Nitrogen-Rich Compounds of the Lanthanoids: The 5,5′-Azobis[1H-tetrazol-1-ides] of some Yttric Earths (Tb, Dy, Ho, Er, Tm, Yb, and Lu)

by **Georg Steinhauser***[a]), **Gerald Giester**[b]), **Christoph Wagner**[c]), **Nicolae Leopold**[c])[d]),
Johannes H. Sterba[a]), **Bernhard Lendl**[c]), and **Max Bichler**[a])

[a]) Vienna University of Technology, Atominstitut der Österreichischen Universitäten, Stadionallee 2,
AT-1020 Vienna (phone: +43-1-5880114189; fax: +43-1-5880114199;
e-mail: georg.steinhauser@ati.ac.at)
[b]) University of Vienna, Institute of Mineralogy and Crystallography, Althanstr. 14, AT-1090 Vienna
[c]) Vienna University of Technology, Institut für Chemische Technologie und Analytik,
Getreidemarkt 9/164, AT-1060 Vienna
[d]) Faculty of Physics, Babeş-Bolyai University, Kogalniceanu 1, RO-400084 Cluj-Napoca

A set of N-rich salts, **3**–**9**, of the heavy lanthanoids (terbium, **3**; dysprosium, **4**; holmium **5**; erbium, **6**; thulium, **7**; ytterbium, **8**; lutetium, **9**) based on the energetic 5,5′-azobis[1H-tetrazole] (H_2ZT) was synthesized and characterized by elemental analysis, vibrational (IR and *Raman*) spectroscopy, and X-ray structure determination. The synthesis of the lanthanoid salts **3**–**9** was performed by crystallization from concentrated aqueous solutions of disodium 5,5′-azobis[1H-tetrazol-1-ide] dihydrate ($Na_2ZT \cdot 2 H_2O$; **1**) and the respective $Ln(NO_3)_3 \cdot 5 H_2O$ and yielded large rhombic crystals of the type $[Ln(H_2O)_8]_2(ZT)_3 \cdot 6 H_2O$ in *ca.* 70% of the theoretical yield. The compounds **3**–**9** are isostructural (triclinic space group $P\bar{1}$) to the previously published yttrium salt **2**; they show, however, a clear lanthanoid contraction of several crystallographic parameters, *e.g.*, the cell volume or the $Ln-O$ bond lengths of the Ln^{3+} ions and the coordinating H_2O molecules. The lanthanoid contraction influences the strengths of the H-bonds, which can be observed as a red shift by 4 cm^{-1} in the characteristic IR band, in particular from 3595 cm^{-1} (**3**) to 3599 cm^{-1} (**9**). In good agreement with previous works, **2**–**9** are purely salt-like compounds without a coordinative bond between the tetrazolide anion and the Ln^{3+} cation.

Introduction. – In 2008, Austria is celebrating the 150th birthday of *Carl Auer von Welsbach* (1858–1929), one of the pioneers in the chemistry of the rare earth elements (REE). He discovered the elements praseodymium and neodymium in 1885 [1]. From 1905 to 1907 *Auer von Welsbach* worked on a substance, which the Swiss chemist *Jean Charles Gallisard de Marignac* (1817–1894) had proposed as a new element ('ytterbium') in 1878. As presaged by many colleagues of his time, *Auer von Welsbach* found that *Marignac*'s ytterbium was actually a mixture of two constituents. He isolated both elements, named them aldebaranium (Ad, atomic number 70) and cassiopeium (Cp, atomic number 71), and determined their atomic mass (172.90 g · mol^{-1} for Ad, and 174.23 g · mol^{-1} for Cp) [2][1]). Approximately one month earlier, the french chemist *Georges Urbain* (1872–1938) published his results on the separation of *Marignac*'s ytterbium: he found atomic masses of 'not far from 170' and 'not much

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1) Today, the relative atomic masses are known as precisely as 173.04 for element 70 (Yb) and 174.967 for element 71 (Lu), resp.

more than 174' for 'his' elements which he named neo-ytterbium and lutecium, respectively [3]. After more than two decades of controversy on the priority of this discovery, the two elements were finally named ytterbium and lutetium, respectively, by the International Committee [4]. Although 'there is no doubt that *Auer von Welsbach* was the first to separate *Marignac*'s ytterbium into reasonably pure components' [5], the fame of discovery of the elements 70 and 71 is finally shared between three scientists, namely *Carl Auer von Welsbach*, *Georges Urbain*, and the U.S. chemist *Charles James* (1880–1928), who did not publish his results.

Due to their extremely similar chemical behavior, the separation of the lanthanoids exhibited a true chemists' challenge at the end of the 19th century. It was observed that some minerals (cerite, orthite, monazite, and others) preferably accumulate light REE, whereas other minerals (*e.g.*, gadolinite, xenotime, euxenite, yttrialite, and fergusonite) mainly accumulate yttrium and heavier REE. Due to the main element constituents in these minerals, the elements cerium and yttrium, respectively, were eponymous for both groups of the lanthanoids (Ln): the cerite earths (La, Ce, Pr, Nd, and Sm) and the yttric earths (Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y, and Sc). The yttric earths can be classified further into five subgroups: 1. terbine earths (Eu, Gd, Tb), 2. erbine earths (Dy, Ho, Er, Tm), 3. ytterbine earths (Yb, Lu), 4. yttrium, and 5. scandium [6].

In chemistry and/or physics, anomalous chemical behaviors occur near the middle of the lanthanoid series despite their extreme similarity. This phenomenon has been referred to as the 'gadolinium break' in literature [7–11] and results from the introduction of supplementary electrons into the half-filled 4f shell. The 'gadolinium break' has been observed in numerous studies on the chemical behavior of the rare earths, *e.g.*, the charge separation reaction (*Eqn. 1*) of hydrated Ln^{3+} ions in the gas phase [12] and their solution hydrolysis constants [13].

$$[Ln(H_2O)_n]^{3+} \rightleftharpoons [Ln(OH)(H_2O)_{n-m-1}]^{2+} + H^+(H_2O)_m \qquad (1)$$
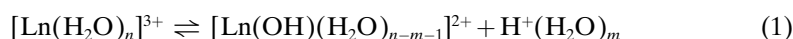
The d-block element yttrium is closely related to the heavier lanthanoids due to its trivalent charge and its similar ion radius, a consequence of the lanthanoid contraction (which roots in the poor shielding between the nucleus and the $5s^2 5p^6$ valence shell by the 4f electrons). It is known that, *e.g.*, dysprosium and yttrium are difficult to separate due to their similar ion radii (1.159 Å for Y^{3+} (CN = 8) and 1.167 Å for Dy^{3+} (CN = 8)) (CN = coordination number)). Even the name dysprosium (Greek δυσπρόσιτος: inaccessible, hidden, unfriendly) implied these difficulties. Scandium has a significantly smaller ion radius (1.010 Å for Sc^{3+} (CN = 8)) than the heaviest lanthanoid Lu (1.117 Å for Lu^{3+} (CN = 8)), thus the similarities are less evident. Nevertheless, scandium as well as yttrium are included in the term 'rare earths' together with the lanthanoids of the f-block.

