

Nitrogen-Rich Compounds of the Lanthanoids: Highlights and Summary

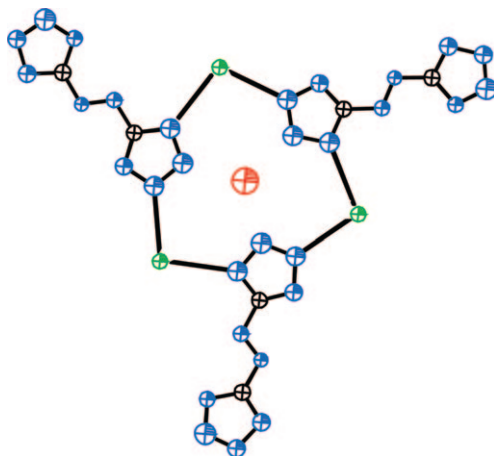
by Georg Steinhauser^{*a)}, Gerald Giester^{b)}, Nicolae Leopold^{c)}, Christoph Wagner^{d)}, Mario Villa^{a)}, and Andreas Musilek^{a)}

^{a)} Vienna University of Technology, Atominstitut der Österreichischen Universitäten, Stadionallee 2, AT-1020 Vienna (phone: +43 158801 14189; fax: +43 158801 14199; e-mail: georg.steinhauser@ati.ac.at)

^{b)} University of Vienna, Institute of Mineralogy and Crystallography, Althanstrasse 14, AT-1090 Vienna

^{c)} Babeş-Bolyai University, Faculty of Physics, Kogalniceanu 1, RO-400084 Cluj-Napoca

^{d)} Vienna University of Technology, Institut für Chemische Technologie und Analytik, Getreidemarkt 9/164, AT-1060 Vienna



‘There is a beauty in discovery. There is mathematics in music, a kinship of science and poetry in the description of nature, and exquisite form in a molecule.’

Glenn T. Seaborg

In this third part of our research on the 5,5'-azobis[1*H*-tetrazol-1-ides] (ZT) of the lanthanoids, we present two compounds with $\text{La}_2(\text{ZT})_3$ moieties with very different coordination modes between the cations and the anions. One $\text{La}_2(\text{ZT})_3$ -containing compound is interesting, because it contains trimeric $\text{La}_3(\text{ZT})_3^{\text{III}}$ cations, which are arranged in a windmill-like structure. Moreover, the first double salt of a ZT compound, namely the carbonate compound $\text{La}_2(\text{ZT})_2(\text{CO}_3) \cdot 12 \text{H}_2\text{O}$, is presented and discussed. Another highlight of nitrogen chemistry is the first molecular structure of a 5-azido-2*H*-tetrazole (CHN_7) molecule, in the form of the spectacular compound $\text{Dy}_2(\text{ZT})_3 \cdot 4 \text{CHN}_7 \cdot 24 \text{H}_2\text{O}$. This is the first known complete molecular structure of an azidotetrazole molecule (the organic molecule with the highest nitrogen-content: 88.3% N). All compounds have been characterized completely including elemental analyses, vibrational (IR and Raman) spectroscopy, and X-ray crystal-structure determination. We summarize our ‘nitrogen-rich compounds of the lanthanoids’ project and extensively discuss selected literature on this topic and compare previously published results with ours.

Introduction. – In 2008, the scientific community in Austria celebrated the 150th birthday of *Carl Auer von Welsbach*, one of Austria's most famous scientists ever. *Auer von Welsbach* (1858–1929) was a pioneer in several fields of chemical sciences. He not only discovered four rare earth elements (REE) [1][2] and correctly proclaimed the non-existence of element 61 (promethium) in nature [3], but also made fundamental discoveries in the field of nuclear sciences. Ninety-nine years ago, he reported that 'ionium' (^{230}Th) was able to induce radioactivity in other materials (presumably lanthanoids) if stored next to the ionium sample [4]. *Auer von Welsbach* proclaimed that '*in this process, a concussion of the elementary inventory of the irradiated samples takes place as well as changes in their chemical properties*'. Today, we call the observed scenario simply '*neutron activation*'. He was well aware that this observation was '*not quite in agreement with current theories*', but he was confident enough in his separation skills that he did not attribute the radioactivity in the lanthanoid salt to naturally occurring radionuclide impurities, as others interpreted this observation¹⁾. In fact, *Auer von Welsbach* thereby incidentally discovered the production of artificial radionuclides (24 years before *Frédéric Joliot* and *Irène Curie* [6]), (spontaneous) fission (29 years before *Meitner* and *Frisch* [7], and *Hahn* and *Straßmann* [8]), the neutron (22 years before *Chadwick* [5]), and lastly the principle of neutron-activation analysis (26 years before *Hevesy* and *Levi* [9]). *Auer von Welsbach* predicted that this observation '*might be of importance for the field of radioactivity research*'. Stunning.

In this study, we present several novel N-rich compounds of the lanthanoids (Ln) and summarize our previous works on this topic [10–12]. Nitrogen-rich compounds, in particular, tetrazoles, are of interest for several branches of science. Tetrazoles are five-membered rings with four N-atoms and, due to their high N content, can be applied as energetic materials (*e.g.*, [13–25]). Nitrogen-rich compounds gain their energy from high heats of formation and not by intramolecular oxidation of a C backbone like 'conventional' explosives such as TNT or PETN. They are also of interest as ligands in coordination chemistry (*e.g.*, [26–28]). Some of them have interesting optical properties [29–31], and some can even be used as precursors of functional materials [32][33]. With our well-proven preparative technique, we were able to synthesize two different products of lanthanum 5,5'-azobis[1*H*-tetrazol-1-ide] hydrates, as well as a lanthanum 5,5'-azobis[1*H*-tetrazol-1-ide] carbonate hydrate and a dysprosium 5,5'-azobis[1*H*-tetrazol-1-ide] hydrate–5-azidotetrazole adduct. The 5,5'-azobis[1*H*-tetrazol-1-ide] dianion (= 5,5'-(diazene-1,2-diyl)bis[2*H*-tetrazole] ion (2–)) is also called 5,5'-azotetrazolate in literature, has the sum formula $\text{C}_2\text{N}_{10}^{2-}$ and is abbreviated with ZT. The compounds presented in this study are fully characterized using X-ray single-crystal structure analysis, elemental analysis, and vibrational spectroscopy (IR and *Raman*).

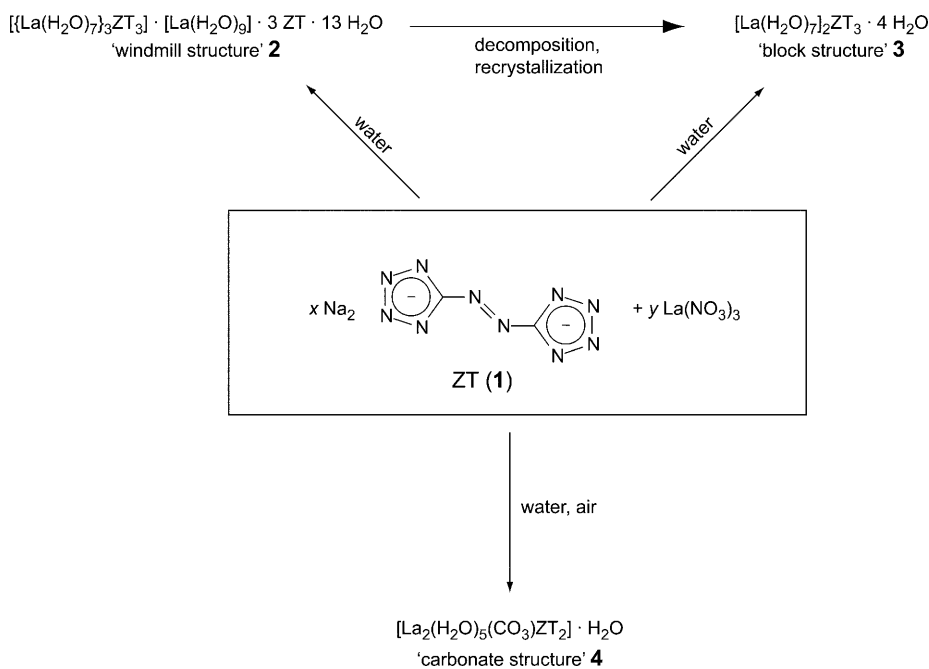
¹⁾ We can only speculate that neutrons emitted in the course of spontaneous fission events of one radionuclide in *Auer von Welsbach's* ^{230}Th sample (eventually ^{230}Th itself) could have been responsible for this observation. In another theory, beryllium impurities in the ^{230}Th sample could have produced neutrons in a $^9\text{Be}(\alpha, n)^{12}\text{C}$ reaction (see [5]). The induced radioactivity in the lanthanoids could, therefore, have been due to the capture of neutrons which are emitted from this sample. The glass containers used and the H_2O of crystallization in the REE compounds probably acted as moderators to the neutrons.

