Three-dimensional networks of lanthanide 1,2,4-triazolates: $^{3}_{\infty}$[Yb(Tz)$_3$] and $^{3}_{\infty}$[Eu$_2$(Tz)$_5$(TzH)$_2$], the first 4f networks with complete nitrogen coordination†

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The solvent-free melt reaction of Eu and Yb with the N-heterocycle 1,2,4-triazole, gives the first three-dimensional networks of the lanthanides with complete nitrogen coordination spheres, further being the first unsubstituted triazolates of the lanthanides and exhibiting different valences.

$^{3}_{\infty}$[Yb(Tz)$_3$] and $^{3}_{\infty}$[Eu$_2$(Tz)$_5$(TzH)$_2$] (Tz$^-$ = 1,2,4-triazolate, C$_2$H$_2$N$_3$$^-$, TzH = 1,2,4-triazole, C$_2$H$_3$N$_3$) mark interesting amides of the rare-earth elements ytterbium and europium as both exhibit network structures. Framework and network chemistry has recently attracted attention and is known for oxygen coordinating ligands, mainly metal carboxylates[1] including the 4f elements.[2] Adsorption materials and nano composites are in the current focus of material science concerning coordination networks.[3] Apart from networks with oxygen coordinated lanthanide atoms the formation of three-dimensional structures proves difficult. We have now succeeded in the synthesis of the first coordination networks of the rare-earth elements displaying complete nitrogen coordination. This was achieved *via* the oxidation of the metals with 1,2,4-triazole under amalgam activation conditions.‡ We previously elaborated this type of solvent free melt reactions with rare-earth elements and amines for a number of N heterocycles[4] observing a trend to one-dimensional coordination polymers.[4,5] By use of the ligand triazole that contains three N atoms in one ring additional backside coordination enabled the formation of multi-dimensional networks.

The syntheses benefit from the high reactivity of the lanthanide metals, which can be directly oxidized with a melt of the amine:

$$Yb + 3\ TzH \rightarrow {}^{3}_{\infty}[Yb(Tz)_3] + 1.5\ H_2 \qquad (1)$$

$$2\ Eu + 7\ TzH \rightarrow {}^{3}_{\infty}[Eu_2(Tz)_5(TzH)_2] + 2.5\ H_2 \qquad (2)$$
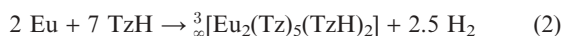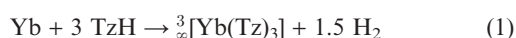
Different from reactions in solution, these high-temperature reactions are a synthetic challenge as aromatic N heterocycles containing three or more N atoms decompose exothermically under release of N$_2$. Though this release is kinetically hindered the temperatures available for the melt reactions are limited by the decomposition temperatures.§ The thermal product stabilities of the networks $^{3}_{\infty}$[Yb(Tz)$_3$] (**1**) and $^{3}_{\infty}$[Eu$_2$(Tz)$_5$(TzH)$_2$] (**2**) are much higher than of triazole in presence of the metals due to strong

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bonds of the triazolate anions to the metal cations.¶ In contrast to a complex ligand design including several syntheses steps, amines of relatively low cost like triazoles can be used for network syntheses instead, rendering them attractive for commercial use, *viz.* we are currently investigating the absorption abilities of small guest molecules such as H$_2$ and N$_2$. $^{3}_{\infty}$[Yb(Tz)$_3$] (**1**) is a homoleptic amide containing only triazolate anions as ligands. Ytterbium is trivalent and shows a nitrogen coodination number of nine, consisting of three triazolate ligands that coordinate η^1, and three that coordinate η^2. These coordination modes are *e.g.* also observed for pyrazolates with two neighbouring nitrogen atoms.[5,6] All ligands in **1** are connecting to another Yb ion resulting in a pseudo-octahedral coordination as polyhedron and establishing the three-dimensional network. **1** thus adopts a common structure type, the ReO$_3$ structure counting each triazolate ligand as one corner of the octahedron.[7] Fig. 1 depicts the coordination and crystal structure of **1**.

