Nitrogen-Rich Compounds of the Lanthanoids: The 5,5′-Azobis[1*H*-tetrazol-1-ides] of the Light Rare Earths (Ce, Pr, Nd, Sm, Eu, Gd)

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On the occasion of *Carl Auer von Welsbach*'s 150th birthday in 2008, we investigated the 5,5′-azobis[1*H*-tetrazol-1-ides] ($C_2N_{10}^{2-}$; $(ZT)^{2-}$) of the light lanthanoids (Ln) cerium, praseodymium, neodymium, samarium, europium, and gadolinium. Their synthesis was performed by crystallization from aqueous solutions of disodium 5,5′-azobis[1*H*-tetrazol-1-ide] and the respective lanthanoid nitrate. All compounds are isotypic (triclinic space group *P*-1) and crystallize according to the general formula $[Ln(H_2O)_7]_2(ZT)_3 \cdot 10\,H_2O$. The crystal structures of all compounds were determined. A distinct lanthanoid contraction could be established, clearly observable by the decrease in the bond lengths in the $LnNO_7$ polyhedra from the Ce to the Gd compound. Further, and in contrast to the previously published 5,5′-azobis[1*H*-tetrazol-1-ides] of the heavy yttric earths, the light Ln cations in this study are coordinated not only by H_2O molecules but also by one $(ZT)^{2-}$ anion. Further characterization was performed by vibrational (IR and *Raman*) spectroscopy and elemental analysis.

Introduction. – The lanthanoids (Ln) are an interesting group of elements with respect to their applicability in various fields of science and technology. The term 'lanthanoid' comprises the elements of the f-block elements of the 6th period of the periodic table (La – Lu). The chemically closely related elements scandium and yttrium form, together with the lanthanoids, the so-called 'Rare Earth Elements' (REE). The 17 REE share similar chemical properties. This can be used, for example, in earth sciences, as their concentration is a highly reliable indicator that can be used for both the investigation of geochemical processes as well as the establishment of a chemical fingerprint, *e.g.*, for provenance studies [1]. Some minerals (*e.g.*, cerite, orthite, monazite, and bastnäsite) preferably accumulate cerium and the light REE, whereas other minerals (*e.g.*, gadolinite, xenotime, euxenite, yttrialite, and fergusonite) mainly accumulate yttrium and heavier REE. The elements cerium and yttrium, respectively, are the main REE constituents in these minerals and are eponymous for both subgroups of the lanthanoids: 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). Accordingly, the mineral cerite with the very general formula $Ce^{III}_9Fe^{III}(SiO_4)_6[(SiO_3(OH)](OH)_3$ not only contains cerium but also other lanthanoids, preferably the light ones. In the early 1840s, *Carl*

Gustav Mosander 'isolated' from cerite earth what he erroneously believed to be a new element: salts of a novel substance, which he named 'didymium', Greek for 'twin' (of lanthanum). Ironically, the lanthanum's 'twin' didymium turned out to be a twin itself: the Austrian chemist and pioneer in the REE chemistry, *Carl Auer von Welsbach* (1858–1929), isolated the elements praseodymium (Greek for 'green twin') and neodymium ('new twin') from didymium in 1885 by fractional crystallization. By using separation techniques like this, it took dozens of repetitions to separate two REE compounds. The trickiest challenge in this respect was, in general, the separation of two neighboring elements in the periodic table as they have very similar ionic radii, thus complicating their separation. However, already at *Auer von Welsbach*'s time, it was comparably easy to separate the 'neighboring' elements neodymium (today known to have the atomic number 60) and samarium (62). As a consequence, and after hundreds of experiments searching for the missing link, *Auer von Welsbach* postulated the absence of even traces of the element with the atomic number 61 in nature [2], without having an explanation for this phenomenon at first glance. Indeed, the missing element – promethium (Pm) – was discovered as a short-lived and thus highly radioactive fission product of uranium not earlier than in 1945. And, indeed, it does not exist naturally [3]. If viewed from a formal rather than from a chemical point of view, the only natural source of Pm is the spontaneous fission of the actinides, yielding a few atoms Pm per gram uranium or thorium only. In the authors' opinion, the correct prediction of the complete absence of an element can be regarded as a more noteworthy merit than even the discovery of an element. The present study was undertaken in memory of *Carl Auer von Welsbach* on the occasion of his 150th birthday which was celebrated by the Austrian scientific community in 2008.

This study is on novel N-rich compounds of the lanthanoids, a field with very recent advances [4][5]. N-Rich heterocycles such as tetrazoles are of interest in coordination chemistry. Due to their extremely low-lying π^*-orbtials, they are excellent π-acceptors [6][7]. Such compounds have the potential to serve with their electrochemical or optical properties, in particular as electronic devices [8–10]. Further, they may be interesting with respect to their luminescent or nonlinear optic properties [4][11]. The preparation of tetrazoles is performed in straightforward 'click chemistry' reactions [4][12].

N-Rich, energetic ionic liquids based on lanthanoid nitrate complex anions have been suggested for propellants recently [5]. Interestingly, these compounds are promising propellants in spite of the high relative atomic mass of the lanthanoids (which is usually a drawback to propellants, see [13]), obviously due to the high content of volatile low-atomic-number constituents in the compounds (high N-content in the organic cations, strong oxidizers in the anions). Tetrazole derivatives are one of the most promising class of compounds for novel energetic materials and the topic of very recent research, see, *e.g.*, [5][13–21].
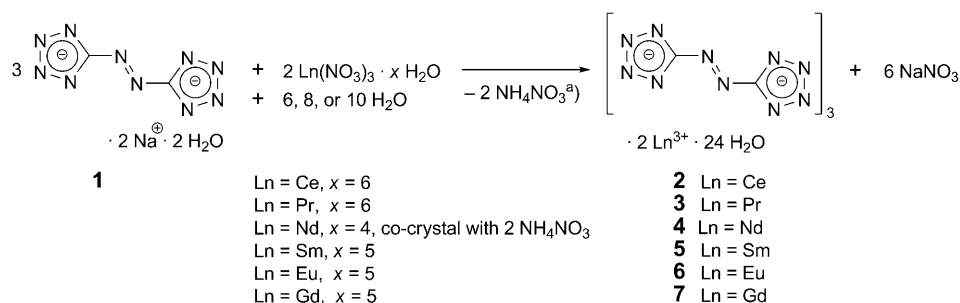
This article is the second contribution of our work on N-rich compounds of the lanthanoids, and follows [22]. In the present study, we report on the synthesis, crystal structures, and vibrational spectroscopy of the isotypic 5,5′-azobis[1*H*-tetrazol-1-ides] ((ZT)$^{2-}$) of the type [Ln$_2$(ZT)$_3$]·24 H$_2$O, where Ln = Ce, Pr, Nd, Sm, Eu, and Gd (see **2**–**7**). The synthesis of several ZT salts of the light lanthanoids, in particular those of La, Ce, Nd, and Gd, has been attempted previously [23]. Crystal structures, however,

