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$_{\infty}^{3}$[Eu(Tzpy)$_2$]: A Homoleptic Framework Containing {Eu^{II}N$_{12}$} Icosahedra**

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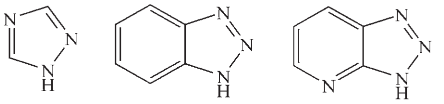
Since the introduction of metal–organic frameworks (MOFs), framework structures of coordination polymers have become a focus of chemistry research.[1] These structures are, for example, promising absorbers for the storage of hydrogen and other gases.[2] The chemistry of the rare-earth metals should offer a new angle on this research, as their large ionic radii, considering their relatively low oxidation numbers, enable a large bandwidth of coordination numbers (CNs; CN = 3–16) in molecular complexes, depending on the steric demand of the ligands.[3] Thus, a large variety of linkage patterns should be available for coordination polymers. Because of the extraordinary oxophilicity of the rare-earth elements, the framework chemistry of these metals is mainly based on oxygen coordination polymers.[4] Only a few rare-earth MOFs are known in which the metal ions are coordinated by nitrogen atoms, and these contain the five-membered aromatic nitrogen heterocycles 1,2,4-triazole or imidazole.[5]

Solvent-free syntheses in the melt of the corresponding amine[6] have been used to produce amide frameworks of the lanthanide (Ln) metals [Eq. (1)]. Attempts to use the UV absorber[7] 1*H*-1,2,3-benzotriazole to attain extended conjugated systems of triazoles led instead to one-dimensional coordination polymers, some of which exhibit interesting luminescence properties.[8]. The backbone of CH groups from the benzotriazole ligands prevents higher-dimensional connectivity in this system.

$$\mathrm{Ln} + x\,\mathrm{HNR_2} \xrightarrow{\Delta T} \mathrm{Ln(NR_2)}_x + x/2\,\mathrm{H_2} \tag{1}$$

Herein, we present the construction of a complex three-dimensional network, $_{\infty}^{3}$[Eu(Tzpy)$_2$] (Tzpy$^-$ = $C_5H_4N_4{}^-$), through the use of 1*H*-1,2,3-triazolo[4,5-*b*]pyridine. The introduction of an additional nitrogen atom into the benzotriazole ligand enables 1,3-chelate bonding, which allows multidimensional connectivity. With respect to the synthetic strategy, a transition from the chemistry of the triazoles, which contain three nitrogen atoms, to the high-temperature chemistry[6] of N_4 ligands is also achieved (see Scheme 1).



Scheme 1. 1*H*-1,2,4-triazole, 1*H*-1,2,3-benzotriazole, 1*H*-1,2,3-triazolo-[4,5-*b*]pyridine (from left to right).

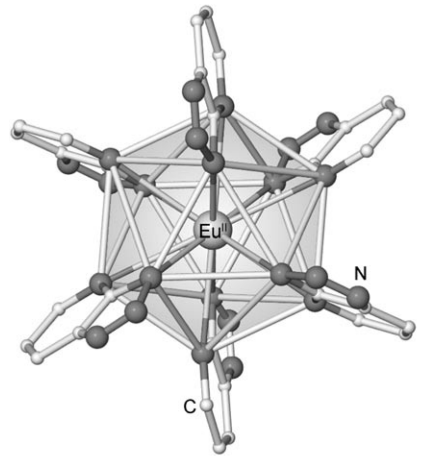


Figure 1. The icosahedral coordination environment of Eu3 in $_{\infty}^{3}$[Eu-(Tzpy)$_2$]. Six pyridinotriazolate ligands form 1,3-chelate bonds to the Eu^{II} center, resulting in a coordination number of 12. The coordination polyhedron is depicted by lines between nitrogen atoms, which do not represent bonds. Hydrogen atoms are omitted.