Results and Discussion. – *Synthesis. Caution!* Although no problem occurred during the synthesis and handling of the salts investigated in this work, ZTs 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 [34].

Disodium 5,5'-azobis[1*H*-tetrazol-1-ide] dihydrate ($\text{Na}_2\text{ZT} \cdot 2 \text{H}_2\text{O}$; **1**) was prepared according to Thiele [35] and Singh *et al.* [36] by oxidation of 1*H*-tetrazol-5-amine monohydrate with KMnO_4 in aqueous solution of NaOH , and subsequent partial dehydration of the pentahydrate, as described in [11].

For a simplified graphical illustration of the synthesis of the La compounds **2–4**, see Scheme 1. Their synthesis was performed according to the same preparative concept of the Vienna research group (see [11] and [12]). In summary, the compounds crystallized from aqueous solutions of lanthanum nitrate and Na_2ZT (**1**). Crystallization sets in only a few days later than the previously investigated $\text{Ln}_2(\text{ZT})_3$ compounds and is completed after *ca.* 10 days. If crystallization does not start, it is recommended to slowly let the H_2O evaporate from the solution. In any case, this simple and effective procedure yields a crystalline product of $\text{La}_4(\text{ZT})_6 \cdot 43 \text{H}_2\text{O}$ (**2**) in the form of needles. In a previous study, the syntheses of the ZTs of several lanthanoids (*i.e.*, La, Ce, Nd, and Gd) have been attempted by Klapötke and co-workers [37]; however, their preparative approach failed to produce a product suitable for single-crystal X-ray diffraction.

Scheme 1. Synthesis of the Lanthanum ZT Compounds by Crystallization from Aqueous Solutions



Klapötke and co-workers tried the metathesis reaction of BaZT and the respective $\text{Ln}_2(\text{SO}_4)_3$ [37]. The Vienna approach, in contrast, not only yielded a product better suited for complete characterization, but also avoided one unnecessary reaction step, namely the production of BaZT from Na_2ZT . BaZT is a relatively sensitive, explosive compound. Lastly, the dispensable reaction step only decreases the yield of the final product.

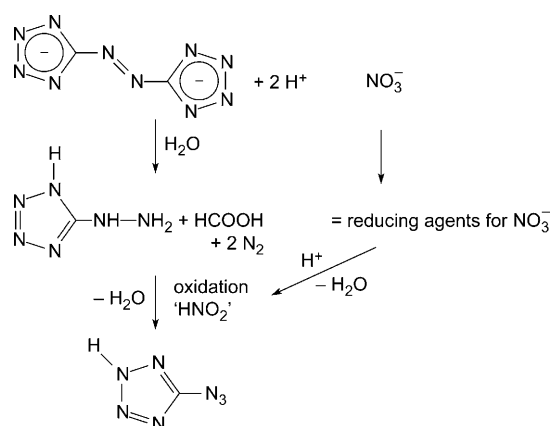
We observed that, commonly, after several weeks of storage in the mother liquid, thin needles of **2** decompose, and a new crystal type, blocks of isometric shape, forms. This second product, $\text{La}_2(\text{ZT})_3 \cdot 18 \text{H}_2\text{O}$, was defined as compound **3**. Both compounds **2** and **3** are stable enough to perform full characterization by means of single-crystal X-ray diffraction, vibrational spectroscopy (IR and *Raman*), and elemental analyses (see below). We have not yet clarified the circumstances (temperature, changes in the concentration of the solution, *etc.*) that are responsible for the decomposition of **2** and lead to the formation of **3**. However, both products are easily obtainable. In their study on several ZT salts, *Klapötke* and co-workers [37] provided elemental analytical data on a $\text{La}_2(\text{ZT})_3$ compound: C 6.1, H 3.8, N 34.7%. The comparison with our values listed in the *Exper. Part* suggests that they might have synthesized rather **2** than **3**. However, without a crystal-structure analysis, the assignment is not conclusive.

When synthesis of **2** and/or **3** is not performed in airtight polyethylene vials, but in *Teflon* vials, which are loosely closed with a *Teflon* lid, we observed the crystallization of $\text{La}_2(\text{ZT})_2(\text{CO}_3) \cdot 12 \text{H}_2\text{O}$ (**4**) in the form of small brown prisms. The formation of carbonate, of course, is characterized by little tolerance against acidic conditions: the pH of the reaction mixture is *ca.* 7.5 right after synthesis. Obviously, the slightly basic character of **1** compensates the acidic character of the $\text{La}(\text{NO}_3)_3$ solution. After 1 day, the pH of the solution reaches 6.5, and when measured after *ca.* 50 days, it finally dropped to 5.5. At this pH, the crystals of **4** are still undecomposed. There are two possible C sources for the formation of CO_3^{2-} : first, CO_2 from the atmosphere, and second, CO_2 as the oxidation product of formate, which is a decomposition product of ZT itself (see *Scheme 2*). We can assume that nitrate in the reaction mixture can accelerate the oxidation of formate. In any case, the ZT solution buffers large amounts of H_3O^+ ions, so that the decrease in pH is moderate.

Another highlight of the chemistry of N-rich compounds of the f-block elements certainly is compound **5**: octaaquadyprosium(III)–5-azido-2*H*-tetrazole–5,5'-azobis[1*H*-tetrazol-1-ide]–water (2:4:3:8). It forms, when the ‘simple’ octaaquadyprosium(III) 5,5'-azobis[1*H*-tetrazol-1-ide] docosahydrate ($\text{Dy}_2(\text{ZT})_3 \cdot 22 \text{H}_2\text{O}$) described in [11] is stored in its mother liquor for several months. Thereby, an interesting set of decomposition/redox reactions takes place, leading to azidotetrazole (CHN_7 , a molecule with 88.3% N), as shown in *Scheme 2*.

According to *Scheme 2*, the first step in the formation of azidotetrazole must be the acidic decomposition of the $(\text{ZT})^{2-}$ anion, yielding 5-hydrazinotetrazole. The decomposition of this type is primarily known when mineral acids are applied. In our case, the *Lewis* acid Dy^{III} must act as the protonating agent. In a second step, we assume that nitrate ions are reduced by the hydrazinotetrazole or the formate, forming nitrite ions. Nitrite in acidic solution, however, is known to oxidize hydrazino groups, forming the azide, which, therefore, must be the third step of this reaction. Finally, during crystallization, four chemical species are incorporated into the crystal, namely *a*)

Scheme 2. Simplified Scheme of Acidic Decomposition of ZT Yielding 5-Hydrazinotetrazole in Aqueous Media, and Redox Reactions for the Oxidation of 5-Hydrazinotetrazole Yielding 5-Azidotetrazole



[Dy(H₂O)₈]³⁺ as the cations, *b*) (ZT)²⁻ as the anions, *c*) 5-azidotetrazole molecules as neutral adducts, and *d*) H₂O of crystallization.