Yb–N distances are 235(2)–241(2) pm and thereby in the range of other Yb^{III} amides.[8] Furthermore $^{3}_{\infty}$[Yb(Tz)$_3$] (**1**) shows an interesting crystallography. The Tz$^-$ ligands are ordered only
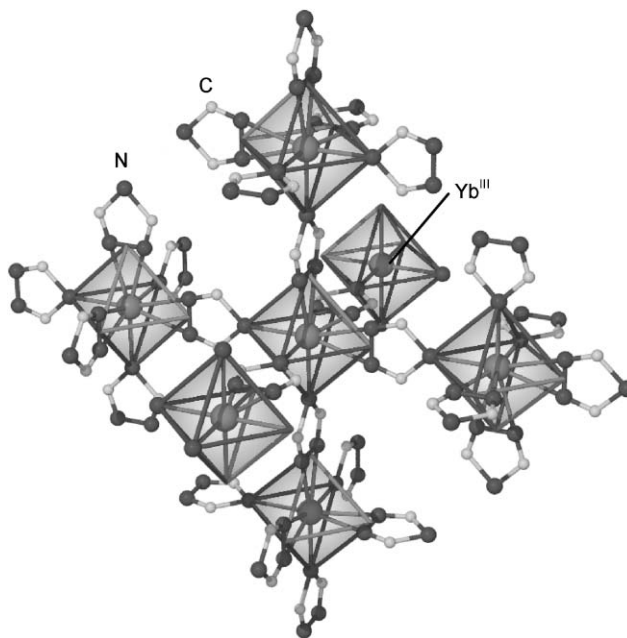

Fig. 1 The crystal structure of $^{3}_{\infty}$[Yb(Tz)$_3$] (**1**). The coordination polyhedra around the Yb atoms as well as one set of ligand orientations are depicted. H atoms are omitted for clarity.

along one-dimensional chains of the octahedra whilst the other two respective directions including neighbouring chains of octahedra are free to adopt any of four possible overall orientations of the ligand rings. This results in a three-dimensional disorder phenomenon that can be identified by diffuse scattering along the *hkl* planes throughout the complete reciprocal space. No diffuse scattering is observed between the *hkl* planes. Refinement in the cubic crystal system and the space group $Pm\bar{3}m$ reflects all four possible ligand orientations.‖**

$^{3}_{\infty}[Eu_2(Tz)_5(TzH)_2]$ (**2**) is mixed valent, contains Eu^{II} and Eu^{III} as well as triazolate anions and triazole molecules. The presence of molecules is supported by the vibration ν(N–H) at 3417 cm^{-1} in the mid-IR spectrum. The overall metal to ligand ratio is 1:3.5. This corroborates the larger radius of europium cations compared to ytterbium cations[9] as well as the mixed-valent character of europium in **2**. The redox potentials $E_{Eu(II/III)} = 0.35$ and $E_{Yb(II/III)} = 1.04$[10] also correspond to trivalent Yb in **1** whereas Eu in **2** is partially divalent due to its less positive potential. The other lanthanide triazolates can thus all be expected to be trivalent as the $E_{Ln(II/III)}$ potentials of the remaining rare-earth elements are more positive than of Eu and Yb.[10] A similar coherence is observed *e.g.* for lanthanide pyrazolates and carbazolates.[4–6] In **2**, Eu^{II} and Eu^{III} are found in a ratio of 1:1. The coordination sphere of the larger Eu^{II} ions is saturated with TzH molecules, whereas the coordination sphere of Eu^{III} is identical to Yb^{III} in **1**. The Eu–N distances range from 244(3) to 281(3) pm, the large distances originating from Eu^{II}, the short from Eu^{III}. Both are in good accordance with other divalent[11] and trivalent europium amides.[12] The coordination numbers are eight and nine, giving pseudo-octahedra as in **1** and distorted square antiprisms as coordination polyhedra. Eu^{II} and Eu^{III} are arranged in layers co-planar with the *ab* plane. All Tz$^-$ ligands are linking two metal centres and are thus responsible for the formation of the network whereas the TzH molecules coordinate η^1 end on.

The coordination modes of Tz$^-$ anions in **2** match with **1**. Fig. 2 depicts the coordination polyhedra in **2**, Fig. 3 the crystal structure of the network. $^{3}_{\infty}[Eu_2(Tz)_5(TzH)_2]$ (**2**) also exhibits a challenging crystallography as it crystallizes in systematic twins with a mirror plane perpendicular to the *c* axis as twin element. A false small centrosymmetric monoclinic C centred unit cell is obtained. The true metric is orthorhombic with the space group *Fdd*2 $^{3}_{\infty}[Eu_2(Tz)_5(TzH)_2]$ showing an additional tetragonal-pseudo symmetry.‖
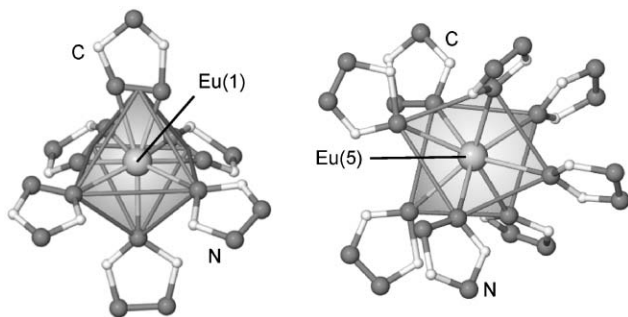