$_{\infty}^{3}$[Eu(Tzpy)$_2$] is novel, as the chelate bonds of six pyridinotriazolate anions to a single Eu^{II} atom (Eu3) result in a coordination number of 12, the highest known for europium, and in a coordination environment that is a nearly undistorted icosahedron (Figure 1). Icosahedral coordination has not previously been reported for coordination polymers and frameworks. It results in an unprecedented complexity in the topology of a lanthanide coordination polymer. This extraordinary type of Ln–N coordination polyhedron is only known for the monomeric salts [Pr($C_8H_6N_2$)$_6$][ClO$_4$]$_3$,[9a] in which six 1,8-naphthyridine ligands coordinate the Pr^{III} atom through 1,3-chelate bonds, and [La($C_6H_9N_3$)$_4$]-[ClO$_4$]$_3$·CH$_3$CN,[9b] in which the cation contains four three-fold-coordinating ligand caps. The cations in the few known networks of rare-earth amides have lower coordination

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numbers of six for $\mathrm{Ln^{III}}$ in ${}^{3}_{\infty}[\mathrm{Yb(Tz)_3}]$ ($\mathrm{Tz^-}$ = 1,2,4-triazolate) and ${}^{3}_{\infty}[\mathrm{Tb(Im)_3}]@\mathrm{NH_3}$[5a,c] ($\mathrm{Im^-}$ = imidazolate), or eight for $\mathrm{Eu^{II}}$ in ${}^{3}_{\infty}[\mathrm{Eu(Tz)_5(TzH)_2}]$.[5a]

Additionally, the crystal structure of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ contains two further europium sites, which are eightfold (Eu2) and ninefold (Eu1) coordinated by η^1:η^1:η^1- and η^2:η^1-triazolate rings of $\mathrm{Tzpy^-}$ ions. The different coordination numbers are also reflected by the Eu–N distances, which range from 258(2)–284(2) pm for CN = 8 (Eu2), to 263(1)–294(2) pm for CN = 9 (Eu1), to 296(1)–311(1) pm for CN = 12 (Eu3) in the icosahedron. Note that the chelate bonds consist of nitrogen donor interactions exclusively, whereas the shorter Eu–N distances represent cation–anion interactions. The Ln–N distances in the icosahedron of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ are in good agreement with those in $[\mathrm{Pr(C_8H_6N_2)_6}][\mathrm{ClO_4}]_3$ (Pr–N 274–277 pm) and $[\mathrm{La(C_6H_9N_3)_4}][\mathrm{ClO_4}]_3\cdot\mathrm{CH_3CN}$[9] (La–N 273–283 pm), because the bonds in these compounds also significantly exceed the expected values for $\mathrm{La^{III}}$ and $\mathrm{Pr^{III}}$.[9,10] Assuming that none of the ligands in ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ is reduced to a dianion, all three europium sites contain $\mathrm{Eu^{II}}$,[10] in accordance with other europium amides.[11] ^{151}Eu Mößbauer spectroscopy confirms that the europium cations in ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ are divalent.[12]

The framework of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ consists of interlinked coordination polyhedra around the different europium sites. The icosahedra are responsible for the linkages along the *c* axis, and the other two types of polyhedra are responsible for the linkages within the a_1–a_2 plane (Figure 2). This connectivity results in a large rhombohedral unit cell with an extraordinarily long *c* axis of 6940.9(6) pm.[13]