could not be obtained in that work, and only for the La and Ce salts elemental analytical values were given, allowing the rough estimation of the H_2O content in the compounds.

Results and Discussion. – *Synthesis.* **Caution!** *Although no problem occurred during the synthesis and handling of the salts investigated in this work, azobis[1H-tetrazol-1-ides] are high-energy density materials 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.*

In contrast to the previously attempted, ineffective metathesis reactions (for $La_2(ZT)_3$, $Ce_2(ZT)_3$ (**2**), $Nd_2(ZT)_3$ (**4**), and $Gd_2(ZT)_3$ (**7**) by the reaction of Ba(ZT) and the respective $Ln_2(SO_4)_3$ [23], we synthesized the title compounds by a simple crystallization reaction from the respective REE nitrate and disodium 5,5′-azobis[1*H*-tetrazol-1-ide] dihydrate (**1**) in aqueous solution at elevated temperature in the initial phase of the reaction (*Scheme*). After five days, crystallization started and led to a pure, crystalline product with a satisfactory yield (between 25 and 67%). The yield was smaller than in the case of the previously studied heavier and more acidic REE [22]. This fact evidences that acidic decomposition of the $(ZT)^{2-}$ by the *Lewis* acidic Ln^{3+} cannot be responsible for the lower yield. Only in the reaction with Sc^{3+} – the smallest REE ion – typical signs of acidic decomposition of $(ZT)^{2-}$ were observed (evolving N_2 gas) [22].

Scheme. *Synthesis of the ZT Salts by Crystallization from Aqueous Solutions*

Ln = Ce, x = 6	**2** Ln = Ce
Ln = Pr, x = 6	**3** Ln = Pr
Ln = Nd, x = 4, co-crystal with 2 NH_4NO_3	**4** Ln = Nd
Ln = Sm, x = 5	**5** Ln = Sm
Ln = Eu, x = 5	**6** Ln = Eu
Ln = Gd, x = 5	**7** Ln = Gd

a) In the case of Ln = Nd.

Disodium 5,5′-azobis[1*H*-tetrazol-1-ide] dihydrate (**1**) was prepared according to *Thiele* [24] and *Singh et al.* [25] by oxidation of 1*H*-tetrazol-5-amine monohydrate with $KMnO_4$ in aqueous NaOH solution. Compound **1** was obtained as a very pure product (see elemental analysis in [22]), suitable as a starting material for the attempted syntheses. We used Na_2ZT in the form of the dihydrate instead of the pentahydrate that has been used in previous studies on ZT compounds as a starting material. The dihydrate was obtained by further dehydration under high vacuum and careful heating, as described in our previous study [22]. The use of the dihydrate offers no advantage or disadvantage because it is as stable as the pentahydrate and very soluble in H_2O as well.

However, we need to warn that dehydration must not yield a completely H_2O-free product, because H_2O-free ZT salts are highly sensitive and explosive [23].

In laboratories like ours, dedicated to the preparation of samples for neutron activation analysis, the work with REE must be performed with utmost care, as many of them have an extremely high cross section for the capture of thermal neutrons (especially Eu and Gd in this study). A contamination of the lab (and consequently of future samples) with these elements may cause major disturbances in future analyses [26].

Compared to the ZTs of the heavy yttric earths (prepared by an analogous synthesis) [22], the yield was somewhat smaller (*ca.* 70 *vs.* 25 – 67%, resp.). The crystals of **2 – 7** are generally smaller than the crystals of heavy yttric earth ZTs, they are brittle and of nonuniform shape. Our crystalline products **2 – 7** did not decompose (by the loss of H_2O and acidic decomposition of the ZT) as dramatically as described in [23]. If stored in the mother liquor, they last for at least months. Even if stored as a pure compound in air-tight vials, the typical signs of decomposition (loss of color) could not be observed either after several months. This increased stability may be due to the advantageous surface-to-volume ratio of larger crystals compared to the powder obtained by *Klapötke* and co-workers [23].

Elemental Analyses. As stated in the *Exper. Part*, elemental analyses of N-rich compounds are generally regarded as tricky, because, even for very pure compounds, the values obtained may deviate significantly from the calculated ones. This phenomenon was also observed in the very pure, crystalline materials analyzed in this study and previously in [22]. The values for N were in a good or at least acceptable range around the theoretical values. The C values, however, were found a little increased, whereas the H values appear a little decreased compared to the calculated values. This systematic deviation has already been observed in *Klapötke* and co-workers' previous study [23] – with consequences concerning the calculation of the H_2O content in the cerium compound (presumably **2**): *Klapötke* and co-workers found the values C 6.8, H 2.8, and N 36.6%. They consequently calculated the number of H_2O molecules of crystallization to be 14 – 18. From the crystal structure analysis of this study, however, we know that the true value is six to ten H_2O molecules higher, namely 24, if we assume that *Klapötke* and co-workers' compound was identical with this study's **2** (calculated values C 5.98, H 4.02, and N 34.88%). Elemental analysis alone, therefore, provides only unsufficient information about the title compounds.