Fig. 2 The distorted pseudo-octahedral coordination of trivalent Eu (left) and square-antiprismatic coordination of divalent Eu (right) in $^{3}_{\infty}[Eu_2(Tz)_5(TzH)_2]$ (**2**) represented by the crystallographic independent atoms Eu(1) and Eu(5).
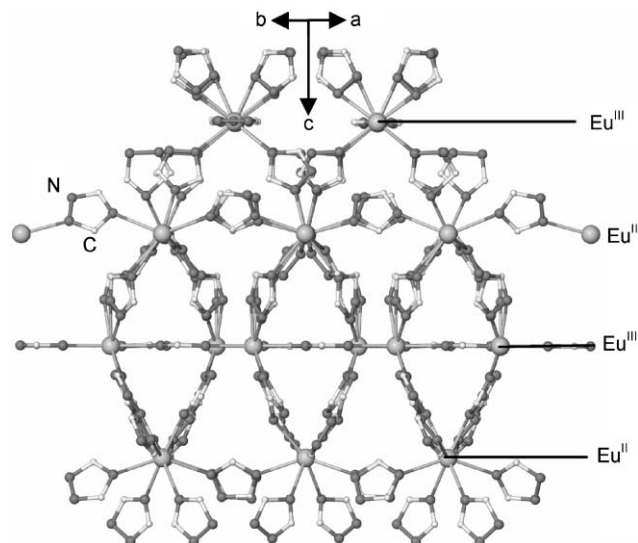

Fig. 3 Section of the network structure of $^{3}_{\infty}[Eu_2(Tz)_5(TzH)_2]$ (**2**) with alternating layers of Eu^{III} and Eu^{II} along the *c* axis.

Whereas the ReO_3 structure of **1** is a rather close packing and is not likely to absorb external molecules, the structure of **2** shows void volumes of about 5 Å diameter, large enough for the absorption of guest atoms and small molecules such as H_2 and N_2. DTA/TG experiments show that **2** endothermically absorbs 8% of N_2 between 110 and 140 °C followed by desorption finished at 190 °C.

Notes and references

diffractometer, $6.01 \leqslant 2\theta \leqslant 63.84°$, $\Delta\Omega = 2°$, $R_{\text{int}} = 0.088$, 143 reflections (for all $I > 2\sigma(I)$) for 15 parameters, $R_1 = 0.027$ and $wR = 0.067$ for all reflections, GOOF = 1.066, residual electron density = $+1.87/-1.62$ e 10^6 pm^3 (0.64×10^2 pm from Yb1).

$^3_\infty$[Eu$_2$(Tz)$_5$(TzH)$_2$] (**2**): C$_{14}$H$_{16}$N$_{21}$Eu$_2$, $M = 782.4$, orthorhombic, space group $Fdd2$ (no. 43), $a = 2012.4(4)$, $b = 2010.9(4)$, $c = 4470(2)$ pm, $V = 18089 \times 10^6$ pm^3, $Z = 32$, $T = 170$ K, λ(Mo-Kα) = 0.71073×10^2 pm, STOE IPDS-II diffractometer, $3.01 \leqslant 2\theta \leqslant 50.00°$, $\Delta\Omega = 2°$, racemic twin, $R_{\text{int}} = 0.119$, 7754 reflections, 6250 with $I > 2\sigma(I)$ for 629 parameters, $R_1 = 0.092$ for $I > 2\sigma(I)$, $R_1 = 0.138$ and $wR = 0.213$ for all reflections, GOOF = 1.085, residual electron density = $+1.26/-0.84$ e 10^6 pm^3 (0.90×10^2 pm from Eu5).

CCDC 296983 and 296984. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b601450j

** $^3_\infty$[Yb(Tz)$_3$] (**1**): One crystallographically independent N atom is the η^1 coordinating tip of the heterocyclic ring and is located at the site $4m.m$, the other N atom is located at $m..$ and marks the η^2 coordinating edge of the ring. The C atom is located at $mm2..$ altogether with the N atoms giving the four different ring orientations. Reduction to the chemical formula $^3_\infty$[Yb(Tz)$_3$] implies that all ring atom positions have reduced site occupancies. The N at the tip of the ring and the C atom have half occupancies as two of the four ring orientations use the same atom positions, whereas the N atom at the ring edge has a different position for each orientation rendering an occupancy of only one fourth.

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