In this work, we investigated salts of the lanthanoids with the N-rich anion 5,5′-azobis[1*H*-tetrazol-1-ide] (= 5,5′-(diazene-1,2-diyl)bis[2*H*-tetrazole] ion(2−); $C_2N_{10}^{2-}$; $(ZT)^{2-}$). Formerly, 5,5′-azobis[1*H*-tretrazol-1-ide] was called 5,5′-azotetrazolate. In contrast to conventional explosives which are based on the intermolecular or intramolecular oxidation of a C-backbone, N-rich high-energy density materials (HEDM) obtain their high energy content from a high heat of formation. Two classes of compounds have been shown to be most promising for this purpose, namely 1*H*-

tetrazoles (five-membered rings with four N-atoms) and tetrazines (six-membered rings with four N-atoms in 1,2,4,5- or 1,2,3,5-position) [14][15]. Both ring systems are stabilized by their aromaticity. In general, the heat of formation of a cation or anion increases as the number of N-atoms in this respective ion increases [16]. In previous studies, the 5,5′-azobis[1*H*-tetrazol-1-ides] have been reported as promising materials for primary or high explosives, eventually in combination with N-rich energetic cations [14][17–21]. The sensitivity of tetrazole derivatives generally depends very much on the content of crystal H_2O. Anhydrous compounds showed to be extremely sensitive, whereas the sensitivity decreases with the amount of H_2O of crystallization in the molecule [21]. In this project, we present the synthesis and complete structural as well as vibrational spectroscopical characterization of the 5,5′-azobis[1*H*-tetrazol-1-ides] of all lanthanoids. N-Rich compounds (bis[1*H*-tetrazol-1-ides]) of lanthanoids have been object of recent investigations [22], but not as energetic materials: N-rich heterocycles such as 1*H*-tetrazoles are also of interest in coordination chemistry. Due to their extremely low-lying π^*-orbtials, they are excellent π-acceptors [23][24]. Such compounds have the potential to serve with their electrochemical or optical properties, in particular, as electronic devices [25–27] or luminescent or nonlinear optic materials [22][28].

As starting materials for the synthesis of the titel compounds, $Na_2ZT \cdot 2\,H_2O$ (**1**) and the respective lanthanoid nitrate hydrates ($Ln(NO_3)_3 \cdot 5\,H_2O$) were used. In total, the pure hydrates of ZT salts of the lanthanoids were found to crystallize in four independent crystallographical groups, where the largest group, the isotypic series of the heavy yttric earth salts $Ln_2(ZT)_3 \cdot 22\,H_2O$ ($Ln = Tb, Dy, Er, Tm, Yb$, and Lu) is the topic of this article. We have been able to obtain single crystals suitable for X-ray crystallography of all lanthanoid ZTs, where previous attempts were in vain [21], except for the transition metal yttrium (octaaquayttrium(3+) 5,5′-azobis[1*H*-tetrazol-1-ide] hydrate (2:3:6); **2**).

Results and Discussion. – *Synthesis.* Disodium 5,5′-azobis[1*H*-tetrazol-1-ide] dihydrate (**1**) was prepared as a starting material (with a slight modification, *i.e.*, the crystal H_2O content) according to *Thiele* [29] and *Klapötke* and co-workers [21] by oxidation of 1*H*-tetrazol-5-amine monohydrate with $KMnO_4$ in aqueous NaOH solution. The obtained crystalline product contained five molecules of H_2O of crystallization. We observed that three H_2O molecules can easily be removed upon drying of the product by careful heating on a water bath and under high vacuum (HV), yielding the dihydrate. Elemental analysis established the purity of this compound (anal. calc. for $C_2H_4N_{10}Na_2O_2$ (246.099): C 9.76, H 1.64, N 56.91%; found: C 9.71, H 1.77, N 56.02%). Both, the pentahydrate and the dihydrate of Na_2ZT are stable at room temperature and can be regarded as relatively innocuous. Nonetheless, complete dehydration should be avoided due to the highly sensitive and explosive character of the anhydrous ZT salts.

In contrast to the previously attempted, ineffective metathesis reactions (for $La_2(ZT)_3$, $Ce_2(ZT)_3$, $Nd_2(ZT)_3$, and $Gd_2(ZT)_3$ by the reaction of BaZT and the respective $Ln_2(SO_4)_3$) [21], we synthesized the title compounds by a simple crystallization reaction from the respective REE nitrate and Na_2ZT in aqueous solution at elevated temperature (*Scheme*). In contrast to the behavior of many

transition-metal ions (including the REE ion Sc^{3+}), no immediate precipitation took place in the concentration ranges described in the *Exper. Part*. After 2–5 d, crystallization set in and led to a pure, large-crystalline product (with crystals of up to 150 mg a piece) within a good yield (*ca.* 70%, whereas the known **2** was obtained with a yield of only 24% [21]). Thus, the crystallization from relatively concentrated solutions of the Ln nitrates and **1** is a very effective way of synthesizing **3**–**9**.