Crystal Structures. All 5,5′-azobis[1*H*-tetrazol-1-ides] of the light and trivalent lanthanoids Ce, Pr, Nd, Sm, Eu, and Gd have isotypic crystal structures. Therefore, only one compound will be discussed in detail unless significant differences justify a separate discussion. One of those differences, due to the lanthanoid contraction, is the decrease of the cell volume from **2** to **7** (see *Table 1*). The lanthanoid contraction is the consequence of the poor shielding between the nucleus and the $5s^2 5p^6$ valence-shell by the 4f electrons. In contrast to other groups of elements in the periodic table, the ionic radii of the lanthanoids and actinoids, therefore, decrease with increasing atomic number.

The structure and numbering scheme of **2** are illustrated in *Fig. 1*. The three-dimensional packing in the crystal is shown in *Fig. 2*. The Ln cations are eight-coordinated (distorted tetragonal antiprisms) to seven O-atoms of H_2O molecules and

Table 1. *Crystallographic Data and Structure-Determination Details for Compounds* **2** – **7**. *All compounds crystallize in the triclinic space group P*-1. *The general formula is* $[Ln(H_2O)_7]_2(ZT)_3 \cdot 10\,H_2O$, $Z = 1$ *(number of molecules in the unit cell).*

	2	**3**	**4**	**5**	**6**	**7**
Ln	Ce	Pr	Nd	Sm	Eu	Gd
M_r [g·mol^{-1}]	1204.87	1206.45	1213.11	1225.43	1228.55	1239.13
a [Å]	9.244(1)	9.225(1)	9.206(1)	9.161(1)	9.142(1)	9.125(1)
b [Å]	9.963(1)	9.961(1)	9.956(1)	9.942(1)	9.938(1)	9.932(1)
c [Å]	12.454(1)	12.449(1)	12.442(1)	12.423(1)	12.418(1)	12.413(1)
α [°]	108.11(1)	108.07(1)	108.05(1)	107.94(1)	107.86(1)	107.80(1)
β [°]	93.89(1)	93.89(1)	93.86 (1)	93.83(1)	93.83(1)	93.84(1)
γ [°]	97.33(1)	97.32(1)	97.27(1)	97.18(1)	97.15 (1)	97.13(1)
V [Å^3]	1074.2(2)	1071.6(2)	1068.7(2)	1061.4(2)	1058.9(2)	1056.3(2)
$\rho_{calc.}$ [g·cm^{-3}]	1.863	1.870	1.885	1.917	1.927	1.948
μ [mm^{-1}]	2.203	2.358	2.514	2.852	3.047	3.225
Reflections collected	18303	18267	18130	18079	18041	17958
Ind. reflections	9791	9762	9689	9663	9636	9585
R_{int}	0.024	0.024	0.041	0.029	0.026	0.025
Obs. reflections	8866	8866	7773	8499	8664	8606
$F(000)$	602	604	606	610	612	614
R_1[a])	0.030	0.032	0.056	0.038	0.033	0.033
wR_2[b])	0.055	0.062	0.074	0.066	0.061	0.060
Weighting scheme[c])	0.020, 0.50	0.025, 0.75	0.025, 0.50	0.025, 0.75	0.025, 0.75	0.025, 0.75
Goodness of fit	1.105	1.064	1.069	1.074	1.048	1.042
No. of parameters	369	369	369	369	369	369
CCDC Number	722671	722672	722673	722674	722675	722676

[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]) $w = [\sigma_c^2(F_o^2) + (xP)^2 + yP]^{-1}$,　$P = (F_o^2 - 2F_c^2)/3$.

to one N-atom. The coordination bonds from Ln to N(1) exhibit a zig-zag-like structure. The $(ZT)^{2-}$ anions are packed in a stacked structure with intercalated hydrated Ln^{3+} cations.

The previously mentioned lanthanoid contraction can be cleary observed in the bond lengths of the $LnNO_7$ polyhedron. With increasing charge density – a result of decreasing ionic radii at constant trivalent charge – the bond lengths of the central Ln ion to its ligands become smaller. This is true for the ligating H_2O molecules (O(1) to O(7)) as well as for the tetrazole ligand, as shown in *Fig. 3*. The decrease in the bond lengths in the complex is almost linear (for Ln−N(1): regression line $y = -0.0122x + 2.6494$, coefficient of determination $R^2 = 0.9971$; for the average Ln−O bonds: $y = -0.0143x + 2.505$, $R^2 = 0.9972$). According to the regression lines of *Fig. 3*, the bond lengths in the respective promethium compound can be predicted. For example, Pm−N(1) was calculated to be 2.60 Å. A synthesis of this compound is not feasible from several points of view: Even disregarding the consequences with respect to radiation protection for the experimenters and the commercial unavailability of any Pm starting material, we also doubt that macroscopic amounts of such a highly radioactive substance can be used as a starting material for the synthesis of N-rich compounds
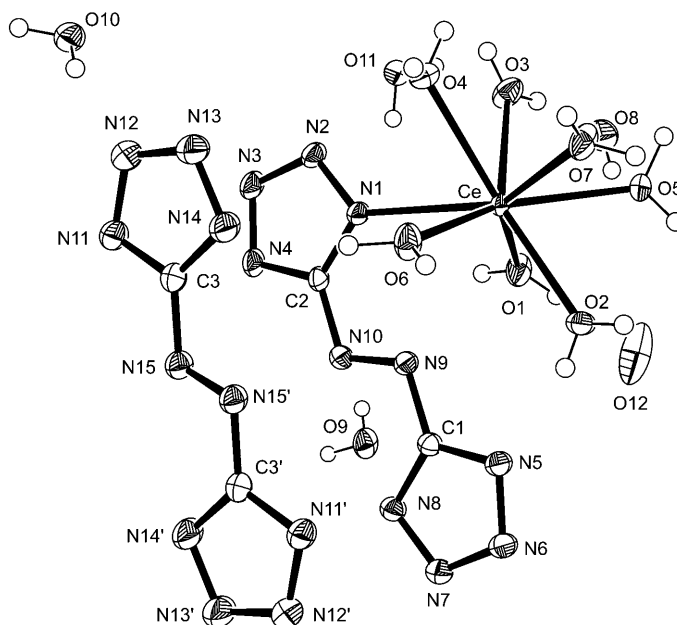
Fig. 1. *X-Ray crystal structure of* **2**. Thermal ellipsoids represent 50% probability. Arbitrary atom numbering.

without causing radiolytic disintegration of the $(ZT)^{2-}$ anion. Even the measurement of a single crystal certainly cannot be performed on a regular X-ray diffractometer due to the interferences of the highly active substance with the CCD detector.

