
26 tetramethyl-4,4'-bipyrazolate anion, $\text{C}_{10}\text{H}_{13}\text{N}_4^-$, $\text{Me}_4\text{BpzH}_2 = 3,3',5,5'$ -tetramethyl-4,4'-
27 bipyrazole, $\text{C}_{10}\text{H}_{14}\text{N}_4$, is obtained by a high-temperature oxidation of the metal europium with
28 a self consuming melt of 3,3',5,5'-tetramethyl-4,4'-bipyrazole above 300 °C. The framework
29 structure initiates from a three-dimensional linkage of Eu centres and bridging ligands that
30 coordinate with one N atom of each aromatic ring linking $\eta^1:\eta^1$ via front and backside of the
31 bicyclic ring system. The framework has a (4,8) topology and is the first example of a rare
32 earth bipyrazolate. Thus for the trivalent eightfold by nitrogen atoms coordinated europium a
33 sterically rather crowded ligand with four methyl groups is able to yield a 3D-framework. The
34 crystal structure was refined from systematically eight-fold twinned crystals as merohedric
35 fourfold twins with a subsequent racemic twinning of the fourfold twin individuals.
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54 **Keywords:** Metal Organic Frameworks; Lanthanides; Europium; Coordination polymers;
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56 Twinning
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13 14 15 16 17 **Introduction** 18

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22 Among network and framework structures of coordination polymers [1] MOFs (Metal Or-
23 ganic Frameworks) [2 - 6] have attracted reasonable attention. Concerning N-donor ligand
24 substituted frameworks imidazolates were recently highlighted as ZIFs (Zeolite Imidazolate
25 Frameworks) as they adopt zeolite structures, if four-fold coordinated metal ions are used like
26 zinc and cobalt, promising fruitful sorption abilities [7 - 9]. For the large rare earth ions higher
27 coordination numbers are observed in imidazolates [10, 11]. This includes other aromatic N
28 heterocyclic amide linkers such as triazolates [12 - 15], pyridino- and benzotriazolates [16,
29 17] with coordination numbers ranging from 6 to 12 for Ln-N-MOFs. The linkers that were
30 successfully used for a 3D linkage in rare earth amides so far were sterically hardly crowded.
31 Accordingly, the utilization of the 3,3',5,5'-tetramethyl-4,4'-bipyrazole ligand, which is
32 known as a successful linker for extended frameworks from main group and transition metal
33 chemistry [18 - 21], was attractive as a benchmark for both the steric demand together with
34 high C.N. centres for a MOF construction and the thermal stability needed for a redox melt
35 reaction above 300° C. For europium the reaction yielded single crystalline
36 $\infty[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$, $\text{Me}_4\text{BpzH}^- = 3,3',5,5'$ -tetramethyl-4,4'-bipyrazolate anion,
37 $\text{C}_{10}\text{H}_{13}\text{N}_4^-$, $\text{Me}_4\text{BpzH}_2 = 3,3',5,5'$ -tetramethyl-4,4'-bipyrazole, $\text{C}_{10}\text{H}_{14}\text{N}_4$. Systematic eight-
38 fold twinning made structure resolution and refinement procedures additionally challenging.
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Experimental

All manipulations were carried out under inert atmospheric conditions using glove box, ampoule as well as vacuum line techniques. Heating furnaces were equipped with Al₂O₃ tubes and EURO THERM 2416 control elements. Hg (Riedel-de-Haen) of 99.99% purity was used for amalgam activation, europium metal (CHEMPUR, 99.9%) was used as purchased. 3,3',5,5'-tetramethyl-4,4'-bipyrazole was prepared according to the well known procedure [22]. The EDX analysis and successful stability tests vs. a REM beam were carried out on a REM JSM-6500F instrument (Fa. JEOL). Micro analyses were carried out on the crystalline product on a Vario Microcube and Vario EL (Fa. Elementar) elemental analyzers. The yield of the reaction was calculated according to the amount of ligand used for the synthesis.

Synthesis of ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$:

Eu metal (0,5 mmol, 76 mg) and 3,3',5,5'-tetramethyl-4,4'-bipyrazole (Me₄BpzH₂, 1 mmol, 380 mg) together with Hg (0.1 mmol) were sealed in an evacuated DURAN™ glass ampoule and heated to 302° C in 55 h. The temperature was held for 336 h and then cooled to 250° C in 520 h and finally to room temperature in another 44 h. The reaction resulted in a single crystalline and in the majority microcrystalline yellow product. Yield: 184 mg = 82 %. Anal. calc. EuC₄₀H₅₃N₁₆; M = 909.9 g mol⁻¹: C, 52.80; N, 24.63; H, 5.87. Found: C, 52.46; N, 24.58; H, 6.64.