Scheme. *Synthesis of the ZT Salts* **3**–**9** *by Crystallization from Aqueous Solutions of* **1** *and the Respective* $Ln(NO_3)_3$

$$Ln = Tb, Dy, Ho, Er, Tm, Yb, Lu$$

3 – 9
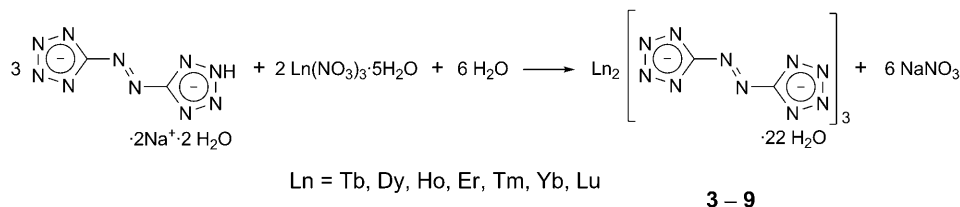
The work with dysprosium – probably the radiochemists' preferred stable element – required special care in our lab. With a total cross-section of $2.7 \cdot 10^3$ barn for the capture of thermal neutrons in the nuclear reaction $^{164}Dy(n,\gamma)^{165}Dy$ and a natural abundance of ^{164}Dy of 28.18%, dysprosium is the element of the periodic table that can be detected with the highest sensitivity by neutron-activation analysis (NAA). The detection limit is *ca.* 10^{-14} $g \cdot g^{-1}$. Also, many other lanthanoids have excellent nuclear properties for NAA. This explains why the preparative work with REE and especially dysprosium compounds in an analytical laboratory that is dedicated to NAA has to be performed with utmost care to avoid contaminations. Even minor explosions of explosive REE compounds would contaminate the lab and thwart future analyses of these elements [30].

Crystal Structures. Since the compounds **3**–**9** are isotypic, only dysprosium salt **4** will be discussed as an example in the following, unless the differences in the compounds justify a separate discussion of all compounds. The structure, numbering scheme, and H-bonding of **4** is illustrated in *Figs. 1* and *2*. For selected data from the data collection and refinement, see *Table 1*.

The salts **3**–**9** are isostructural to the previously reported yttrium salt **2** [21]. Selected bond lengths, angles, and H-bonds are given in *Tables 2* and *3*, respectively. The hydrated Ln^{3+} ions were shown to be eight-coordinated by H_2O molecules in a deformed square antiprismatic configuration. In aqueous solution, the heavy Ln^{III} ions prefer a coordination by eight H_2O molecules in a square antiprismatic coordination mode, see *Persson* and co-workers [7] and refs. cit. therein. According to these publications, the light Ln^{III} ions (lighter than Ho) are nine-coordinated in relatively regular tricapped trigonal-prismatic configurations.

In the crystal structures described in this study, two ZT dianions are present, one with and one without an inversion center. The bonding parameters (see *Table 2* for compound **4**) of the $(ZT)^{2-}$ ions of **3**–**9** are highly similar to previously published crystal structures. For comparison with the literature, the bond lengths of the crystal structures of azobis[1*H*-tetrazol-1-ides] with solely metallic cations were chosen, in
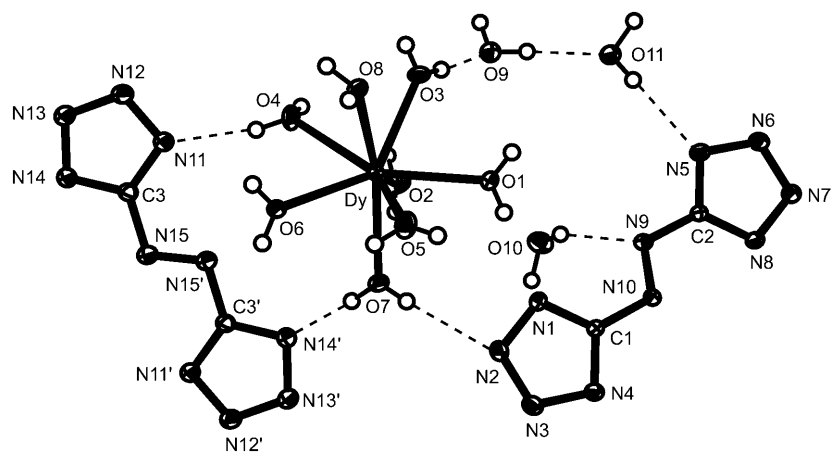
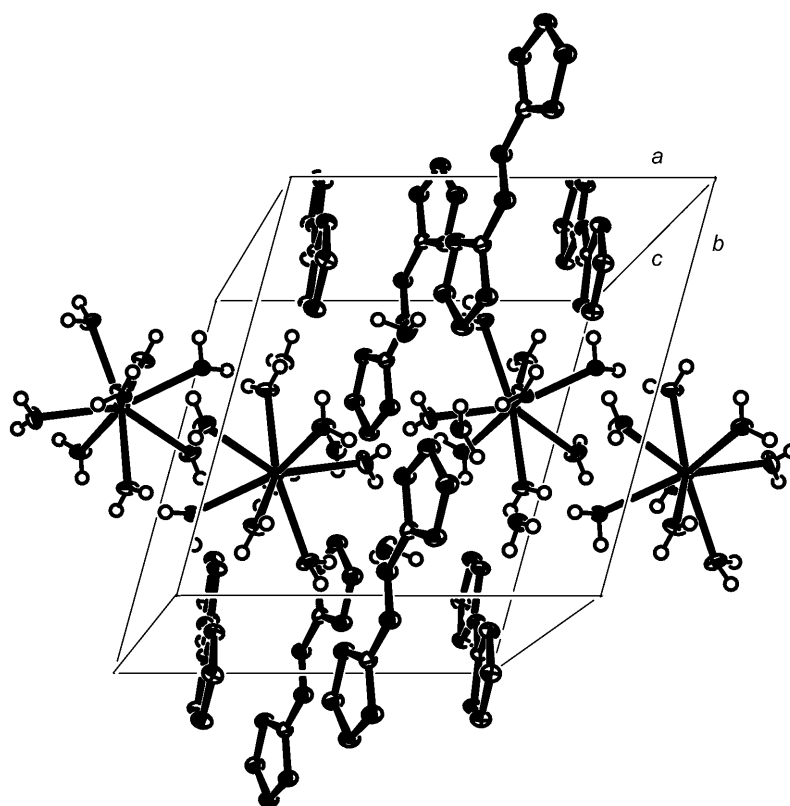Fig. 1. *Structure and intramolecular H-bonding of dysprosium salt* **4**. Thermal ellipsoids represent 50% probability.

Fig. 2. *Stacks of 5,5′-azobis[1H-tetrazol-1-ide] anions intercalated with hydrated Dy³⁺ ions in the unit cell of* **4**. View on (001); thermal ellipsoids represent 50% probability.

Table 1. *Crystallographic Data and Structure Determination Details for Compounds* **3**–**9**. All compounds crystallize in triclinic $P\bar{1}$. The general formula is $[Ln(H_2O)_8]_2(ZT)_3 \cdot 6\,H_2O$, $Z = 1$.