The trend of the decreasing Ln–O bond lengths observed is in good agreement with recent (but randomly chosen) literature on crystal structures of aqua complexes of the respective lanthanoids. The deviation of this study compared with the reported Ln–O bond length (or the average of all bond lengths in case of multiple complexation by H_2O) is less than 2.5% (relative), for the selected structure reports [27–32].

A comprehensive selection of bond lengths and angles found in the cerium compound **2** is compiled in *Table 2*. For all other compounds studied, *i.e.*, **3–7**, only the bond lengths and angles of the $(ZT)^{2-}$ ligand and anion are given in *Table 3*, showing that both parameters found in **2–7** are extremely similar. Only minute deviations (without a significant trend) can be observed. This is also true for the angle N(2)–N(1)–C(2) (N(1) being the contact atom for the coordination bond to the Ln ions). Due to the lanthanoid contraction and the decreasing bond length between Ln and N(1), one might expect changes from **2** to **7** affecting the angle N(2)–N(1)–C(2) as a consequence of the increasing force on the Ln–N(1) bond from **2** to **7**. This angle, however, does not become significantly more acute with increasing atom number. The angle in the samarium compound **5** is, for example, even more obtuse than the angle in the neodymium compound **4** or the praseodymium compound **3**. The coordinating $(ZT)^{2-}$ ligand is, therefore, not affected by the lanthanoid contraction.
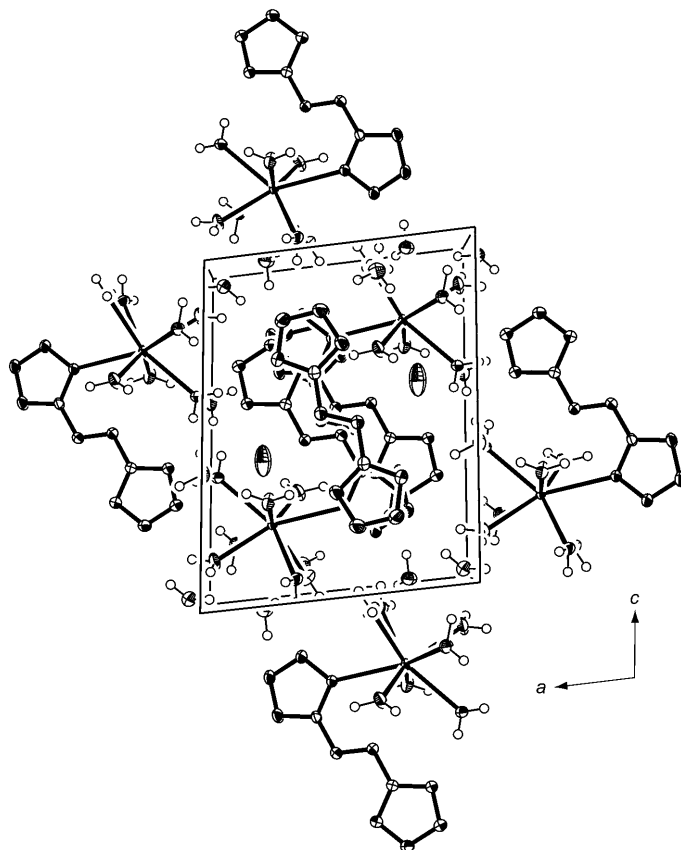
Fig. 2. *Stacks of 5,5′-azobis[1H-tetrazol-1-ide] anions intercalated with hydrated Ce³⁺ ions in the unit cell of* **2**. Perspectivic view *ca.* on (010), thermal ellipsoids represent 50% probability.

With remarkable consistency, all compounds showed a disordered H_2O molecule (O(12)) in the crystal structure. Due to the disorder, it was impossible to calculate the position of the respective H-atoms for this O-atom. In principle, a local symmetry violation (centrosymmetric – noncentrosymmetric ambiguity) [33] could be a possible reason for this effect as well, but a definitive solution of this problem cannot be offered here. The effect described in [33] was observed with purely organic molecules and, therefore, can not be translated to our heavy-atom compounds in equal measure. If it truly is a static disorder, however, we believe that H-bonds may be responsible for it, in particular O(1)−H(12)···O(12) (O(1)···O(12) = 2.751(3) Å) as well as O(12)−H(12)x···O(9) (O(9)···O(12) = 2.887(3) Å). Including these, half of the H-bonds present in the compounds is found between the H_2O molecules (O(3)−H(31)··· O(4), O(3)−H(32)···O(8), O(4)−H(41)···O(11), O(5)−H(52)···O(10), O(6)−H(62)···O(9), O(7)−H(71)···N(3), O(7)−H(72)···O(10), O(9)−H(92)··· O(9), O(10)−H(101)···O(11), and O(11)−H(112)···O(8), in addition to the previously mentioned). For the other half, N-atoms of the (ZT)²⁻ ions act as H-bond
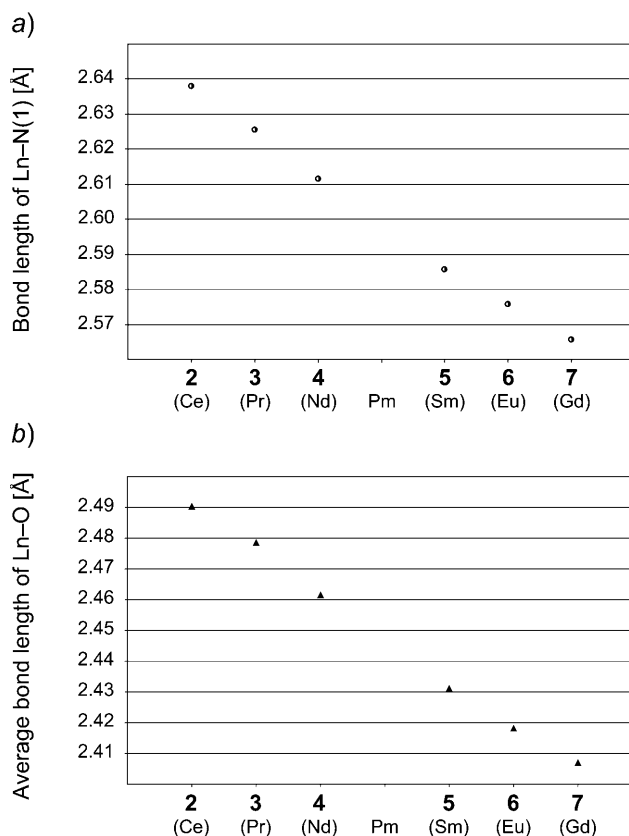
a)

b)