Crystal Structure Determination

The best suitable single crystal of the compound ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ was selected for the single crystal X-ray investigation under glovebox conditions and sealed in a glass capillary. The data collection was carried out on a STOE IPDS-II diffractometer (Mo K_α radiation λ = 0.7107 Å) at 170 K. The structure was determined using direct methods [23]. Crystals of

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3 $^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ show as systematic twinning. After data collection four cells of
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6 the same dimensions, but different orientations could be indexed. The four cells are tetragonal
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8 and can be transferred by a fourfold axis along [1-10] into one another (See Figure 1).
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11 A data set for one of the individuals was created and a structure solution in the non-
12 centrosymmetric space group *I422* was carried out. A centrosymmetric space group setting is
13 contradicted by the ligand symmetry and positioning. The structure refinement [24] as a
14 meroedric fourfold twin resulted in a Flack-X parameter [25] of 0.4. Consequently each of the
15 four individuals forms an additional racemic twin giving an overall eightfold twinning. Two
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17 of the seven twin factors are smaller than the others. This could indicate a domain eightfold
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19 twin with two orientations less represented.
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27 All non-H atoms were refined anisotropically by least squares techniques [25]. The hydrogen
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29 atom positions were calculated into preset positions adjusting their thermal parameters to 1.2
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31 of the referring carbon atoms except for the N-H hydrogen atom, which had to be neglected.
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34 Because of the twin refinement no absorption correction was applied. Crystallographic data
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36 are summarised in Table 1. Further information was deposited at the Cambridge Crystallo-
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38 graphic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44
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40 1223336033 or e-mail: deposit@ccdc.cam.ac.uk) and may be requested by citing the deposi-
41
42 tion number CCDC-xxxxx, the names of the authors and the literature citation.
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46 The compound was also investigated on powder samples of the bulk products in sealed capil-
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48 laries on a STOE STADI P transmission diffractometer (Cu $K\alpha_1$ radiation $\lambda = 1.540598 \text{ \AA}$,
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50 focussed single crystal germanium monochromator). The diffraction pattern of bulk
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52 $^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ shows large similarity with the simulated diffractogram. All
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54 reflections of the single crystal structure could be indexed in the powder as well [26]. Seven
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56 additional reflections in the powder pattern reveal another unknown crystalline phase that is
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58 neither the ligand nor europium metal.
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Results and Discussion

Synthesis

${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ is formed by a solvent free reaction [27] of europium metal with a self consuming melt of 3,3',5,5'-tetramethyl-4,4'-bipyrazole (see Scheme 1). In this redox reaction the metal is oxidized by the ligand and hydrogen gas is formed. One additional molecule from the melt is needed to saturate the coordination sphere of europium:



With a reaction temperature above 300° C needed, a referring thermal stability of the organic ligand is vital, and the crystallization of the framework product is hindered. We consider this the main reason why it has not yet been successful to characterize also the other lanthanide 3,3',5,5'-tetramethyl-4,4'-bipyrazolates. Reactions of other metals are proceeding at comparable conditions, but so far no crystallization was achieved.

Crystal Structure

The crystal structure of ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ consists of a three-dimensional framework. It is built up by europium ions linked by 3,3',5,5'-tetramethyl-4,4'-bipyrazolate ligands and one bipyrazole ligand. Each ligand coordinates asymmetrically η^1 with the non-H bearing N atom of each pyrazole ring to one europium cation. The second N atom is too far from Eu (Eu-N = 315 pm) that it cannot be counted for coordination. Eight ligands coordinate to one europium centre, so that an eight-fold coordination of a distorted square antiprism results (see Figure 2). Thus not all ligands can be anionic, as Eu-N distance of 257,1(13) pm indicates Eu^{III} , viz. three ligands are anions Me_4BpzH^- and one is a Me_4BpzH_2 molecule. They cannot