	3	**4**	**5**	**6**	**7**	**8**	**9**
Ln	Tb	Dy	Ho	Er	Tm	Yb	Lu
M_r	1206.45	1213.60	1218.46	1223.12	1226.47	1234.68	1238.54
a [Å]	10.137(2)	10.128(2)	10.119(2)	10.110(2)	10.099(2)	10.096(2)	10.088(2)
b [Å]	10.399(2)	10.384(2)	10.376(2)	10.364(2)	10.359(2)	10.342(2)	10.334(2)
c [Å]	10.462(2)	10.454(2)	10.450(2)	10.443(2)	10.433(2)	10.426(2)	10.425(2)
α [°]	73.09(3)	73.05(3)	73.00(3)	72.95(3)	72.91(3)	72.89(3)	72.87(3)
β [°]	78.64(3)	78.63(3)	78.65(3)	78.67(3)	78.72(3)	78.71(3)	78.73(3)
γ [°]	74.74(3)	74.76(3)	74.76(3)	74.79(3)	74.76(3)	74.82(3)	74.83(3)
V [Å³]	1009.2(3)	1006.0(3)	1003.8(3)	1001.0(3)	998.2(3)	995.8(3)	994.0(3)
ρ_{calc} [g·cm⁻³]	1.985	2.003	2.016	2.029	2.040	2.059	2.069
μ [mm⁻¹]	3.587	3.797	4.025	4.276	4.528	4.780	5.050
Reflns. collected	17226	17204	17162	17037	17093	17087	17029
Ind. reflections	9205	9219	9170	9100	9141	9128	9097
R_{int}	0.025	0.029	0.026	0.032	0.024	0.026	0.025
Obs. reflections	8441	8700	8469	8105	8447	8567	8536
$F(000)$	596	598	600	602	604	606	608
R_1[a])	0.025	0.025	0.024	0.031	0.024	0.024	0.021
wR_2[b])	0.045	0.053	0.044	0.046	0.042	0.049	0.042
Weighting scheme[c])	0.015, 0.3	0.02, 0.5	0.015, 0.4	0.01, 0.5	0.01, 0.5	0.02, 0.4	0.013, 0.4
Goodness-of-fit	1.060	1.111	1.027	1.035	1.066	1.071	1.068
No. of parameters	360	360	360	360	360	360	360

[a]) $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.   [b]) $R_w = [\Sigma(F_o^2 - F_c^2)/\Sigma w(F_o)^2]^{1/2}$.   [c]) $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$, $P = (F_o^2 - 2F_c^2)/3$.

particular Na^+ [21][31], Li^+, Rb^+, Ca^{2+}, Ba^{2+}, Y^{3+} (**2**) [21], Mn^{2+} [32], and Tl^+ (as a crown ether complex) [33] and illustrated in *Fig. 3*. For each bond a–g, two values are given. Bold figures represent the average bond lengths of the ZT ions in **2**–**9**. The figures in brackets represent the average values of ZT ions of all previously published inorganic ZT compounds listed above. The maximum deviations from the average are
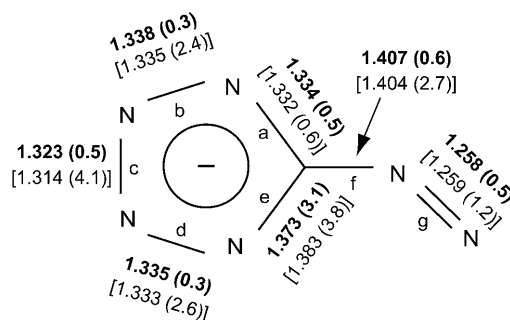

Fig. 3. *Average bond lengths of the ZT ions in* **2**–**9** (bold) *and of all previously published crystal structures of ZTs with a metal cation* (in brackets). The maximum deviations from the mean values, resp., are given in parentheses in rel. percent.

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *in Compound* **4**. Arbitrary atom numbering.

Bond lengths					
Dy−O(1)	2.335(1)	N(2)−N(3)	1.323(2)	N(10)−C(1)	1.400(2)
Dy−O(2)	2.345(2)	N(3)−N(4)	1.336(2)	N(11)−N(12)	1.335(2)
Dy−O(3)	2.359(1)	N(4)−C(1)	1.337(2)	N(1)−C(3)	1.331(2)
Dy−O(4)	2.376(1)	N(5)−C(2)	1.337(2)	N(12)−N(13)	1.319(2)
Dy−O(5)	2.462(2)	N(5)−N(6)	1.337(2)	N(13)−N(14)	1.335(2)
Dy−O(6)	2.338(1)	N(6)−N(7)	1.325(2)	N(14)−C(3)	1.341(2)
Dy−O(7)	2.352(2)	N(7)−N(8)	1.333(2)	N(15)−N(15′)	1.257(2)
Dy−O(8)	2.411(1)	N(8)−C(2)	1.338(2)	N(15)−C(3)	1.412(2)
N(1)−N(2)	1.338(2)	N(9)−N(10)	1.260(2)		
N(1)−C(1)	1.336(2)	N(9)−C(2)	1.405(2)		

Bond angles					
O(1)−Dy−O(2)	80.83(7)	N(5)−N(6)−N(7)	109.6(1)	N(15)−N(15′)−C(3)	112.4(2)
O(1)−Dy−O(3)	71.89(6)	N(6)−N(7)−N(8)	109.6(1)	N(1)−C(1)−N(10)	127.1(1)
O(1)−Dy−O(4)	142.22(6)	N(7)−N(8)−C(2)	104.3(1)	N(4)−C(1)−N(10)	120.5(1)
O(1)−Dy−O(5)	73.47(6)	N(10)−N(9)−C(2)	113.4(1)	N(1)−C(1)−N(4)	112.4(1)
O(1)−Dy−O(6)	145.13(6)	N(9)−N(10)−C(1)	114.1(1)	N(5)−C(2)−N(9)	120.5(1)
O(1)−Dy−O(7)	85.13(6)	N(12)−N(11)−C(3)	104.2(2)	N(8)−C(2)−N(9)	127.3(1)
O(1)−Dy−O(8)	100.57(6)	N(11)−N(12)−N(13)	109.9(2)	N(5)−C(2)−N(8)	112.3(1)
N(1)−N(2)−N(3)	109.5(1)	N(12)−N(13)−N(14)	109.4(2)	N(11)−C(3)−N(14)	112.2(2)
N(2)−N(3)−N(4)	109.7(1)	N(2)−N(1)−C(1)	104.2(1)	N(11)−C(3)−N(15)	128.4(2)
N(3)−N(4)−C(1)	104.2(1)	N(13)−N(14)−C(3)	104.3(2)	N(14)−C(3)−N(15)	119.4(2)
N(6)−N(5)−C(2)	104.1(1)				

given in percent in parentheses. For the calculation of the average bond lengths, only complete $(ZT)^{2-}$ dianions were taken, *i.e.*, identical bond lengths of ions with an inversion center along the N=N bond were counted twice for the calculation.