Crystal Structures. For selected data from the data collection and refinement, see Table 1.

As discussed before, the first reaction product of Na₂ZT (**1**) and La(NO₃)₃ in aqueous solution is a crystalline product in the form of lemon-yellow fine needles: La₄(ZT)₆·43 H₂O (**2**). The crystal structure of this compound is characterized by two different motifs. Around *z* = 0, the compound consists of isolated [La(H₂O)₉]³⁺ cations and (ZT)²⁻ anions, which do not exhibit a coordinative bond to any of the La^{III} ions (see Fig. 1, *a*). The La^{III} ions in this layer are coordinated in the form of a distorted tricapped trigonal prism (LaO₉).

Around *z* = 0.5, however, the La^{III} and (ZT)²⁻ ions form a spectacular and unique ‘windmill’-like structure, which is built of three [La(H₂O)₇]³⁺ cations and three (ZT)²⁻ anions (see Fig. 1, *b*). Each of the (ZT)²⁻ ions of the windmill coordinates two La^{III} ions *via* one tetrazole ring as a bridging ligand in the respective N(1) and N(3) position. In the center of the windmill, there is a threefold axis or a pseudo-axis. For the previously published 5,5’-bitetrazolates of the lanthanoids [31], N-atoms of both tetrazole rings are incorporated into the coordination sphere of the light lanthanoids (including La). In compound **2**, only one tetrazole ring of the ZT moiety acts as a ligand. The La^{III} ions are coordinated in strongly distorted tricapped trigonal prisms (LaN₂O₇). In total, this windmill system can be regarded as a La₃N₉ heterocycle, which, so far, has only been described once in a completely different compound [38]. In that case, the three bridging N-atoms are azido groups, which are almost linear (179.0°). The respective La–N bond lengths were 2.556 and 2.535 Å. In compound **2** of our study, the angles of the three bridging N-atoms vary between 107.3° and 110.7°, and the La–N bond lengths are in the range of 2.778–2.853 Å. The La–La distances of **2** are *ca.* 7.45 Å, which makes it a larger ring than the trimeric azide product of [38] (7.14 Å).

Table 1. Crystallographic Data and Structure-Determination Details for Compounds **2–5**

	2	3	4	5
Sum formula	C ₁₂ H ₈₆ La ₄ N ₆₀ O ₄₃	C ₆ H ₃₆ La ₂ N ₃₀ O ₁₈	C ₅ H ₂₄ La ₂ N ₂₀ O ₁₅	C ₁₀ H ₅₀ Dy ₂ N ₅₈ O ₂₄
Crystal system	trigonal	triclinic	monoclinic	triclinic
Space group	<i>P</i> 3	<i>P</i> $\bar{1}$	<i>C</i> 12/ <i>c</i> 1	<i>P</i> $\bar{1}$
Weight [g · mol ⁻¹]	2314.8	1094.5	882.3	1691.9
<i>a</i> [Å]	36.502(5)	9.4732(19)	16.978(3)	7.2443(7)
<i>b</i> [Å]	36.502(5)	9.863(2)	6.605(1)	11.612(2)
<i>c</i> [Å]	6.774(1)	11.020(2)	23.867(5)	19.456(2)
α [°]	90	113.50(3)	90	90.428(9)
β [°]	90	92.08(3)	93.65(3)	100.141(7)
γ [°]	120	107.10(3)	90	104.60(1)
<i>V</i> [Å ³]	7816(2)	888.5(3)	2671.1(9)	1556.8(3)
<i>Z</i>	4	1	4	1
ρ_{calc} [g · cm ⁻³]	1.967	2.046	2.194	1.805
μ [mm ⁻¹]	2.270	2.483	3.257	2.496
Ind. reflections	29019	8129	6129	6066
Obs. reflections $F_o > 4\sigma(F_o)$	19597	7675	5393	4984
R_{int}	0.08	0.043	0.042	0.033
R_1^{a}	0.129	0.0208	0.0309	0.0359
wR_2^{b}	0.228	0.0441	0.0637	0.0539
Weighting scheme ^c)	0.08; 95	0.015; 0.5	0.03; 4	0.026; 0
Goodnes-of-fit	1.093	1.009	1.071	0.970
No. of parameters	1430	326	240	584

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

The ZTs of both layers form stacks, which are favored because of the aromatic $\pi-\pi$ interaction of the tetrazole rings. The isolated $[\text{La}(\text{H}_2\text{O})_9]^{3+}$ cations are located between these ZT stacks, as shown in *Fig. 1, b*. There are 20 H₂O molecules of crystallization in both layers and between them.

It is interesting to note that the structure of **2** comprises some characteristics of both the heavy [11] and the light lanthanoid ZTs [12]. In particular, bonding partners of the La^{III} ions in this compound are not uniform: there exist isolated hydrated La ions (as observed with the heavy REE salts) and La ions that are coordinated by both H₂O molecules and (ZT)²⁻ ions (as characteristic to the light REE compounds of ZT). A significant difference, however, is that the La^{III} ions in **2** are nine-coordinated, whereas the ZT compounds of the other REE (Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu) are eight-coordinated. The ‘borderline between coordination and salt-like compounds’ of the lanthanoids, therefore, appears not as clear as suggested in [31].

The decomposition product of **2**, however, shows a very different picture: in compound **3**, all (ZT)²⁻ ions are coordinated to one La^{III} ion, as expected from the behavior of the light REE described in [12][31]. *Fig. 2* shows the molecular structure of **3**.

The centrosymmetric (ZT)²⁻ ion connects two La^{III} ions *via* N(1). In contrast to the previously discussed compound **2**, both tetrazole rings of this anion are involved in the coordination of the cations. The second ZT anion coordinates the cation *via* N(7).