Fig. 3. *Lanthanoid contraction observed from **2** to **7** for* a) *the bond length of Ln−N(1) and* b) *the average of all seven Ln−O bond lengths per compound*

acceptors (in particular O(1)−H(11)···N(8), O(2)−H(21)···N(5), O(2)−H(22)···N(4), O(4)−H(42)···N(2), O(5)−H(51)···N(6), O(6)−H(61)···N(14), O(7)−H(71)···N(3), O(8)−H(82)···N(13), O(9)−H(91)···N(11), O(10)−H(102)···N(12), and O(11)−H(111)···N(7)).

In good agreement with a previous study on REE compounds of 5-substituted tetrazolides [4], the 5,5′-azobis[1*H*-tetrazol-1-ides] of this study act as ligands to the light trivalent cations Ce, Pr, Nd, Sm, Eu, and Gd, whereas the respective compounds of the heavier yttric earths (Tb, Dy, Ho, Er, Tm, Yb, and Lu) are built up as salt-like compounds without a coordination bond between the metal ions and the $(ZT)^{2-}$ anions [22]. In this respect, the light lanthanoids thus behave like the ZT compounds of Li^+ [23], Na^+ [23][25], Rb^+, Sr^{2+}, Ba^{2+} [23], and Mn^{2+} [34].

Vibrational Spectra. The IR spectra of compounds **2**–**7** are very similar. This also holds true for the comparison with the previously published representatives of the yttric earths [22]. Most of the strong modes appear in both studies. They can be assigned as discussed in [22]. Only few additional (weak) bands appeared in the present study, for

Table 2. *Selected Bond Lengths* [Å] *and Angles* [°] *of the Cerium Complex* **2**

Bond lengths			
Ce−O(1)	2.477(2)	N(5)−C(1)	1.334(2)
Ce−O(2)	2.482(1)	N(6)−N(7)	1.326(2)
Ce−O(3)	2.502(2)	N(7)−N(8)	1.332(2)
Ce−O(4)	2.544(1)	N(8)−C(1)	1.338(2)
Ce−O(5)	2.522(2)	N(9)−N(10)	1.263(2)
Ce−O(6)	2.468(2)	N(9)−C(1)	1.407(2)
Ce−O(7)	2.438(2)	N(10)−C(2)	1.399(2)
Ce−N(1)	2.638(1)	N(11)−C(3)	1.337(2)
N(1)−N(2)	1.335(2)	N(11)−N(12)	1.333(2)
N(1)−C(2)	1.339(2)	N(12)−N(13)	1.320(2)
N(2)−N(3)	1.321(2)	N(13)−N(14)	1.340(2)
N(3)−N(4)	1.335(2)	N(14)−C(3)	1.331(2)
N(4)−C(2)	1.335(2)	N(15)−C(3)	1.404(2)
N(5)−N(6)	1.334(2)	N(15)−N(15′)	1.259(2)

Bond angles			
O(1)−Ce−O(2)	84.98(5)	O(7)−Ce−N(1)	143.97(5)
O(1)−Ce−O(3)	76.64(5)	N(2)−N(3)−N(4)	110.0(1)
O(1)−Ce−O(4)	135.61(4)	N(3)−N(4)−C(2)	104.1(1)
O(1)−Ce−O(5)	68.76(5)	N(6)−N(5)−C(1)	104.3(1)
O(1)−Ce−O(6)	130.49(5)	N(5)−N(6)−N(7)	109.5(1)
O(1)−Ce−O(7)	139.90(5)	N(6)−N(7)−N(8)	109.6(1)
O(1)−Ce−N(1)	75.26(5)	N(7)−N(8)−C(1)	104.2(1)
O(2)−Ce−O(3)	142.80(5)	N(10)−N(9)−C(1)	112.0(1)
O(2)−Ce−O(4)	139.32(5)	N(9)−N(10)−C(2)	112.4(1)
O(2)−Ce−O(5)	73.65(5)	N(12)−N(11)−C(3)	104.5(1)
O(2)−Ce−O(6)	81.01(5)	N(11)−N(12)−N(13)	109.4(2)
O(2)−Ce−O(7)	75.56(5)	N(12)−N(13)−N(14)	109.7(2)
O(2)−Ce−N(1)	125.93(4)	N(2)−N(1)−C(2)	104.3(1)
O(3)−Ce−O(4)	67.20(5)	Ce−N(1)−C(2)	126.9(1)
O(3)−Ce−O(5)	69.62(5)	Ce−N(1)−N(2)	128.8(1)
O(3)−Ce−O(6)	135.04(5)	N(1)−N(2)−N(3)	109.4(1)
O(3)−Ce−O(7)	98.26(5)	N(13)−N(14)−C(3)	104.2(2)
O(3)−Ce−N(1)	80.34(4)	N(15′)−N(15)−C(3)	112.8(1)
O(4)−Ce−O(5)	117.93(5)	N(8)−C(1)−N(9)	127.5(1)
O(4)−Ce−O(6)	69.96(5)	N(5)−C(1)−N(9)	120.2(1)
O(4)−Ce−O(7)	72.35(5)	N(5)−C(1)−N(8)	112.3(1)
O(4)−Ce−N(1)	74.09(4)	N(4)−C(2)−N(10)	121.1(1)
O(5)−Ce−O(6)	146.80(5)	N(1)−C(2)−N(4)	112.3(1)
O(5)−Ce−O(7)	72.21(5)	N(1)−C(2)−N(10)	126.7(1)
O(5)−Ce−N(1)	137.21(5)	N(11)−C(3)−N(15)	120.5(1)
O(6)−Ce−O(7)	81.05(5)	N(14)−C(3)−N(15)	127.4(2)
O(6)−Ce−N(1)	75.47(4)	N(11)−C(3)−N(14)	112.2(2)

example the weak band at 2444 cm^{-1}, which was even weaker for heavy yttric earths (and has not been listed there). The modes corresponding to the vibrations of the Ln−N bond can be expected in the region of the low wavenumbers and could not be observed by ATR (attenuated total reflection) spectroscopy. The peaks in the