From *Fig. 3*, one can easily see that the bond lengths within the compounds **2**–**9** are highly similar and subject to only minute fluctuations. Also the mean values of the other azobis[1*H*-tetrazol-1-ides] are similar to those of this study, the maximum deviations, however, are higher in most cases. The most obvious difference was observed with the crystal structure of bis[1,4,7,10,13,16-tetraoxacyclooctadecane)thallium(I)] 5,5′-azobis[1*H*-tetrazol-1-ide] of [33]. In this case, bond g was longer, bond e was very much longer and bonds b, c, d, and f were shorter than the average shown in *Fig. 3*.

The characteristic lanthanoid contraction can be observed with several parameters of the structures of **2**–**9**. For example, the cell volume decreases from 1009.2(3) Å^3 for Tb compound **3** to 994.0(3) Å^3 for Lu compound **9** as shown in *Fig. 4*. The cell volume of the yttrium salt **2** (1004.82(3) Å^3) [21] lies, as expected from the ion radius, between those of the Dy compound **4** and the Ho compound **5**. The minimum and maximum Ln−O distances decrease, according to the lanthanoid contraction, from **3** to **9** as shown in *Table 4*. The Ln−O bond lengths of the lighter yttric earths of this study (Tb, Dy, Ho, and Er) are significantly shorter (up to *ca.* 2.5%) than the respective hydrated ions of recently published solid Ln^{III} trifluoromethanesulfonate salts (EXAFS data) [7]. The heavier lanthanoids of this study (Tm, Yb, and Lu), however, compare somewhat better to these Ln−O bond lengths with deviations of *ca.* 1%.

Table 3. *H-Bonding in* **4**

D–H···A [°]	D–H [Å]	H···A [Å]	D···A [Å]	D–H···A [°]
O(1)–H(11)···O(8)[a]	0.78(4)	2.19(4)	2.959(2)	173(3)
O(1)–H(12)···N(1)	0.74(3)	2.01(3)	2.747(2)	174(4)
O(2)–H(21)···O(10)[b]	0.83(4)	1.95(4)	2.727(2)	155(4)
O(2)–H(22)···O(9)[b]	0.66(4)	2.11(4)	2.743(2)	160(5)
O(3)–H(31)···O(9)	0.84(3)	1.88(3)	2.722(2)	175(3)
O(3)–H(32)···N(8)[c]	0.69(4)	2.13(4)	2.816(2)	174(4)
O(4)–H(41)···O(10)[b]	0.75(3)	2.01(3)	2.758(2)	169(3)
O(4)–H(42)···N(11)	0.80(4)	2.01(4)	2.795(2)	168(4)
O(5)–H(51)···N(7)[d]	0.71(4)	2.21(4)	2.901(2)	166(5)
O(5)–H(52)···N(2)[e]	0.81(4)	2.58(4)	3.376(2)	168(4)
O(6)–H(61)···N(6)[f]	0.75(4)	2.05(4)	2.793(2)	170(4)
O(6)–H(62)···N(4)[e]	0.72(4)	2.13(4)	2.841(2)	169(4)
O(7)–H(71)···N(2)	0.70(4)	2.18(4)	2.880(2)	175(4)
O(7)–H(72)···N(14)[g]	0.82(3)	1.90(3)	2.714(2)	176(3)
O(8)–H(81)···O(11)[a]	0.82(3)	1.87(3)	2.679(2)	169(3)
O(8)–H(82)···N(10)[c]	0.79(3)	2.05(3)	2.841(2)	178(4)
O(9)–H(91)···O(11)	0.84(3)	1.95(3)	2.785(2)	174(3)
O(9)–H(92)···N(13)[h]	0.75(3)	2.13(3)	2.849(2)	161(3)
O(10)–H(101)···N(12)[i]	0.86(3)	1.91(3)	2.775(2)	178(4)
O(10)–H(102)···N(9)	0.81(4)	2.21(4)	2.962(2)	155(4)
O(11)–H(111)···N(5)	0.73(3)	2.13(3)	2.859(2)	175(3)
O(11)–H(112)···N(3)[j]	0.88(4)	1.93(4)	2.796(2)	166(4)

Symmetry codes: [a] $-x, 1-y, 1-z$. [b] $1-x, 1-y, 1-z$. [c] $x, -1+y, z$. [d] $-x, 2-y, 1-z$. [e] $-x, 1-y, 2-z$. [f] $x, -1+y, 1+z$. [g] $1-x, -y, 2-z$. [h] $1-x, -y, 1-z$. [i] $x, 1+y, z$. [j] $x, y, -1+z$.
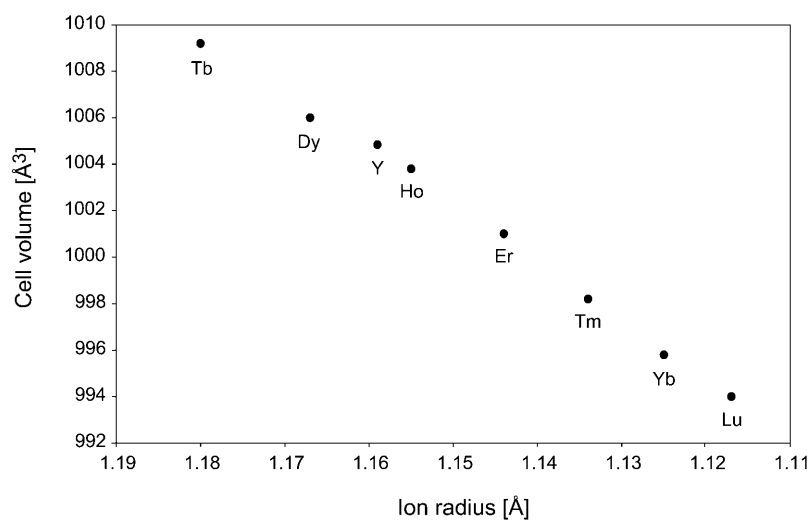

Fig. 4. *Lanthanoid* (REE) *contraction observed with the cell volumina of the salts* **2–9** *of the type* *Ln₂(ZT)₃·22 H₂O. Tb*, **3**; *Dy*, **4**; *Y*, **2**; *Ho*, **5**; *Er*, **6**; *Tm*, **7**; *Yb*, **8**; *Lu*, **9**. All cell-volumina values from this study, except for **2**, taken from [21]. Ionic radii for Ln^{3+} and CN = 8 taken from [43].