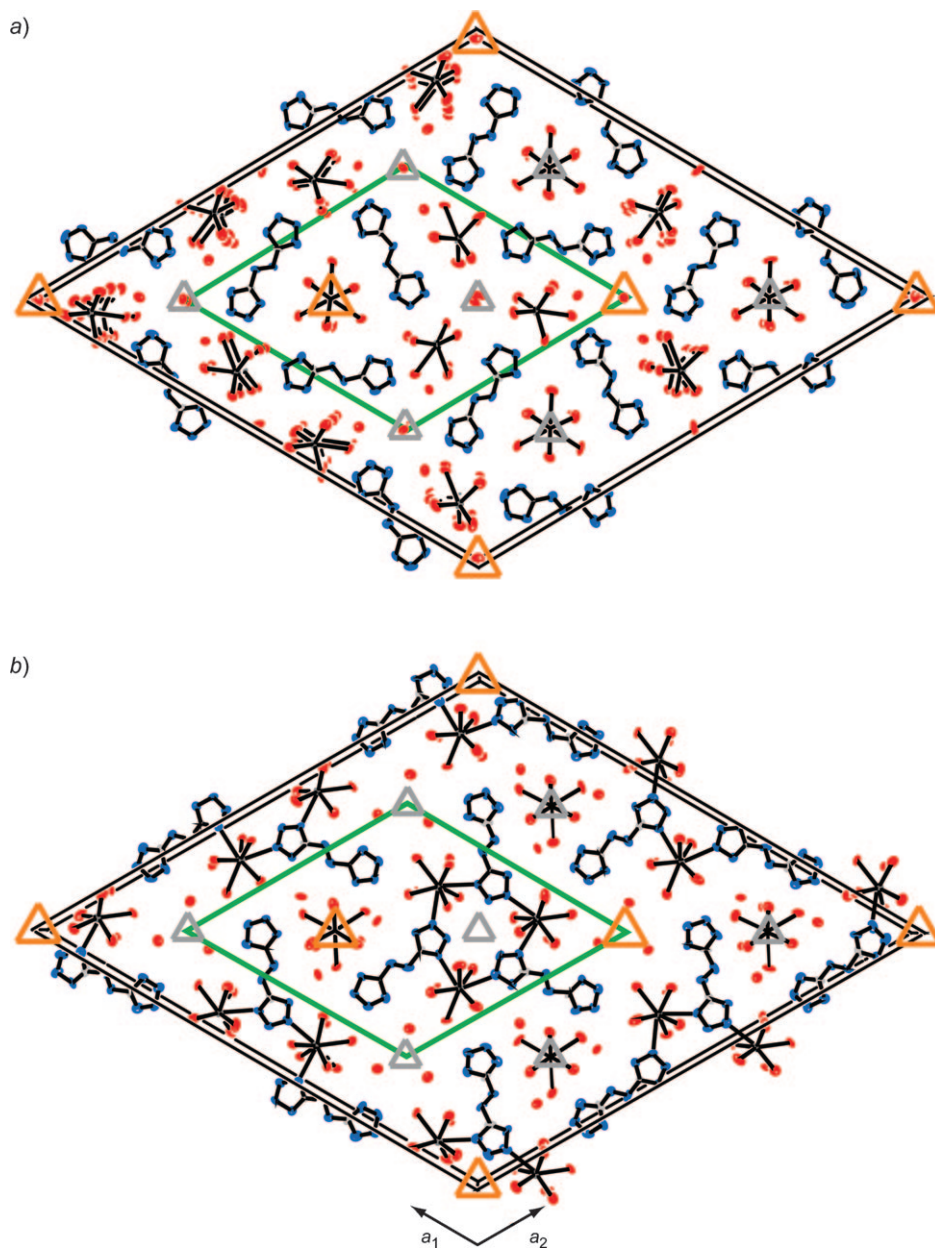


Fig. 1. Motifs in the crystal structure of **2**, from a) $z = -0.25$ to $z = 0.25$, as well as from b) $z = 0.25$ to $z = 0.75$. H-Atoms are omitted. Orange triangles indicate the threefold axes, and grey triangles threefold pseudo-axes. A potential 'subcell' is indicated in green.

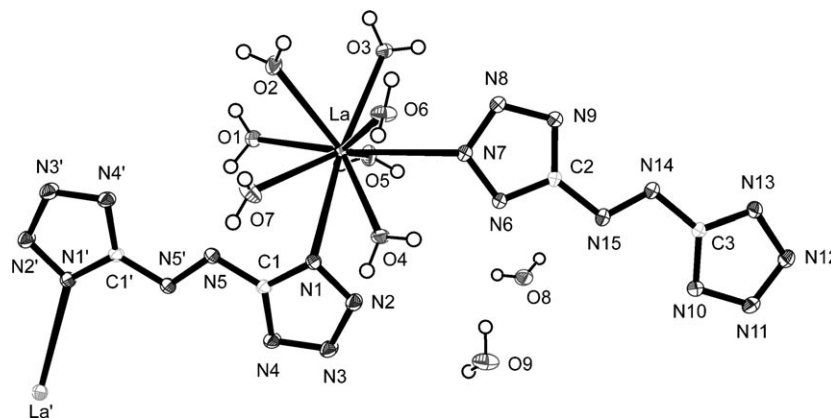


Fig. 2. Molecular structure of **3**

Consequently, each La^{III} ion is coordinated by two tetrazole ligands, forming a distorted tricapped trigonal prism (LaN_2O_7). The ZT ions in this structure again form stacks, which are intercalated with La complexes.

A third compound containing La and ZT, namely $\text{La}_2(\text{ZT})_2(\text{CO}_3) \cdot 12 \text{H}_2\text{O}$ (**4**), proves, to our best knowledge, to be the first double salt with one $(\text{ZT})^{2-}$ anion ever reported in literature. At first glance, carbonate can be mistaken for nitrate in X-ray structures. Although nitrate was present in the reaction mixture, there is no doubt that, for several reasons, the XO_3 species must be a bidentate carbonate and not nitrate ligand:

- For reasons of charge balance, two La^{III} ions require more negative counterions than two $(\text{ZT})^{2-}$ and one speculative NO_3^- ion. Since there are no other elements present in the reaction mixture than La, N, C, H, and O, the only possibly ‘missed’ and reasonable counteranion could be hydroxide. With basic Ln salts, the $\text{Ln}-(\text{OH})^-$ bond lengths are *ca.* 0.1 Å shorter than the respective $\text{Ln}-\text{OH}_2$ bond lengths (*cf.*, *e.g.*, [39]). Disregarding the bonds of La to the XO_3 ligand, the $\text{Ln}-\text{O}$ bond lengths of **4**, however, fluctuate within a range of *ca.* 0.05 Å at most. The consistency of the $\text{La}-\text{O}$ bond lengths of the aqua ligands, consequently, excludes the ‘nitrate hydroxide hypothesis’.

- Elemental analysis strongly suggests carbonate and not the ‘nitrate hydroxide hypothesis’: values calculated for $\text{C}_4\text{H}_{23}\text{La}_2\text{N}_{21}\text{O}_{15}$ (nitrate hydroxide): C 5.4, H 2.6, N 33.3%; values calculated for $\text{C}_5\text{H}_{24}\text{La}_2\text{N}_{20}\text{O}_{15}$ (carbonate): C 6.8, H 2.7, N 31.8%; values found: C 7.0, H 2.8, N 31.5%

- The structure refinement favors CO_3^{2-} rather than NO_3^- .

- The average X–O distances are typically in the range of 1.29 Å for carbonate (*e.g.*, [40]) and 1.25 Å for nitrate (*e.g.*, [41]). The average X–O distance found in the structure of **4** is 1.291 Å.

- Although the *Raman* and IR spectra of carbonate and nitrate are quite similar, the small band at 1099 cm^{-1} in the IR can only be explained by the presence of carbonate, as will be discussed later.

In this structure, two La^{III} ions are connected *via* the carbonato ligand, which acts as a bridging bidentate ligand (see *Fig. 3*).

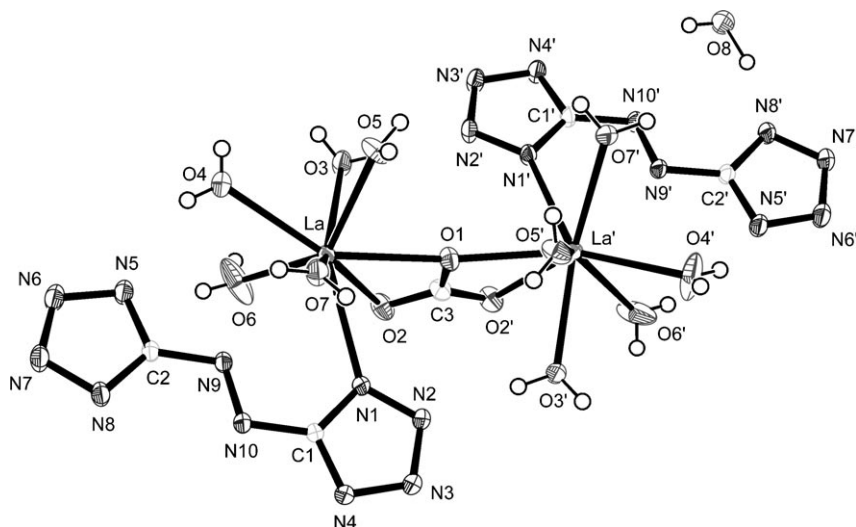


Fig. 3. Molecular structure of 4

La in compound **4** is only eight-coordinated, which is in contrast to the other ZT compounds of La discussed before. One ligand is an N-atom belonging to the ZT ion, two O-atoms belong to the carbonato ligand, and five ligands are O-atoms of H_2O molecules. The LaNO_7 polyhedron forms a strongly distorted dicapped trigonal prism. In compound **4**, only 5 H_2O ligands and $\frac{1}{2}$ free H_2O molecule occur per La^{III} ion. It is, therefore, the ZT compound of the lanthanoids with the lowest H_2O content.