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3 be crystallographically distinguished. As the symmetry reduces amide and N-donor contacts
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5 to one average Eu-N distance a comparison with other amides containing Eu^{III} exhibits aver-
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7 age Eu-N distances of 254 pm and square antiprismatic coordination in
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9 [Eu(Pybiz)₂(PybizH)₂][Eu(Pybiz)₄] [28], Pybiz⁻ = pyridylbenzimidazolate, N₃C₁₂H₈⁻, PybizH
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11 = N₃C₁₂H₉, whereas Eu^{II} containing amides vary in their Eu-N average distances between 257
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13 pm in Eu(Cbz)₂(thf)₄ [29] for a C.N. of six, 263 pm for a C.N. of five in ¹_∞[Eu(Cbz)₂] [30],
14
15 Cbz⁻ = carbazolate anion, C₁₂H₈N⁻, and 275 pm for a C.N. of eight in ³_∞[Eu(Tzpy)₂] [16],
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17 Tzpy⁻, pyridinotriazolate. Eu-N distances in Eu(Cbz)₂(thf)₄ [28] are shorter as only amide N-
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19 Eu bonds are present and no average with longer N-donor bonds. The N-Eu-N angles reflect
20
21 the distortion of the square-antiprismatic N-coordination being 85.6(6) for the angle between
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23 Eu and one square face (N-Eu-N^{II}) and 162.8(9) for the angle between Eu and opposing cor-
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25 ners of both square faces (N-Eu-N^V).

26
27 The overall framework ³_∞[Eu(Me₄BpzH)₃(Me₄BpzH₂)] (see Figure 3) has a (4,8)-topology and
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29 is thus different from structures of Co and Ag containing bipyrazolate MOFs [31, 32] that
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31 have a connectivity of four or two. The high connectivity of eight in
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33 ³_∞[Eu(Me₄BpzH)₃(Me₄BpzH₂)] limits the overall possible free space of the MOF, which none-
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35 theless is about 8% of the cell volume counting only the accessible space on base of the van-
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37 der-Waals-spheres [33].

38 39 40 41 42 43 44 45 46 47 48 49 **Conclusion**

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51 With ³_∞[Eu(Me₄BpzH)₃(Me₄BpzH₂)] a first bipyrazolate MOF of a rare earth element was suc-
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53 cessfully prepared. Both the solvent free synthesis and crystallography with eight-fold twin-
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55 ning prove challenging, so that this is the first and only example of a rare earth element char-
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57 acterized so far, although the other elements also show reaction at comparable conditions.
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59 However an advantage of the high-temperature melt synthesis is the tendency towards ho-
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moleptic compounds by avoiding solvent co-coordination. The bipyrazolate ligand is essential

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3 for a 3D-linking and thus the construction of a framework as monopyrazolates result in for-
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5 mation of small molecules [34 - 36] or 1D-coordination polymers [36, 37]. The MOF is po-
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7 tentially attractive concerning selectivity of sorption as it exhibits window sizes of the cavities
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9 of 3.4 – 4.2Å.
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Legends for Figures

Fig. 1 Selection of the Ewald sphere of the single crystal X-ray data collection of ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ indicating the matrices of two twin orientations and the C_4 twin element along $[1-10]$ as well as an intensity summation of the diffraction experiment (within and at the borders of the depiction). The transformation matrix for the twin refinement as a four-fold twin is given. The eight-fold twins results from additional racemic twinning.

Fig. 2 The distorted square antiprismatic coordination sphere of N atoms around Eu^{III} in ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ as well as the subsequent linkage via the ligands. Edges of the polyhedra do not represent bonds. Symmetry operations: I: $-y, x, z$; II: $-x, -y, z$; III: $y, -x, z$; IV: $x, -y, -z$; V: $-x, y, -z$; VI: $y, x, -z$; VII: $-y, -x, -z$.

Fig. 3 The crystal structure of ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ with a view along $[100]$. Cavities in the structure are emphasized by shaded ellipsoids. Eu atoms are depicted as large grey balls, N atoms as dark, C atoms as light grey balls. H atoms are omitted for clarity.

Scheme 1 The amide ligand 3,3',5,5'-tetramethyl-4,4'-bipyrazole.