Table 4. *Minimum and Maximum Ln–O Bond Lengths* [Å] *in Compounds* **2**–**9**. Data for **2** are taken from [21].

	3	4	2	5	6	7	8	9
Min. Ln–O(1)	2.348(1)	2.335(1)	2.322(2)	2.323(1)	2.312(2)	2.302(1)	2.290(1)	2.282(1)
Max. Ln–O(5)	2.473(1)	2.462(2)	2.450(2)	2.451(2)	2.441(2)	2.430(2)	2.423(2)	2.416(2)

In **3**–**9**, no coordinative bonds exist between the $(ZT)^{2-}$ anions und the Ln^{3+} cations, which is in contrast to the respective ZT salts of Li^+, Na^+, Rb^+, Sr^{2+}, Ba^{2+} [21], and Mn^{2+} [32] as well as to those of the light earths (Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+}) which will be topic of our next publications. By and large, this is in good agreement with the work of *Klein*, *Maggiarosa*, and co-workers [22] who published a similar observation with the 5,5′-bis[1*H*-tetrazol-1-ide] compounds of some selected lanthanoids: only the REE cations heavier than Tb^{3+} form salt-like compounds. For lighter REE cations, the 1*H*-tetrazole ring usually acts as a bridging or chelating ligand in a complex.

Vibrational Spectra. The characteristic vibrational-spectroscopic bands for the isostructural **2** have been reported to be 1403 and 727 cm^{-1} (IR) and 1487 and 1388 cm^{-1} (*Raman*), respectively [21][34]. The compounds of this study exhibited bands in these regions as well. In general, all vibrational spectra of **2**–**9** are extremely similar. The IR spectra of the salts are characterized by absorptions of the ZT anions and the H_2O molecules present in the crystal structure. It is interesting to note that hardly any shift in the absorption spectrum of the anion can be observed. The IR band at 724 cm^{-1} corresponds to the azo group's antisymmetric stretching mode as well as the out-of-plane bending of the 1*H*-tetrazole ring (in-phase), the band at 1402 cm^{-1} to the antisymmetric C–N(1) stretching mode, the IR bands at 1174 cm^{-1} reflect the antisymmetric stretching mode of the 1*H*-tetrazole ring and the 1048 cm^{-1} band corresponds to the antisymmetric in-plane bending of the 1*H*-tetrazole ring. A set of absorptions was calculated and published at the B3YLYP level of theory previously [35][36]. Due to the large number of combination modes in the IR spectra, however, not all modes of the anion are assignable. The strongest IR band is due to the coupling of in-phase and out-of-phase modes of the H_2O ligands, which appear as one broad unresolved band in all spectra. Contrary to the constant frequencies corresponding to the azobis[1*H*-tetrazol-1-ide] anions in **3**–**9**, there is a significant red shift of the stretch vibrations of the H_2O bands around 3599 cm^{-1}, which are not part of the broad and unresolved band, when going from **3** to **9**. This general observation can be interpreted as follows. The nature of the hydrated cation hardly affects the anion which explains that their IR bands remain constant. However, the difference in the volume/charge ratio of the cation does affect the H-bonding and coordination with H_2O molecules. A stronger coordination of the O-atom of the H_2O molecule can be expected in case of a smaller diameter at constant charge. The stronger the coordination in Ln^{3+}–O, the weaker the force constant of the respective H–O bond of the H_2O molecule. This, as a consequence, reduces the frequencies of the related symmetric and antisymmetric stretch vibrations, which is reflected in the red shift observed in case of **9** when compared to **3**. Since in these salts, the minute changes from one cation to the next

heavier one can hardly be spotted, we discuss this shift in the most characteristic band from the salt **3** with the largest cation, Tb^{3+} (3595 cm^{-1}), to the band of the salt **9** with the smallest cation, Lu^{3+} (3599 cm^{-1}), in *Fig. 5*. IR Spectra of hydrated Ln^{3+} ions with similar observations have been the topic of a very recent publication [12]. Unfortunately, the respective region in the IR spectrum has not been discussed in the article by *Klein*, *Maggiarosa*, and co-workers [22] on 1*H*-tetrazole derivatives of some lanthanoids. It would be highly interesting to compare the IR spectra of both studies.
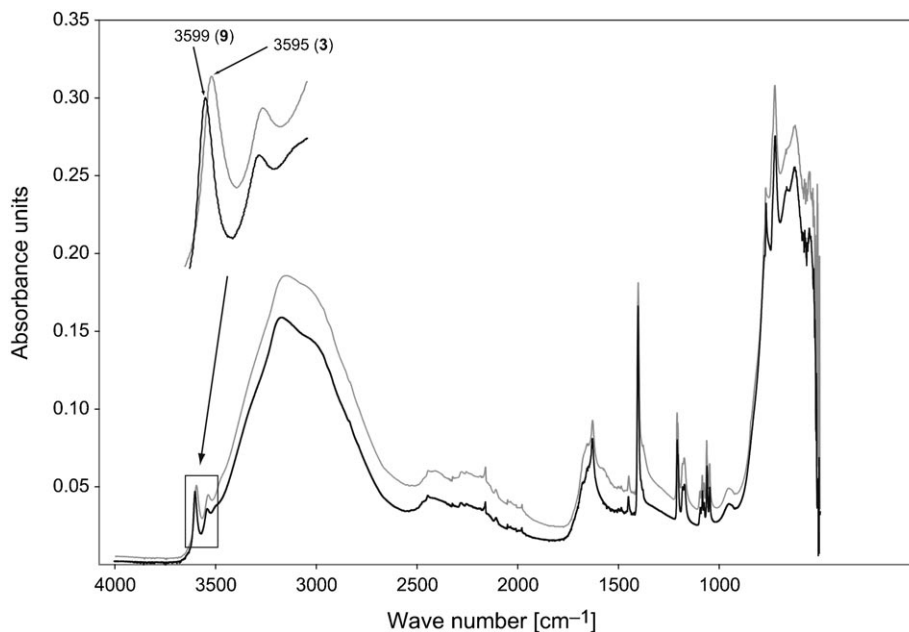
Fig. 5. *IR Spectra of* **3** (grey) *and* **9** (black) *illustrating the shift in the stretching modes of H$_2$O molecules in the ZT salts* **3** *and* **9** *of Tb^{3+} and Lu^{3+}, resp.*

The $(ZT)^{2-}$ anion is known to be very *Raman* active, consequently a couple of the very intense *Raman* bands could be observed and identified, *i.e.*, a symmetric $C-N_{azo}$ stretching mode (around 1386 cm^{-1}) and an $N-N$ stretching mode of the azo group (around 1486 cm^{-1}), respectively, in good agreement with the literature [21].