Table 3. *Bond Lengths* [Å] *and Angles* [°] *of the 5,5′-Azobis[1*H-*tetrazolato] Ligand and the 5,5′-Azobis[1*H-*tetrazol-1-ide] Ion of* **3**–**7**

	3 (Pr)	**4** (Nd)	**5** (Sm)	**6** (Eu)	**7** (Gd)
N(1)−N(2)	1.338(2)	1.337(3)	1.340(2)	1.338(2)	1.337(2)
N(1)−C(2)	1.342(2)	1.344(3)	1.339(2)	1.339(2)	1.340(2)
N(2)−N(3)	1.316(2)	1.313(3)	1.316(2)	1.314(2)	1.315(2)
N(3)−N(4)	1.338(2)	1.338(3)	1.337(3)	1.335(2)	1.337(2)
N(4)−C(2)	1.334(2)	1.336(3)	1.335(3)	1.334(2)	1.332(2)
N(5)−N(6)	1.335(2)	1.337(3)	1.333(2)	1.337(2)	1.335(2)
N(5)−C(1)	1.332(2)	1.330(3)	1.331(3)	1.329(2)	1.331(2)
N(6)−N(7)	1.325(2)	1.325(3)	1.324(3)	1.323(2)	1.325(2)
N(7)−N(8)	1.333(2)	1.331(3)	1.335(2)	1.333(2)	1.333(2)
N(8)−C(1)	1.340(2)	1.340(3)	1.337(2)	1.343(2)	1.342(2)
N(9)−N(10)	1.262(2)	1.269(3)	1.264(2)	1.264(2)	1.260(2)
N(9)−C(1)	1.405(2)	1.406(3)	1.407(2)	1.403(2)	1.405(2)
N(10)−C(2)	1.399(2)	1.396(3)	1.399(2)	1.400(2)	1.402(2)
N(11)−C(3)	1.333(2)	1.331(3)	1.333(3)	1.336(3)	1.334(3)
N(11)−N(12)	1.335(2)	1.336(3)	1.335(3)	1.333(3)	1.334(3)
N(12)−N(13)	1.317(3)	1.318(4)	1.315(3)	1.316(3)	1.315(3)
N(13)−N(14)	1.341(3)	1.345(3)	1.345(3)	1.341(3)	1.341(3)
N(14)−C(3)	1.333(3)	1.331(4)	1.327(3)	1.331(3)	1.329(3)
N(15)−C(3)	1.403(2)	1.407(3)	1.404(3)	1.402(3)	1.403(3)
N(15)−N(15′)	1.263(2)	1.258(3)	1.257(2)	1.260(2)	1.261(2)
N(2)−N(3)−N(4)	110.0(1)	110.0(2)	110.1(2)	110.0(2)	110.0(2)
N(3)−N(4)−C(2)	104.0(1)	104.1(2)	104.0(2)	104.1(2)	104.0(2)
N(6)−N(5)−C(1)	104.5(1)	104.3(2)	104.4(2)	104.6(2)	104.6(2)
N(5)−N(6)−N(7)	109.4(1)	109.5(2)	109.5(2)	109.3(2)	109.3(2)
N(6)−N(7)−N(8)	109.7(1)	109.7(2)	109.6(2)	109.8(2)	109.8(2)
N(7)−N(8)−C(1)	104.2(1)	104.2(2)	104.1(2)	104.1(2)	104.1(2)
N(10)−N(9)−C(1)	112.1(1)	112.2(2)	112.3(2)	112.5(2)	112.6(2)
N(9)−N(10)−C(2)	112.4(1)	112.3(2)	112.2(2)	112.1(2)	112.1(2)
N(12)−N(11)−C(3)	104.6(2)	104.5(2)	104.6(2)	104.6(2)	104.7(2)
N(11)−N(12)−N(13)	109.4(2)	109.4(2)	109.4(2)	109.4(2)	109.3(2)
N(12)−N(13)−N(14)	109.7(2)	109.6(2)	109.6(2)	109.7(2)	109.7(2)
N(2)−N(1)−C(2)	104.0(1)	104.0(2)	104.1(2)	104.0(1)	103.9(1)
N(1)−N(2)−N(3)	109.6(1)	109.8(2)	109.5(2)	109.6(2)	109.7(1)
N(13)−N(14)−C(3)	104.1(2)	104.0(2)	104.2(2)	104.2(2)	104.3(2)
N(15′)−N(15)−C(3)	112.9(2)	113.1(2)	113.1(2)	113.1(2)	113.0(2)
N(8)−C(1)−N(9)	127.4(2)	127.6(2)	127.6(2)	127.6(2)	127.6(2)
N(5)−C(1)−N(9)	120.4(1)	120.1(2)	120.0(2)	120.2(2)	120.2(2)
N(5)−C(1)−N(8)	112.2(1)	112.4(2)	112.4(2)	112.2(2)	112.2(2)
N(4)−C(2)−N(10)	121.2(1)	121.1(2)	121.0(0)	121.0(2)	121.0(2)
N(1)−C(2)−N(4)	112.3(1)	112.1(2)	112.4(2)	112.3(2)	112.5(2)
N(1)−C(2)−N(10)	126.5(2)	126.7(2)	126.7(2)	126.6(2)	126.5(2)
N(11)−C(3)−N(15)	120.5(2)	120.6(2)	120.7(2)	120.6(2)	120.6(2)
N(14)−C(3)−N(15)	127.2(2)	126.9(2)	127.0(2)	127.4(2)	127.4(2)
N(11)−C(3)−N(14)	112.2(2)	112.5(2)	112.3(2)	112.1(2)	112.0(2)

asymmetric-stretch-vibration region of H_2O (around 3600 cm^{-1}) appear more diffuse and less resolved in this work than in [22]. The comparison with the IR data provided in [23] shows good agreement. *Klapötke* and co-workers' work allows the comparison of the vibrational spectra of the cerium, neodymium, and gadolinium compounds **2**, **4**, and **7**, respectively: several bands appear in both [23] and this work, *e.g.*, for compound **2** at 1624, *ca.* 1452, 1408, 1361, 1208, 1184, 1169, 1048, 768, 743, and 570 cm^{-1}. Some bands described in [23] could not be found in our study. Since we analyzed large single crystals, we can only speculate that these bands may be due to some impurities in their powdery products. This, however, does not affect the overall comparability of both works. The density-functional-theory (DFT) calculation of vibrational modes of ZT published in [35] is in quite good agreement with this work (better for IR than for *Raman* spectroscopy), when disregarding from the minor shifts of some cm^{-1}.