The packing of **4** is characterized by layers of ZT stacks arranged parallel to the *c* axis. These layers are intercalated with layers of slightly inclined $[\text{La}(\text{H}_2\text{O})_5]-\text{O}-\text{CO}_2-[\text{La}(\text{H}_2\text{O})_5]$ moieties.

Dy in compound **5** is similarly coordinated as in the $\text{Dy}_2(\text{ZT})_3 \cdot 22 \text{H}_2\text{O}$ compound published previously [11]. The Dy^{III} ions are eight-coordinated by H_2O ligands only. The 5-azido-2*H*-tetrazole adducts described in this compound were the first CHN_7 molecules completely characterized by X-ray crystal-structure analysis [10]. Since both azidotetrazole molecules in **5** are almost identical, only one will be discussed in more detail (see *Fig. 4*).

One of the most interesting features of this molecule is the position of the H-atom. Previous calculations [42] predicted the 2*H*-tautomer to be more aromatic and thus more stable than the 1*H*-tautomer. Therefore, it came as a surprise that, in a previous report [43] on the structure of this molecule, the H-atom was located on N(1). Since the quality of the structure refinement in [43] (*cf.* R_1 , wR_2 and GOOF in *Table 2*) was rather poor, many questions, especially with respect to the position of the H-atom remained

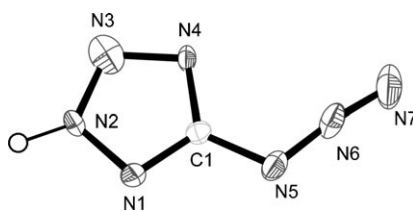


Fig. 4. Molecular structure of the 5-azidotetrazole adduct found in **5**

open. Although compound **5** is a heavy-atom compound making it difficult exactly to locate the position of a H-atom, there is no doubt that the 5-azidotetrazole molecules in compound **5** are protonated at N(2) because of the further H-bond arrangement as shown in *Fig. 5*: one can see that the position N(1) is blocked, because it is already part of a H-bridge, in this case an $N \cdots H-O$ bridge to H_2O molecules coordinating the Dy^{III} cation.

With exception of the location of the H-atom, the other main structural parameters in the 5-azidotetrazole molecule by and large have been confirmed in [44], shortly after our submission to the Austrian Academy of Sciences [10]. For easier comparison, the main characteristics of all reports on the molecular structures of 5-azidotetrazole are summarized in *Table 2*. Some geometric details in the preliminary structural determination of 5-azidotetrazole [43] are not easily obtainable, because those authors did not submit the cif file to an open data base.

In our preliminary report on the structure of compound **5**, we mentioned a disorder [10]. Herein, we present the refined structure of compound **5** and can conclude that the disordered area includes $\frac{1}{2} (ZT)^{2-}$ anion and a free H_2O molecule (and not NO_3^-). The improved structure refinement, vibrational spectroscopy (to be discussed later), as well as elemental analysis support this model: calculated for $C_4H_{24}DyN_{25}O_{14}$ (containing NO_3 ; alternative model): C 5.9, H 3.0, N 43.3%; calculated for $C_{10}H_{50}Dy_2N_{58}O_{24}$ (containing $(C_2N_{10})/2$ and one additional H_2O molecule; this study's model): C 7.1, H 3.0, N 48.0%; found: C 9.7, H 2.8, N 41.8%. Keeping in mind that only a minute amount of material (0.88 mg) was available for elemental analysis which usually suffers systematic problems described in the *Exper. Part*, these values agree well with the calculated ones. For a heavy-ion bearing compound, this one is *extremely* N-rich (it is, to the best of our knowledge, the N-richest dysprosium compound that has ever been structurally characterized).

With the bond lengths determined in the crystal-structure analysis, one can calculate the valence-bond parameters $R(Ln-O)$ as well as $R(Ln-N)$ of the complexes presented herein. The valence-bond parameters mathematically connect bond valences and bond lengths. For Ln metal ions coordinated only by O ligands, $R(Ln-O)$ is calculated as shown in *Eqn. 1* [45], where $V(Ln)$ is the formal valence of the Ln central atom, $d(Ln-O)$ is the bond length between Ln and the O ligand, and $b = 0.37 \text{ \AA}$ is the universal constant [46]. This equation can be used for the $[Dy(H_2O)_8]^{3+}$ ions in compound **5**, as well as for the nonaqua complexes of La(1) and La(2) in compound **2**.

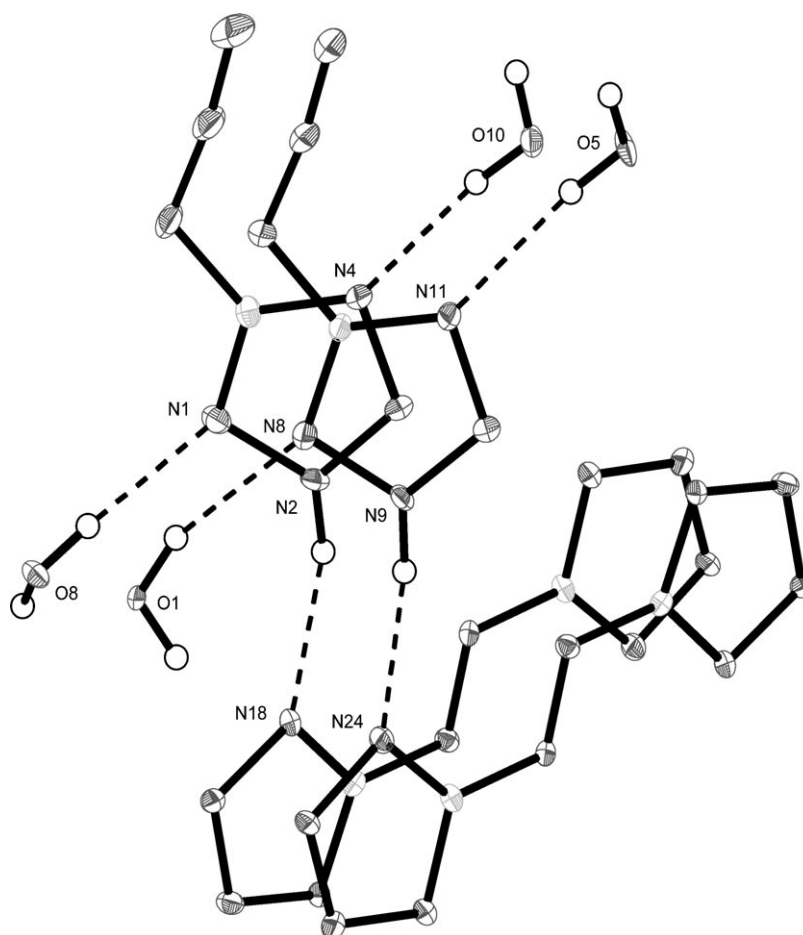


Fig. 5. Hydrogen bonding in **5**, according to [10]

$$R(\text{Ln-O}) = b \cdot \ln \left(\frac{V(\text{Ln})}{\sum_i \exp \left[\frac{-d(\text{Ln-O})_i}{b} \right]} \right) \quad (1)$$

For the complexes with two different ligands (like O and N in case of compounds **2**, **3**, and **4**), *Eqn. 1* has to be modified as shown in *Eqn. 2* [47]. In this modification, the contribution of the Ln–O bonds to the total valence of Ln is subtracted from the formal valence of $V(\text{Ln})=3$. This is done based on the literature values of $R(\text{Ln-O})$ [48] for the respective trivalent Ln ion and with the respective coordination number (CN) (*Eqn. 2*).