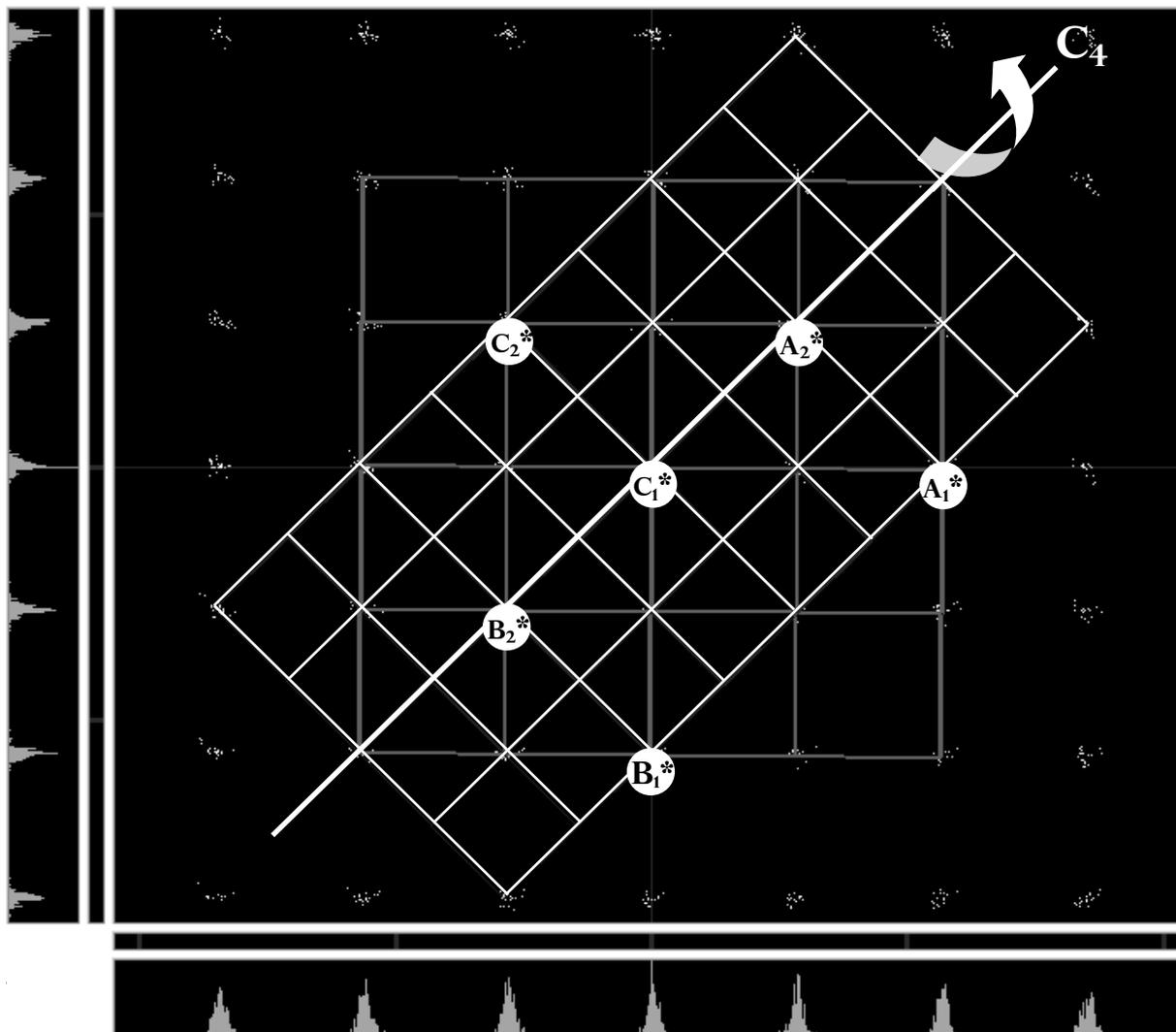
Scheme 2 Schematic drawing of the structure of ${}^3_{\infty}[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$ centred on an Eu^{III} ion.

Table 1 Crystallographic Data for ${}^3\infty[\text{Eu}(\text{Me}_4\text{BpzH})_3(\text{Me}_4\text{BpzH}_2)]$. Deviations given in brackets.

formula	C₄₀ H₅₃ N₁₆ Eu
formula weight	909.92
crystal system	tetragonal
space group	<i>I</i> 422
a / pm	1065.9(2)
c / pm	1510.1(3)
BASF [23]	0.15, 0.12, 0.08, 0.12, 0.18, 0.19, 0.07
V / (10 ⁶ pm ³)	1715.7(5)
Z	2
<i>d</i> _{calcd} / (g·cm ⁻³)	1.7611
μ / cm ⁻¹	18.9
T / K	170(2)
data range	4.68 ≤ 2θ ≤ 49.88
X-ray radiation / pm	Mo-K _α , λ = 71.073
diffractometer	STOE Image Plate Diffraction System II
no. of unique reflections	760
no. of refined parameters	62
R ₁ ^a for n reflections with F _o >4σ(F _o); n	0.0466; 632
R ₁ (all)	0.0583
wR ₂ ^b (all)	0.1182
remaining electron density (e/pm * 10 ⁶)	+0.55/-0.74 e/pm 10 ⁶