The 5,5′-azobis[1*H*-tetrazol-1-ide] ion is known to be strongly *Raman* active. The agreement of the *Raman* measurements of the present study with those of [23] or [22] is even better than the results of the IR spectroscopy. The most intense band is found around 1395 cm^{-1}, corresponding to the symmetric $C-N_{azo}$ stretching mode. The $N-N$ stretching mode of the azo group is found at *ca.* 1472 cm^{-1}. For further reading on the assignments of vibrational spectroscopical modes of 5-substituted tetrazolides, see, *e.g.*, the work of *Klapötke et al.* [36].

Conclusions. – We reported on the organic solvent-free and thus completely 'green' synthesis of the novel 5,5′-azobis[1*H*-tetrazol-1-ides] of the trivalent ions of cerium, praseodymium, neodymium, samarium, europium, and gadolinium. In contrast to the previously reported [23] ineffective metathesis synthesis with barium 5,5′-azobis[1*H*-tetrazol-1-ide] and the respective lanthanoid sulfates, our synthesis was not only simpler (crystallization in aqueous media), but also produced satisfactory yields, avoided the use of the heavy-metal barium, and avoided BaZT as a starting material, which is relatively sensitive. The yields were somewhat smaller, however, than with the ZT compounds of the heavy lanthanoids described in the first part of this project [22]. The crystal structures of all compounds were determined, showing that they are all isotypic and exhibit a distinct lanthanoid contraction as typical trait of the f-block elements. In good agreement with a previous study on tetrazole compounds of the lanthanoids [4], we observed that Gd^{3+} is the last ion of the lanthanoids that exhibits a coordinative bond to the tetrazole ring. The compounds of the heavier yttric earths are purely salt-like with isolated hydrated metal cations and $(ZT)^{2-}$ anions. Further characterization was performed by elemental analysis and vibrational spectroscopy (IR and *Raman*). The crystal-H_2O content of **2** could be corrected to be more than 14–18 H_2O molecules per $Ce_2(ZT)_3$ unit (suggested in [23]), namely 24 molecules.

Experimental Part

General. All chemicals (except the Nd^{3+} starting compound, see below) used in this work were purchased from *Aldrich* or *Merck*, in *p.a.* quality, and used as supplied without further purification. IR Spectra: *Bruker-Tensor-27* (single-reflection *Diamond-ATR*) spectrometer; between 4000 and 600 cm^{-1} with a resolution of 4 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}; relative intensities in % of the most intense peak. Elemental analyses (CHN): *Perkin-Elmer-2400* CHN elemental analyzer; values in wt-%; due to the fact that elemental-analytical facilities are usually not calibrated for the analysis of highly N-rich compounds, the exper. values may deviate from the calc. ones; this phenomenon has been reported in several previous studies [23][37–40].

General Procedure. For the synthesis of the lanthanoid 5,5′-azobis[1*H*-tetrazol-1-ide] tetracosahydrate salts, **1** (100 mg, 0.41 mmol) was suspended in H$_2$O (3 ml). The mixture was stirred and heated to > 90° in the water bath. As soon as the powder had dissolved, a soln. of the respective Ln(NO$_3$)$_3$ · 5 or 6 H$_2$O (0.27 mmol) in H$_2$O (1 ml) was added. Only for the Nd^{3+} salt, Nd(NO$_3$)$_3$ · 2 NH$_4$NO$_3$ · 4 H$_2$O was used (this starting material was obtained from the University of Vienna and probably originated from *Carl Auer von Welsbach*'s work). 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 container to prevent H$_2$O from evaporation. 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.* 6–10 d, the crystallization was completed. The product was obtained in the form of yellowish crystals in undefinable, flaked shape. Depending on the color of the cation, the color of the product varied from yellow (for colorless cations due to the yellow color of the (ZT)$^{2-}$ anion) to dark yellow (for Ce^{3+}) or bluish (for Nd^{3+} or Pr^{3+}). The crystals were collected from the soln. with tweezers, washed with H$_2$O and acetone, and dried (CaCl$_2$) in a desiccator.

*Cerium(III) 5,5′-Azobis[1*H*-tetrazol-1-ide] Tetracosahydrate (= Heptaaqua{{5,5′-[(1E)-diazene-1,2-diyl]bis[2*H*-tetrazolato]}(2−)-κN^1}cerium Salt with 5,5′-[(1E)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:1:10)*; **2**): Yield 67%. Dark yellow crystals. IR: 3602*m*, 2444*w*, 2161v*w*, 1979*w*, 1680 (sh), 1624*s*, 1466*w*, 1410v*s*, 1369*s*, 1204*m*, 1184*m*, 1170*m*, 1110v*w*, 1050*s*, 934v*w*, 794 (sh), 769*s*, 744*m*, 734v*w*, 569*m*. *Raman:* 1472 (37), 1433 (7), 1418 (5), 1393 (100), 1385 (47), 1108 (11), 1087 (20), 1069 (32), 1049 (20), 932 (6), 920 (4). Anal. calc. for C$_6$H$_{48}$Ce$_2$N$_{30}$O$_{24}$ (1204.87): C 5.98, H 4.02, N 34.88; found: C 6.47, H 3.46, N 34.57.