Table 2. Comparison of the Bonding Parameters of 5-Azidotetrazole Tautomers in the Literature. Bond lengths in Å, angles in °.

	Xiao and co-workers [42]	Klapötke and co-workers [43]	Steinhauser [10]	Klapötke and co-workers [44]
	Time →			
Type of study	Theoretical	Experimental	Experimental	Experimental
Tautomer	2 <i>H</i>	1 <i>H</i> (?)	2 <i>H</i>	1 <i>H</i>
C(1)–N(1)	1.299	1.32(1)	1.311(5)	1.327(2)
N(1)–N(2)	1.315	1.37(1)	1.364(5)	1.355(2)
N(2)–N(3)	1.281	1.30(1)	1.326(6)	1.295(2)
N(3)–N(4)	1.280	1.37(1)	1.358(5)	1.372(2)
N(4)–C(1)	1.345	1.324(9)	1.349(5)	1.321(2)
C(1)–N(5)	1.385	1.41(1)	1.403(5)	1.383(2)
N(5)–N(6)	1.247	1.25(1)	1.245(5)	1.267(2)
N(6)–N(7)	1.093	1.12(1)	1.120(6)	1.117(2)
C(1)–N(1)–N(2)	100.57	107.9(7)	102.2(3)	108.3(1)
N(1)–N(2)–N(3)	114.68	106.2(7)	110.7(3)	106.5(1)
N(2)–N(3)–N(4)	106.66	110.7(7)	109.0(4)	110.6(1)
N(3)–N(4)–C(1)	105.65	105.0(6)	102.5(3)	105.1(1)
N(1)–C(1)–N(4)	112.44	^{a)}	115.5(4)	109.5(2)
N(1)–C(1)–N(5)	–	120.8(7)	119.5(4)	121.0(1)
N(4)–C(1)–N(5)	125.59	^{a)}	124.9(4)	129.5(2)
C(1)–N(5)–N(6)	113.15	113.5(7)	113.6(4)	113.1(1)
N(5)–N(6)–N(7)	173.46	172.5(9)	172.2(5)	171.9(2)
<i>R</i> ₁	–	0.187	0.0369	0.0556
<i>wR</i> ₂	–	0.393	0.0740	0.0806
GOOF	–	2.018	1.054	1.001

^{a)} Value not listed and no cif file deposited with the *Cambridge Crystallographic Data Centre*.

$$R(\text{Ln-N}) = b \cdot \ln \left(\frac{V(\text{Ln}) - \sum_i \exp \left[\frac{R(\text{Ln-O}) - d(\text{Ln-O})_i}{b} \right]}{\sum_i \exp \left[\frac{-d(\text{Ln-N})_i}{b} \right]} \right) \quad (2)$$

In compound **2**, the valence bond parameters $R(\text{Ln-N})$ for the ZT ligands of this study are 2.40 Å for La(3), 2.37 Å for La(4), 2.31 Å for La(5), and 2.49 Å for La(6). In compounds **3** and **4**, these parameters are 2.38 and 2.46 Å, respectively. The $R(\text{Ln-N})$ values are, therefore, higher than the average values of N-ligands [47]. The valence-bond parameters $R(\text{Ln-O})$ of La(1) and La(2) in **2** are both 2.15 Å, and thus slightly higher than the average as well [48]. In compound **5**, the $R(\text{Ln-O})$ of the central Dy-atom is 1.99, which is in very good agreement with the literature [48].

Calculation of the bond-valence sum can be performed using the published $R(\text{Ln-O})$ [48] and $R(\text{Ln-N})$ [47] values according to *Eqns. 3a* and *3b* as well as *4*. For Ln–O bonds, *Eqn. 3a* is applied, for Ln–N bonds *Eqn. 3b*.

$$\nu(\text{Ln-O})_i = \exp\left[\frac{R(\text{Ln-O})-d(\text{Ln-O})_i}{b}\right] \quad (3a)$$

$$\nu(\text{Ln-N})_i = \exp\left[\frac{R(\text{Ln-N})-d(\text{Ln-N})_i}{b}\right] \quad (3b)$$

$$V(\text{Ln}) = \sum_i \nu(\text{Ln-O})_i + \sum_i \nu(\text{Ln-N})_i \quad (4)$$

In case of both La and Dy, the calculated valence $V(\text{Ln})$ should be close to the formal valence of 3 valence units, because no deviation of the trivalent state can be expected in our study. The calculation of the valence thus helps checking the correctness of the crystallographic data. Due to the variability of this method of calculating the valence, a deviation of $\pm ca.$ 0.25 valence units is acceptable. The $V(\text{Ln})$ values are as follows and thus confirm the generally good quality of the crystallographic data: compound **2**: $V(\text{La}(1))=2.92$; $V(\text{La}(2))=2.94$; $V(\text{La}(3))=2.79$; $V(\text{La}(4))=2.86$; $V(\text{La}(5))=2.93$; $V(\text{La}(6))=2.65$. In compound **3**, $V(\text{La})=2.83$; in compound **4**, $V(\text{La})=2.74$; and in compound **5** $V(\text{Dy})=3.07$. Hence, only La(6) of the preliminary structure of compound **2** shows a slightly lower bond-valence sum than this range.

Vibrational Spectroscopy. With certain exceptions, the IR and *Raman* spectra recorded for compounds **2–5** are quite similar. The most characteristic bands were also found in the ZT compounds of the other lanthanoids [11][12]. They can be assigned as reported there. *Fig. 6* shows the *Raman* spectra of these compounds. It must be noted at this point that ZT compounds are very *Raman*-active. Consequently, the intensities of other bands (*e.g.*, of CO_3^{2-}) are lower than expected.

The IR and *Raman* spectra of **2** and **3** are exceptionally similar. This was expected, since both compounds are characterized by an identical set of bonds even though in different arrangement in the crystal.

Vibrational spectroscopy can clarify the nature of the compounds **4** and **5**, which potentially contain other anions than ZT (*cf.* [10]). Characteristic bands for nitrate were missing in the spectra of **5**, thus confirming that the disordered moiety in the crystal structure is a ZT ion with an inversion center plus H_2O of crystallization. On the other hand, in **4** the typical bands for carbonate were found in the IR spectra. Both anions, carbonate and nitrate, exhibit very similar characteristics in vibrational spectra with only few differences. For carbonates, two strong IR bands between 1530 and 1320 cm^{-1} can be expected [49–51], and compound **4** shows bands at 1538 cm^{-1} and 1359 cm^{-1} . Similarly, a weak band at 1100–1020 cm^{-1} is expected in the IR, here we have one characteristic band at 1099 cm^{-1} [49][52]. This band does not coincide with the nitrate fingerprint and, therefore, can be regarded as the most characteristic signature of carbonate in compound **4**. The reported medium-strong IR band between 890–800 cm^{-1} is found at 844 cm^{-1} and corresponds to the $\pi(\text{CO}_3)$ of bidentate carbonate [50][53]. The medium band at 1662 cm^{-1} could be attributed to bridged carbonate, as in [50][54]. In the *Raman* spectra, the band characteristic for carbonates (CO_3 symmetric stretching at *ca.* 1100 cm^{-1}) coincides with a band caused by ZT. This is the reason why the *Raman* spectra of **2**, **3**, and **4** appear very similar (see *Fig. 6*). The *Raman* band around 1076 cm^{-1} is much more intense than in the case of the carbonate-