^a $R_1 = \sum [|F_o| - |F_c|] / \sum [|F_o|]$. ^b $wR_2 = (\sum w (F_o^2 - F_c^2)^2 / (\sum w (F_o^4))^{1/2}$ [23].

Fig. 1



$$\begin{aligned}
 a_1^* &= 0.5 a_2^* - 0.5 b_2^* - c_2^* \\
 b_1^* &= -0.5 a_2^* + 0.5 b_2^* - c_2^* \\
 c_1^* &= 0.5 a_2^* + 0.5 b_2^*
 \end{aligned}
 \longrightarrow
 \begin{pmatrix}
 0.5 & -0.5 & -1 \\
 -0.5 & 0.5 & -1 \\
 0.5 & 0.5 & 0
 \end{pmatrix}$$

$$\begin{aligned}
 &\xrightarrow{\text{invert}} \begin{pmatrix} 0.5 & -0.5 & 1 \\ -0.5 & 0.5 & 1 \\ -0.5 & -0.5 & 0 \end{pmatrix} \xrightarrow{\text{transpose}} \begin{pmatrix} 0.5 & -0.5 & -0.5 \\ -0.5 & 0.5 & -0.5 \\ 1 & 1 & 0 \end{pmatrix} \\
 &\hspace{15em} \text{transformation matrix}
 \end{aligned}$$