Conclusion and Outlook. – The synthesis and characterization (including crystal structure and complete vibrational-spectroscopic characterization) of the 5,5′-azo-bis[1*H*-tetrazol-1-ides] of Tb, Dy, Ho, Er, Tm, Yb, and Lu are presented and discussed. This is the first complete structural characterization of pure $(ZT)^{2-}$ salt hydrates of any f-block element. The 'green' synthesis is completely based on H$_2$O, thus avoiding organic solvents. The REE are characterized by only a low toxicity. Therefore, the compounds presented in this study could hypothetically act as environmentally benign energetic materials. This would require partial or complete dehydration of the compounds in order to increase their sensitivity. In a previous study, however, *Klapötke* and co-workers [21] warned that the complete dehydration of similar azobis[1*H*-

tetrazol-1-ide] salts drastically increased their sensitivity resulting in many explosions. In their hydrated form, the title compounds might have potential for electronic applications, such as organic light-emitting diodes (OLEDs).

The comparison of the crystal structures of **3–9** to the previously reported isotypic yttrium salt **2** confirms the close chemical relation of the heavy lanthanoids to the d-block element yttrium (yttric earths). The lanthanoid contraction in several cell parameters such as the cell volume could be observed as expected. Of all yttric earths, all but three members (Eu, Gd, and Sc) of this REE subgroup react in the above-shown reaction, forming the salts of the type $Ln_2(ZT)_3 \cdot 22\,H_2O$. In contrast to yttrium, scandium reacts like a typical transition metal (like, *e.g.*, Cu^{2+}) and yielded a presumably amorphous precipitate under partial decomposition of the $(ZT)^{2-}$ dianion under identical reaction conditions. A similar decomposition by a *Lewis*-acidic metal ion has been described previously with Ce^{4+} [21]. In this whole study, a gadolinium break could be observed in the way that the ZTs of the light and the heavy REE crystallize in different crystal structures. The other crystal structures include the ZT salts of the cerite earths (Ce, Pr, Nd, and Sm) and the light yttric earths (Eu and Gd) as well as two modifications of the La salt which will be the topic of our next publication[2]). *Sine ira et studio.*

Experimental Part

Caution! *Although no problem occurred during the synthesis and handling of the salts investigated in this work, azobis[1H-tetrazol-1-ides] are HEDMs which may explode violently and unexpectedly, especially when anhydrous. Adequate safety precautions have to be taken, especially when these compounds are prepared on a larger scale or set under physical stress like pressure or heat. In particular, we recommend the utilization of leather or* Kevlar® *gloves, face shields, grounded shoes, and ear protection.*

General. All chemicals used in this work were purchased from *Aldrich* or *Merck*, resp., in *p.a.* quality and used as supplied without further purification. IR Spectra: *Bruker-Tensor-27* (*Diamond-ATR*, 1 reflexion) spectrometer; between 4000 and 600 cm^{-1} with a resolution of 1 cm^{-1}; $\tilde{\nu}$ in cm^{-1}. *Raman* Spectra: micro-*Raman* spectrometer *LabRam HR800* (*Horiba Jobin Yvon*) equipped with a charge coupled detector (CCD) and a HeNe laser emitting at 632.8 nm with power set to 14.5 mW at 25°; slit width 100 μm, ensuring a spectral resolution of *ca.* 4 cm^{-1}; $\tilde{\nu}$ in cm^{-1}, relative intensities in % of the most intense peak. Elemental analyses (CHN): *Perkin-Elmer-2400* CHN elemental analyzer; values in wt-%; it is known from many previous studies that highly N-rich compounds sometimes lead to more-than-marginal deviations of their elemental-anal. values due to their extremely high N-content [20][21][37–39].

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[2]) The cell parameters for $Ce_2(ZT)_3 \cdot 24\,H_2O$ are $a = 9.244(1)$, $b = 9.963(1)$, $c = 12.454(1)$ Å, $\alpha = 108.11(1)$, $\beta = 93.89(1)$, $\gamma = 97.33(1)°$, $V = 1074.20(18)$ Å^3, $Z = 2$; cryst. syst. triclinic, space group $P\bar{1}$ (2); for $Gd_2(ZT)_3 \cdot 24\,H_2O$, $a = 9.125(1)$, $b = 9.932(1)$, $c = 12.413(1)$ Å, $\alpha = 107.80(1)$, $\beta = 93.84(1)$, $\gamma = 97.13(1)°$, $V = 1056.27(18)$ Å^3; cryst. syst. triclinic, space group $P\bar{1}$ (2)); for $La_2(ZT)_3 \cdot 21.5\,H_2O$, $a = b = 36.502(5)$, $c = 6.7740(14)$ Å, $V = 7816(2)$ Å^3, $Z = 12$; cryst. syst. trigonal, space group $P3$ (143); for $La_2(ZT)_3 \cdot 18\,H_2O$, $a = 9.473(2)$, $b = 9.863(2)$, $c = 11.020(2)$ Å, $\alpha = 113.50(3)$, $\beta = 92.08(3)$, $\gamma = 107.10(3)°$, $V = 888.5(3)$ Å^3, $Z = 2$; cryst. syst. triclinic, space group $P\bar{1}$ (2).

General Procedure. For the synthesis of the lanthanoid 5,5′-azobis[1*H*-tetrazol-1-ide] docosahydrate salts, **1** (100 mg, 0.41 mmol) was suspended in H_2O (3 ml), and the mixture stirred and heated to $>90°$ on a water bath. As soon as the powder had dissolved, a soln. of the respective $Ln(NO_3)_3 \cdot 5\ H_2O$ (0.27 mmol) in H_2O (1 ml) was added. After *ca.* 5 min of stirring on the water bath, the clear soln. was transferred to a 50 ml polyethylene (PE) vial and closed with an air-tight lid. For easier crystallization, the bottom of the PE vial was scratched several times with an injection needle. The PE vials were stored in a quiet and dark place, and after *ca.* 4–7 d, the crystallization was completed. The product was obtained in the form of large rhombic yellowish crystals. Depending on the color of the cation, the color of the product varied from lemon yellow (for colorless cations due to the yellow color of the $(ZT)^{2-}$ anion) to dark yellow or orange. The crystals were collected from the soln. with tweezers, washed with H_2O and acetone, and dried over $CaCl_2$ in a desiccator.