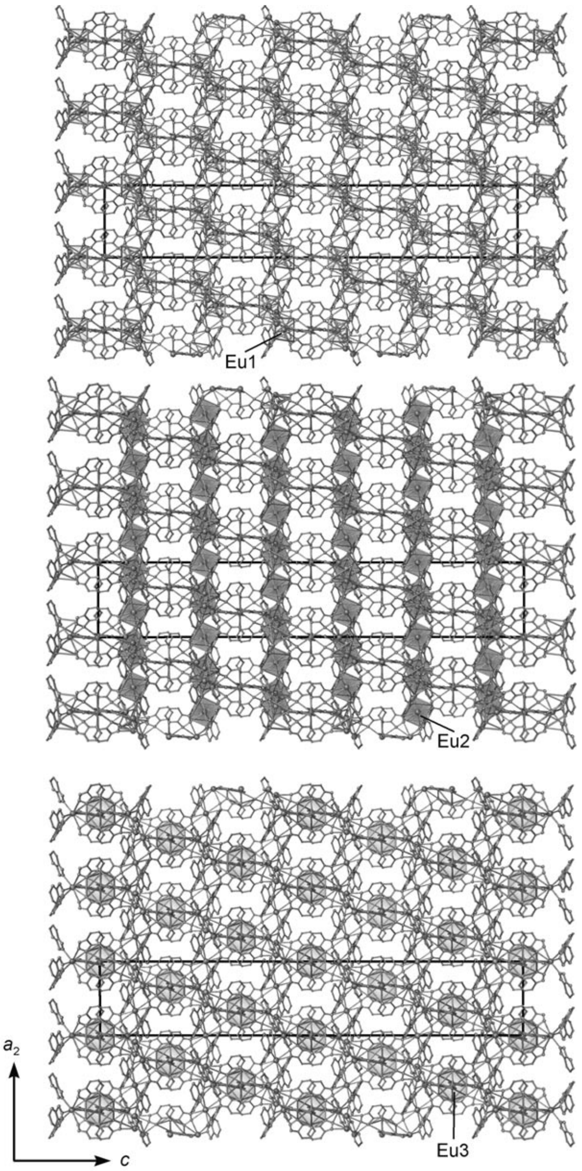

Figure 2. The framework structure of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ viewed along the [100] direction. The coordination polyhedra around the Eu1 (top, CN = 9), Eu2 (middle, CN = 8), and Eu3 (bottom, CN = 12) sites are depicted.

Experimental Section

${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$: Europium (0.5 mmol, 76 mg, ChemPur 99.9 %), 1*H*-1,2,3-triazolo[4,5-*b*]pyridine (TzpyH; 1.5 mmol, 180 mg, Aldrich 98 %), and pyridine (7.5 mmol, 600 mg), as well as mercury (0.1 mmol, 20 mg) for the activation of the europium metal, were filled in a Duran-glass ampoule. The reaction mixture was frozen with liquid nitrogen and degassed three times. The ampoule was sealed under vacuum. The reaction mixture was heated to 100 °C over 4 h and then to 190 °C over 100 h (such that pyridine (b.p. = 115 °C) was under solvothermal conditions), and was held at this temperature for 144 h. It was cooled to 90 °C over 400 h and then to room temperature over 13 h. Along with pyridine and mercury, large amounts of transparent orange crystals of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$, which are air- and moisture-sensitive, were obtained in the reaction. Yield (Eu): 144 mg (86 %). Elemental analysis (%) calcd for $\mathrm{C_{10}H_6N_8Eu}$: C 30.78, H 1.54, N 28.71; found: C 31.0, H 1.6, N 28.5. Mid-IR: $\tilde{\nu}$ = 3135m, 1590m, 1568m, 1517w, 1480w, 1438m, 1402vs, 1343w, 1300m, 1255m, 1176m, 1154m, 1131m, 1111m, 981m, 925w, 802m, 780vs, 704m, 650m, 595w, 563m, 459m cm^{-1}. Far-IR: $\tilde{\nu}$ = 594w, 562m, 458m, 442w, 404w, 288w, 249w, 156sh cm^{-1}.

The reaction was also carried out without pyridine. In this case, a reaction temperature of 205 °C (15 °C higher than that for the pyridine-containing reaction) was necessary using the same heating rates and reaction times. ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ was only obtained as a powder, and any slight overheating results in decomposition of the ligand (decomp 208 °C); thus, the solvothermal synthesis in pyridine is more favorable.

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[12] Two samples of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ were well-mixed with BN or celite (diatomaceous earth), respectively. They were then investigated by ^{151}Eu Mössbauer spectroscopy at 78 K. The spectra of both samples show a main signal at $\delta = -12.9\,\mathrm{mm\,s^{-1}}$, which corresponds to Eu$^{\mathrm{II}}$. Both samples also exhibit a weak signal at $\delta = 0.8\,\mathrm{mm\,s^{-1}}$, which corresponds to Eu$^{\mathrm{III}}$. The resulting ratio of Eu$^{\mathrm{II}}$/Eu$^{\mathrm{III}}$ is 80:20, which could indicate mixed valency in the compound. However, because of the air and moisture sensitivity of ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$, the small amount of Eu$^{\mathrm{III}}$ detected in the spectrum could also be caused by partial decomposition or hydrolysis. Indeed, the powder X-ray diffraction patterns of the samples used for ^{151}Eu Mössbauer spectroscopy show weak reflections indexed to $\mathrm{Eu_2O_3}$ and EuOOH. These compounds are likely responsible for the Eu$^{\mathrm{III}}$ detected. Moreover, the Eu$^{\mathrm{II}}$/Eu$^{\mathrm{III}}$ ratio of 4:1 determined by ^{151}Eu Mössbauer spectroscopy is inconsistent with the results of the single-crystal X-ray diffraction analysis, as all of the Eu–N distances are much too long for Eu$^{\mathrm{III}}$ (by more than 50 pm for the icosahedrally coordinated Eu3 site).[14a] Accordingly, we assume that all the europium cations in ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$ are divalent (see also the Supporting Information).