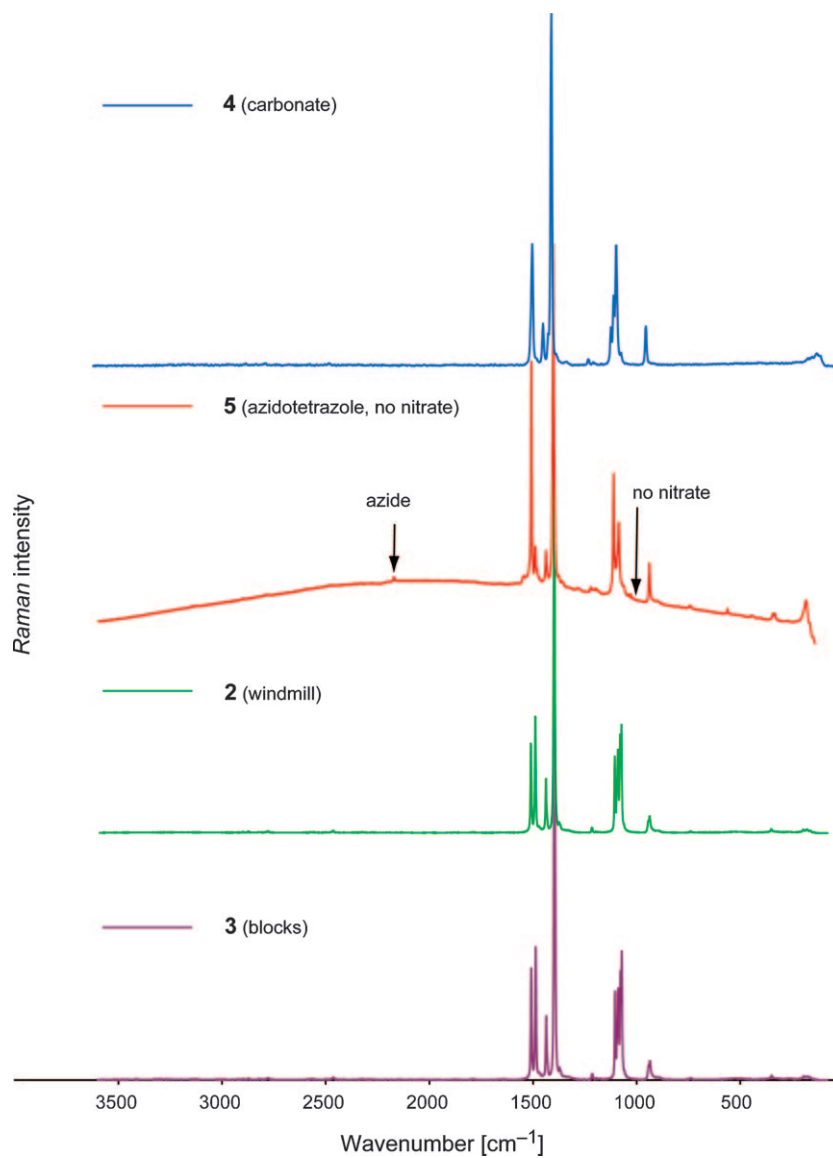


Fig. 6. Raman spectra of 2–5

free compounds **2** and **3**. This may be due to the coincidence of the *Raman* bands caused by $(ZT)^{2-}$ and CO_3^{2-} , since many REE carbonate minerals also exhibit this characteristic band [55]. In conclusion, compound **4** undoubtedly contains both carbonate and ZT anions, but not nitrate. Thereby, this is the first report of a double salt of a ZT compound with another anion.

Probably the most interesting discussion of the vibrational spectroscopical data concerns the existence or nonexistence of the 2150 cm^{-1} band, which is characteristic to the antisymmetric stretching vibration of an azido moiety. This band is quite intense in IR, but it was also observed in the *Raman* spectrum (see *Fig. 6*). According to the crystal-structure analysis of the compounds described herein and in our previous works [11][12], it does not come as a surprise that only the spectra of compound **5** of all 17 compounds show a band at *ca.* 2150 cm^{-1} , because only in this compound a covalent azide is present. *Klapötke* and co-workers previously described the (acidic) decomposition of ZT salts during storing, which could easily be observed by changes in the crystal color [37]. As described above, *Lewis*-acidic decomposition of ZTs is the first step in the formation of 5-azidotetrazole. So, did *Klapötke* eventually observe the formation of analogs to our compound **5**? Interestingly, *Klapötke* and co-workers reported [37] that the lanthanide compounds investigated ($\text{La}_2(\text{ZT})_3$, $\text{Ce}_2(\text{ZT})_3$, $\text{Nd}_2(\text{ZT})_3$, and $\text{Gd}_2(\text{ZT})_3$) indeed showed the typical IR band of a covalent azide. For the cerium(III) ZT, the typical IR band at 2150 cm^{-1} is not listed there; however, close inspection of the original IR spectra clearly shows this peak as well. Although the possible existence of an azide had not been discussed [37], we can speculate, where the typical, but unexpected, azido bands in the REE compounds of ZT in [37] resulted from. Since they used the metathesis reaction of BaZT and the respective REE sulfate, one, at first glance, could imagine that the acidic decomposition of ZT was the consequence of the *Lewis*-acidic character of the Ln^{III} ions, resulting in the formation of 5-hydrazinotetrazole [56]. From what we have learned from the present study, only the heavier Ln^{III} cations such as Dy^{III} are acidic enough for the decomposition of the ZT ion (see compound **5**). An aqueous solution of La^{III} in a 2 : 3 ratio with $(\text{ZT})^{2-}$ is even basic enough to allow for the formation of carbonate (see compound **4**). This makes it improbable that the acidic decomposition step occurred in *Klapötke*'s study to the same degree to form analogs of our compound **5**, at least for the La compound described in [37].

Anyway, even if we assume that the light Ln^{III} cations were acidic enough to decompose ZT and form 5-hydrazinotetrazole, one question yet needs to be answered: where did the additional N-atom come from to form the N_3 group from 5-hydrazinotetrazole? One must keep in mind that *Klapötke* and co-workers used BaZT and $\text{Ln}_2(\text{SO}_4)_3$ and not $\text{Ln}(\text{NO}_3)_3$. There is no final answer to this question; maybe impurities on the surface of the laboratory glassware, which possibly was contaminated with pure 5-azidotetrazole, since investigations on this compound were conducted at approximately the same time in *Klapötke*'s laboratory [43]. With no other reagents utilized than BaZT and $\text{Ln}_2(\text{SO}_4)_3$, it is rather unlikely that *Klapötke* and co-workers produced analogs of **5**, but perhaps only impure $\text{Ln}_2(\text{ZT})_3$ compounds.

Nitrate or Not? We are now able to comment on the anions of the azidotetrazole-containing compound **5** with ultimate distinctiveness (*cf.* [10]). After a certain indication obtained from elemental analysis, vibrational spectroscopy confirms that no nitrate is present in this compound, because its characteristic *Raman* band around 1050 cm^{-1} (symmetric NO_3 stretching, [57]) is lacking (see *Fig. 6*). The relative scattering power of the nitrate's 1050 cm^{-1} band is in the range of approximately 17500 arbitrary units with our *Raman* microscope. This is *ca.* 30% of the most intense ZT-related band in compound **5** (1398 cm^{-1}). Thus, a nitrate band – if present in the

compound – should be clearly visible in the *Raman* spectra of **5**, if nitrate was present in this compound (*cf.* Fig. 6). The disordered constituent in the crystal thus definitely is another half ZT moiety plus one more H₂O molecule, which is confirmed by the improved solution of the crystallographic data. In the same way, compound **4** can be discussed as well: the relative scattering power of the main band of carbonate (1079 cm⁻¹) is only *ca.* 3% of nitrate. Therefore, it is not surprising that the carbonate signature does not show in the vicinity of the very intense ZT bands in the *Raman* spectra.