*Octaaquaterbium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**3**): Yield 71%. Lemon yellow crystals. IR: 3595*m*, 3537*w*, 2160v*w*, 1629*s*, 1449*w*, 1402v*s*, 1209*s*, 1173*m*, 1084*w*, 1062*s*, 1048*m*, 769 (sh), 724*s*. *Raman:* 1492 (39), 1430 (10), 1395 (100), 1370 (3), 1219 (1), 1111 (26), 1093 (21), 1084 (18), 1070 (10), 1058 (3), 941 (5), 742 (1). Anal. calc. for $C_6H_{44}N_{30}O_{22}Tb_2$ (1206.452): C 5.97, H 3.68, N 34.83; found: C 6.35, H 3.41, N 34.37.

*Octaaquadysprosium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**4**): Yield 69%. Yellow crystals. IR: 3595*m*, 3537*w*, 2161*w*, 1630*s*, 1449*w*, 1402v*s*, 1378 (sh), 1209*s*, 1174*m*, 1084*w*, 1062*m*, 1048*m*, 768*m*, 722*s*. *Raman:* 1486 (43), 1422 (12), 1386 (100), 1361 (3), 1101 (19), 1082 (9), 1073 (18), 1059 (12), 935 (3), 923 (3), 731 (1). Anal. calc. for $C_6H_{44}Dy_2N_{30}O_{22}$ (1213.601): C 5.94, H 3.65, N 34.62; found: C 6.14, H 3.16, N 34.67.

*Octaaquaholmium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**5**): Yield 60%. Orange crystals. IR: 3597*m*, 3538*w*, 2160v*w*, 1629*s*, 1450*w*, 1402v*s*, 1209*s*, 1173*m*, 1084*m*, 1062*s*, 1048*m*, 769*m*, 724*s*. *Raman:* 1497 (51), 1433 (14), 1397 (100), 1371 (3), 1215 (1), 1109 (18), 1095 (7), 1086 (27), 1071 (17), 948 (4), 744 (1). Anal. calc. for $C_6H_{44}Ho_2N_{30}O_{22}$ (1218.462): C 5.91, H 3.64, N 34.49; found: C 6.27, H 3.34, N 34.16.

*Octaaquaerbium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**6**): Yield 66%. Orange crystals. IR: 3597*s*, 3538*w*, 2161v*w*, 1629*s*, 1451*w*, 1403v*s*, 1209*s*, 1173*m*, 1084*w*, 1062*m*, 1049*m*, 769*m*, 725*s*. *Raman:* 1485 (38), 1419 (13), 1385 (100), 1360 (3), 1206 (1), 1099 (28), 1081 (14), 1072 (18), 1058 (11), 933 (3), 922 (4), 730 (1). Anal. calc. for $C_6H_{44}Er_2N_{30}O_{22}$ (1223.121): C 5.89, H 3.63, N 34.35; found: C 6.18, H 3.18, N 34.09.

*Octaaquathulium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**7**): Yield 63%. Lemon yellow crystals. IR: 3597*m*, 3539*w*, 2160v*w*, 1630*m*, 1450v*w*, 1403v*s*, 1209*s*, 1173*m*, 1084*w*, 1062*m*, 1048*m*, 769*m*, 725*s*. *Raman:* 1494 (49), 1431 (13), 1394 (100), 1369 (3), 1107 (17), 1091 (5), 1082 (24), 1067 (16), 944 (4), 741 (1). Anal. calc. for $C_6H_{44}N_{30}O_{22}Tm_2$ (1226.470): C 5.88, H 3.62, N 34.26; found: C 6.25, H 3.32, N 33.82.

*Octaaquaytterbium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**8**): Yield 63%. Lemon yellow crystals. IR: 3598*s*, 3540*w*, 2160v*w*, 1629*s*, 1451*w*, 1403v*s*, 1209*s*, 1173*m*, 1084*m*, 1062*s*, 1048*m*, 770*m*, 725*s*. *Raman:* 1496 (46), 1431 (14), 1396 (100), 1371 (3), 1111 (21), 1093 (9), 1085 (20), 1069 (13), 945 (4), 743 (1). Anal. calc. for $C_6H_{44}N_{30}O_{22}Yb_2$ (1234.681): C 5.84, H 3.59, N 34.03; found: C 6.21, H 3.27, N 34.46.

*Octaaqualutetium(3+) Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:3:6)* (**9**): Yield 68%. Lemon yellow crystals. IR: 3599*s*, 3538 (sh), 2160v*w*, 1630*s*, 1451*w*, 1403v*s*, 1210*s*, 1174*m*, 1084*w*, 1062*m*, 1048*m*, 769*m*, 725*s*. *Raman:* 1497 (49), 1433 (14), 1397 (100), 1372 (3), 1219 (1), 1109 (18), 1093 (8), 1085 (24), 1070 (16), 947 (4), 935 (2), 744 (1). Anal. calc. for $C_6H_{44}Lu_2N_{30}O_{22}$ (1238.541): C 5.82, H 3.58, N 33.93; found: C 6.24, H 3.27, N 33.57.

*Reaction of Scandium Nitrate and Disodium 5,5′-Azobis[1*H*-tetrazolide].* In this reaction, a lemon yellow, fine-grained precipitate was formed immediately, and gas was generated (supposingly N_2 from the decomposition of the ZT ion).

X-Ray Crystallography[3]). Crystals were obtained as described above and measured at 200 K. Data were collected on a *Nonius KappaCCD* diffractometer (graphite monochromatized MoK_{α} radiation, λ 0.71073 Å) equipped with a 0.3 mm monocapillary optics collimator. Atomic coordinates were taken from **2** [21] as a starting model. For structure solutions by direct methods and the structure refinements, the programs SHELXS-97 [40] and SHELXL-97 [41] were used, resp. Absorption correction was done by evaluation of partial multiscans. Thermal ellipsoids in ORTEP [42] plots represent a 50% probability.

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