[13] Crystallographic data for ${}^{3}_{\infty}[\mathrm{Eu(Tzpy)_2}]$: $\mathrm{C_{10}H_6N_8Eu}$, $M_r = 390.2\,\mathrm{g\,mol^{-1}}$, crystal size: $0.1 \times 0.1 \times 0.05\,\mathrm{mm^3}$, space group $R\bar{3}c$ (no. 167), $a_{1,2} = 1409.9(2)$, $c = 6940.9(6)$ pm, $T = 170$ K, $Z = 36$, $V = 11\,949(3) \times 10^6\,\mathrm{pm^3}$, $\rho_{\mathrm{calcd}} = 1.952\,\mathrm{g\,cm^{-3}}$, $2\theta_{\max} = 47.98°$, STOE IPDS II diffractometer, ω scans ($\Delta\omega = 2°$, $\phi = 0.90°$), $\mathrm{Mo_{K\alpha}}$ radiation, $\lambda = 0.71073$ Å, 32 697 reflections, 2051 unique reflections, 921 reflections with $I > 2\sigma(I)$, 161 refined parameters, $R_1 = 0.0606$ ($I > 2\sigma(I)$), $wR_2 = 0.0956$ (all data), residual electron density: $+1.15/-0.83\,\mathrm{e/(10^6\,pm^3)}$. The structure was solved using direct methods (SHELXS-97[14a]) and refined by least-squares techniques (SHELXL-97[14b]) for all independent reflections against $|F^2|$. The positions of the hydrogen atoms were calculated, and their thermal parameters were set to 1.2 times that of the neighboring carbon atoms (AFIX 43). Because of the extremely large unit cell, a detector distance had to be chosen that limited the 2θ range. Owing to the low scattering power of the small crystal, it was necessary to refine parts of the pyridyl rings with a "rigid-bond" model.[14b] All non-hydrogen atoms were refined anisotropically. The symmetry and the crystal system were checked separately,[14c] and the lattice parameters were confirmed by powder X-ray diffraction. CCDC-620198 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Selected interatomic distances [pm] and angles [°]: Eu1–N2 263(1), Eu1–N6 285(1), Eu1–N7 294(1), Eu1–Eu2 422.2(1), Eu2–N5 258(2), Eu2–N1 265(2), Eu2–N3 274(2), Eu2–N6 284(2), Eu3–N7 296(1), Eu3–N8 311(1); N2-Eu1-N2$^{\mathrm{I}}$ 87.5(6), N2-Eu1-N6$^{\mathrm{I}}$ 86.8(7), N2-Eu1-N7 95.1(7), N1-Eu2-N6 70.0(8), N5-Eu2-N1$^{\mathrm{II}}$ 88.5(9), N6-Eu2-N6$^{\mathrm{II}}$ 174.5(9), N7-Eu3-N7$^{\mathrm{III}}$ 180(1), N7-Eu3-N7$^{\mathrm{IV}}$ 113.3(8), N7-Eu3-N7$^{\mathrm{I}}$ 66.8(8), N8-Eu3-N8$^{\mathrm{V}}$ 180(1), N8-Eu3-N8$^{\mathrm{VI}}$ 120.0(9), N8$^{\mathrm{I}}$-Eu3-N8$^{\mathrm{III}}$ 60.1(7). Symmetry operations: I: $-y, x-y, z$; II: $y+1/3, x-1/3, -z+1/6$; III: $-x, -y, -z$; IV: $y, -x+y, -z$; V: $-x+1/3, -x+y-1/3, -z+1/6$, VI: $-x+y, -x, z$

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