*Praseodymium 5,5′-Azobis[1*H*-tetrazol-1-ide] Tetracosahydrate (= Heptaaqua{{5,5′-[(1E)-diazene-1,2-diyl]bis[2*H*-tetrazolato]}(2−)-κN^1}praseodymium Salt with 5,5′-[(1E)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:1:10)*; **3**): Yield 32%. Bluish yellow crystals. IR: 3609*m*, 2445*w*, 2160v*w*, 1979*w*, 1685 (sh), 1622*s*, 1466*w*, 1409v*s*, 1396*s*, 1209*m*, 1204*m*, 1186*m*, 1170*m*, 1110v*w*, 1050*s*, 1040 (sh), 933v*w*, 799 (sh), 768*s*, 745*m*, 571*m*. *Raman:* 1472 (36), 1433 (7), 1418 (5), 1393 (100), 1385 (47), 1108 (11), 1087 (20), 1070 (31), 1050 (22), 933 (5), 922 (4). Anal. calc. for C$_6$H$_{48}$N$_{30}$O$_{24}$Pr$_2$ (1206.45): C 5.97, H 4.01, N 34.83; found: C 6.45, H 3.21, N 34.67.

*Neodymium 5,5′-Azobis[1*H*-tetrazol-1-ide] Tetracosahydrate (= Heptaaqua{{5,5′-[(1E)-diazene-1,2-diyl]bis[2*H*-tetrazolato]}(2−)-κN^1}neodymium Salt with 5,5′-[(1E)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:1:10)*; **4**): Yield 25%. Dark yellow crystals. IR: 3588 (sh), 2444v*w*, 2160v*w*, 1652 (sh), 1628*s*, 1462*w*, 1404v*s*, 1363 (sh), 1208*m*, 1185*m*, 1172*m*, 1109v*w*, 1066*m*, 1051*m*, 770*s*, 741*m*, 563*m*. *Raman:* 1470 (39), 1432 (7), 1416 (5), 1392 (100), 1382 (48), 1106 (12), 1085 (21), 1069 (30), 1048 (22), 930 (6), 918 (4). Anal. calc. for C$_6$H$_{48}$N$_{30}$Nd$_2$O$_{24}$ (1213.11): C 5.94, H 3.99, N 34.64; found: C 6.35, H 2.73, N 35.05.

*Samarium 5,5′-Azobis[1*H*-tetrazol-1-ide] Tetracosahydrate (= Heptaaqua{{5,5′-[(1E)-diazene-1,2-diyl]bis[2*H*-tetrazolato]}(2−)-κN^1}samarium Salt with 5,5′-[(1E)-Diazene-1,2-diyl]bis[2*H*-tetrazole] Hydrate (2:1:10)*; **5**): Yield 38%. Yellow crystals. IR: 3589*m*, 2448v*w*, 2161*w*, 1979*w*, 1654 (sh), 1624*s*, 1467v*w*, 1406v*s*, 1396*s*, 1369 (sh), 1208*m*, 1185*m*, 1171*m*, 1112v*w*, 1063 (sh), 1051*s*, 932 (sh), 841 (sh), 769*s*, 742*s*, 567*m*. *Raman:* 1482 (16), 1472 (28), 1430 (4), 1390 (100), 1109 (14), 1065 (21), 1051 (6), 927 (6). Anal. calc. for C$_6$H$_{48}$N$_{30}$O$_{24}$Sm$_2$ (1225.43): C 5.88, H 3.95, N 34.29; found: C 6.29, H 3.01, N 33.90.

*Europium(III) 5,5′-Azobis[1*H-*tetrazol-1-ide] Tetracosahydrate* (= *Heptaaqua{{5,5′-[(1*E*)-diazene-1,2-diyl]bis[2*H-*tetrazolato]}(2 −)-κN¹}europium Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H-*tetrazole] Hydrate (2 : 1 : 10);* **6**): Yield 47%. Yellow crystals. IR: 3607*m*, 2446v*w*, 2160*w*, 1979*w*, 1652*w*, 1617*m*, 1412v*s*, 1395*s*, 1208*m*, 1186*m*, 1170*m*, 1111v*w*, 1051*s*, 933 (sh), 811 (sh), 769*m*, 745*m*. *Raman:* 1474 (42), 1436 (6), 1418 (5), 1396 (100), 1385 (47), 1111 (11), 1087 (19), 1075 (23), 1069 (26), 1052 (24), 934 (5), 923 (4). Anal. calc. for $C_6H_{48}Eu_2N_{30}O_{24}$ (1228.55): C 5.87, H 3.94, N 34.20; found: C 6.21, H 3.32, N 33.75.

*Gadolinium 5,5′-Azobis[1*H-*tetrazol-1-ide] Tetracosahydrate* (= *Heptaaqua{{5,5′-[(1*E*)-diazene-1,2-diyl]bis[2*H-*tetrazolato]}(2 −)-κN¹}gadolinium Salt with 5,5′-[(1*E*)-Diazene-1,2-diyl]bis[2*H-*tetrazole] Hydrate (2 : 1 : 10);* **7**): Yield 29%. Yellow crystals. IR: 3596*m*, 3538*w*, 2444v*w*, 2161v*w*, 1979v*w*, 1654 (sh), 1628*s*, 1449*w*, 1402v*s*, 1209*s*, 1180 (sh), 1173*m*, 1084*m*, 1062*m*, 1048*w*, 769*w*, 724*s*, 556*w*. *Raman:* 1478 (40), 1473 (47), 1427 (15), 1393 (95), 1386 (100), 1108 (17), 1082 (39), 1072 (42), 1066 (33), 1049 (27), 927 (15). Anal. calc. for $C_6H_{48}Gd_2N_{30}O_{24}$ (1239.13): C 5.82, H 3.90, N 33.91; found: C 6.20, H 3.14, N 33.69.

X-Ray Crystallography[1]). 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. For structure solutions by direct methods and the structure refinements, the programs SHELXS-97 [41] and SHELXL-97 [42], resp., were used. Absorption correction was done by evaluation of partial multi-scans. Thermal ellipsoids in ORTEP [43] plots represent a 50% probability. Crystallographic data and structure-determination details for **2** – **7** can be found in *Table 1*.

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[1]) CCDC 722671 – 722676 (see *Table 1*) contain the supplementary crystallographic data for the structures of **2** – **7**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

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