Fig. 2

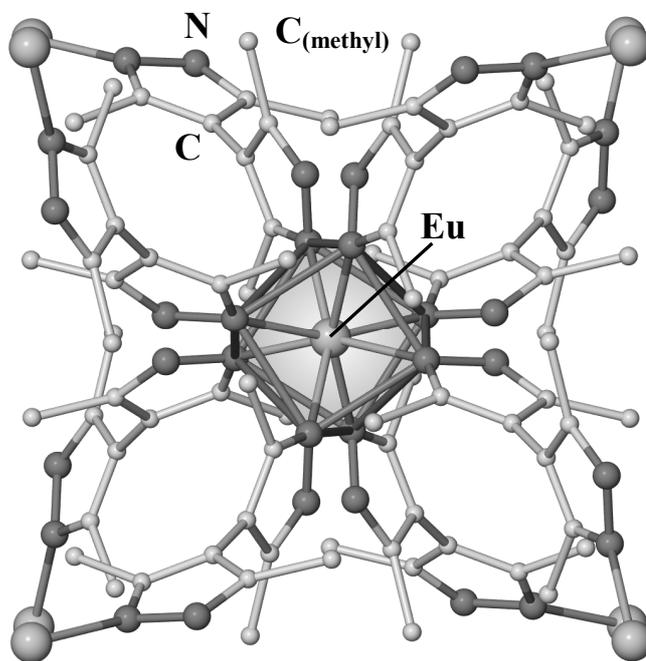
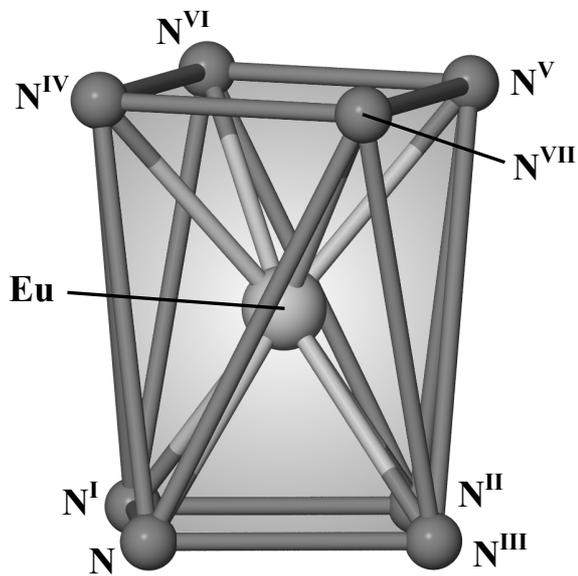
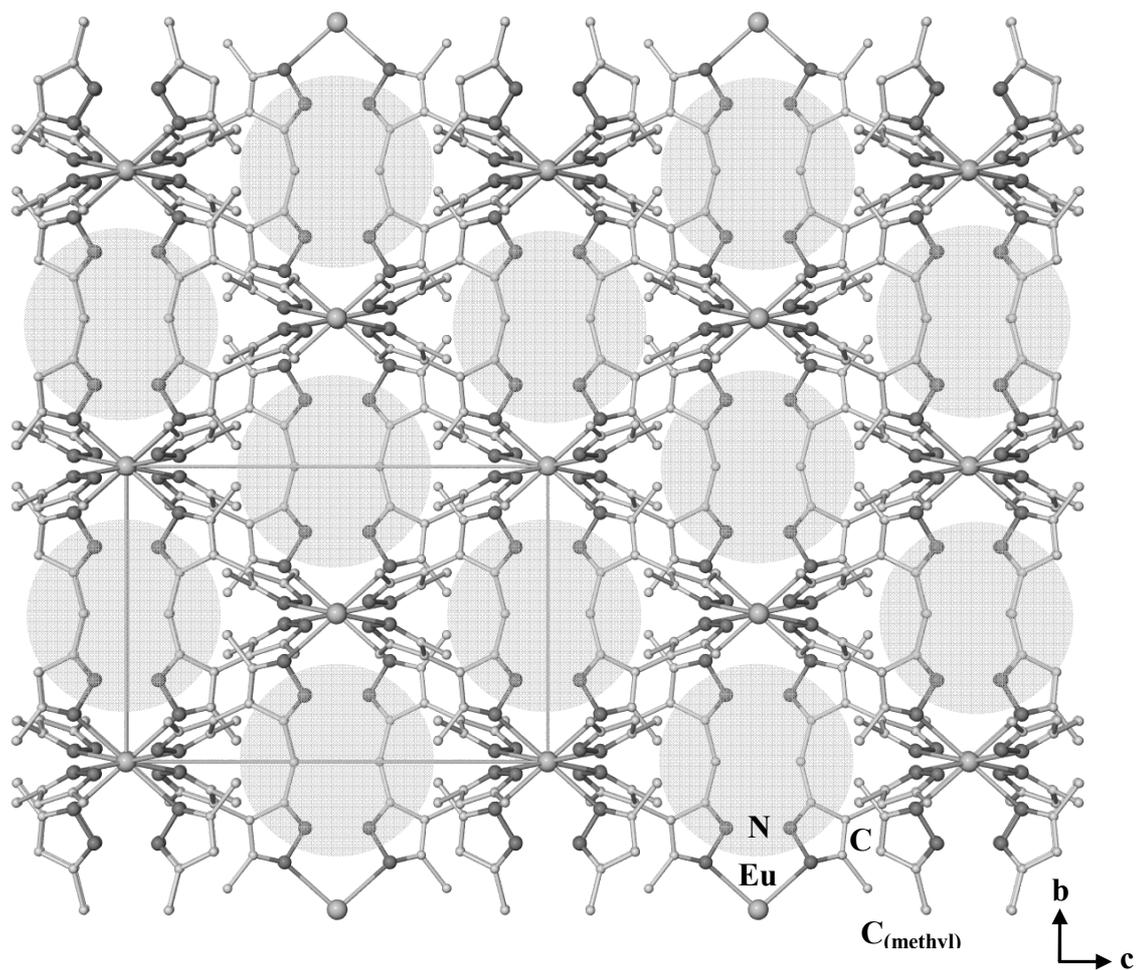
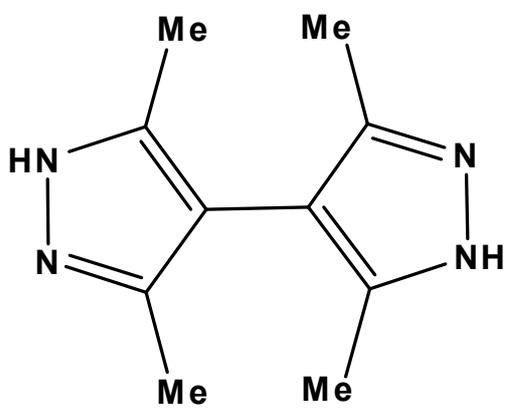


Fig. 3



Scheme 1



Scheme 2