Conclusions. – In the course of our ‘nitrogen-rich compounds of the lanthanoids’ project, we were able to characterize the complete series of the lanthanoid compounds with 5,5′-azobis[1*H*-tetrazol-1-ide]. A brief summary of some interesting characteristics is given in Table 3. The compounds of the light Ln elements (Ce, Pr, Nd, Sm, Eu, and Gd) are isomorphous, as well as those of the heavy ones (Tb, Dy, Ho, Er, Tm, Yb, and Lu), which is in agreement with the theory of the ‘gadolinium break’. In the present work, we presented two extraordinary compounds of La₂(ZT)₃ type, as well as the first double salt of a ZT compound: La₂(ZT)₂(CO₃) · 12 H₂O.

Table 3. Summary of Some Interesting Features of All N-Rich Ln Compounds of Our Research Group

Formula	N Content [%]	N-Atoms per Ln ^{III} ion	H ₂ O Molecules per Ln ^{III} ion	Coordination number of Ln ^{III}	Ref.
La ₄ (ZT) ₆ · 43 H ₂ O (2)	36.31	15	10.75	9 (LaO ₉) and 9 (LaN ₂ O ₇)	This study
La ₂ (ZT) ₃ · 18 H ₂ O (3)	38.40	15	9	9 (LaN ₂ O ₇)	This study
La ₂ (ZT) ₂ (CO ₃) · 12 H ₂ O (4)	31.75	10	6	8 (LaNO ₇)	This study
Ce ₂ (ZT) ₃ · 24 H ₂ O	34.88	15	12	8 (CeNO ₇)	[12]
Pr ₂ (ZT) ₃ · 24 H ₂ O	34.83	15	12	8 (PrNO ₇)	[12]
Nd ₂ (ZT) ₃ · 24 H ₂ O	34.64	15	12	8 (NdNO ₇)	[12]
Sm ₂ (ZT) ₃ · 24 H ₂ O	34.29	15	12	8 (SmNO ₇)	[12]
Eu ₂ (ZT) ₃ · 24 H ₂ O	34.20	15	12	8 (EuNO ₇)	[12]
Gd ₂ (ZT) ₃ · 24 H ₂ O	33.91	15	12	8 (GdNO ₇)	[12]
Tb ₂ (ZT) ₃ · 22 H ₂ O	34.83	15	11	8 (TbO ₈)	[11]
Dy ₂ (ZT) ₃ · 22 H ₂ O	34.62	15	11	8 (DyO ₈)	[11]
Dy ₂ (ZT) ₃ (CHN ₇) ₄ · 24 H ₂ O (5)	41.87	22	12	8 (DyO ₈)	This study and [10]
Ho ₂ (ZT) ₃ · 22 H ₂ O	34.49	15	11	8 (HoO ₈)	[11]
Er ₂ (ZT) ₃ · 22 H ₂ O	34.35	15	11	8 (ErO ₈)	[11]
Tm ₂ (ZT) ₃ · 22 H ₂ O	34.26	15	11	8 (TmO ₈)	[11]
Yb ₂ (ZT) ₃ · 22 H ₂ O	34.03	15	11	8 (YbO ₈)	[11]
Lu ₂ (ZT) ₃ · 22 H ₂ O	33.93	15	11	8 (LuO ₈)	[11]

The coordination modes of tetrazolide compounds of the REE do not entirely agree with a previous study [31]: Klein, Maggiorosa, and co-workers found ‘*coordination compounds for the early M elements, but [...] salt-like compounds for the heavier analogues*’ [31]. Here, we presented an exception with La (compound **2**, which contains isolated [La(H₂O)₉]³⁺ and (ZT)²⁻ ions as well). It is interesting to note that the ZT compounds of La always have a lower H₂O content than the other salts. This makes

compound **3** the N-richest ‘pure’ ZT compound, although it ‘only’ contains 15 N-atoms per La-atom. It is only ‘exceeded’ by another highlight of this study: compound **5** – a $\text{Dy}_2(\text{ZT})_3$ compound with four CHN_7 molecules as adducts. Our first article [10] on this compound **5** was the first publication incorporating a valid molecular structure of this N-richest organic molecule. It is, so far, the only experimental report on a 2*H*-tautomer of this molecule. According to early calculations, this tautomer should be more stable than the 1*H*-tautomer. Moreover, compound **5** is, to the best of our knowledge, the N-richest Dy compound ever structurally characterized. It is the first 5,5'-azobis[1*H*-tetrazol-1-ide] compound with a neutral tetrazole adduct described in literature.

The full characterization of the compounds which were obtained only with minimum yields (*i.e.*, only a few crystals of less than 5 mg), especially the carbonate ZT compound **4** and the azidotetrazole compound **5**, proved to be microchemically challenging. Nevertheless, all compounds listed in *Table 3* have been fully characterized, including crystal structures, vibrational spectroscopy (IR and *Raman*), and elemental analysis. The blue shift (erroneously reported as red shift in [11]) of the stretching vibrations of the H_2O bands in the IR was only clearly observed with the ZTs of the heavy lanthanoids ($\geq \text{Tb}$) [11]. We are still investigating this phenomenon; however, the three (partly very small) bands in this region of the IR spectra could correspond to the three not coordinating H_2O molecules in the crystal. *Sine gratia et ambitione.*

G. S. wishes to express his sincerest thanks to *S. G.* for all his support, as well as to Prof. *Max Bichler* for his generous support in the whole course of this study and for providing space in his analytical laboratories. Furthermore, Prof. *Bernhard Lendl* is gratefully acknowledged for generous allocation of measurement time with the IR and *Raman* spectrometers of his laboratory. We thank Prof. *Karl Buchtela* for financial support of this study and the Vienna University of Technology for the acquisition of chemicals. We thank the University of Vienna (*Alexander Roller*, Institute of Inorganic Chemistry) and the Ludwig-Maximilian University of Munich (*Michael Göbel*, Department of Chemistry and Biochemistry) for the XRD measurements of **2** and **5**, respectively. *G. S.* thanks the *Austrian Science Fund* (FWF) for financial support in the form of an *Erwin Schrödinger-Stipendium* (project No. J2645-N17).

Experimental Part

General. With the exception of $\text{Dy}(\text{NO}_3)_3$, all chemicals used in this work were purchased from *Aldrich* or *Merck*, resp., in *p.a.* quality and used as supplied without further purification. The starting material for compound **5**, $\text{Dy}(\text{NO}_3)_3 \cdot 5 \text{H}_2\text{O}$, has been obtained from the chemical stock of the Atominstitut (99.9%). *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} ; ν in cm^{-1} ; relative intensities in % of the most intense peak. IR Spectra: *Bruker-Tensor-27* (*Diamond-ATR*, 1 reflection); between 4000 and 600 cm^{-1} with a resolution of 4 cm^{-1} ; $\tilde{\nu}$ in cm^{-1} . Elemental analyses (CHN): *Perkin-Elmer-2400 CHN* elemental analyzer (for compounds **1**, **2**, and **3**) and *Carlo Erba's CHNS* facility *EA 1108 CHNS-O* (for compounds **4** and **5**, which were obtained only in minute amounts of less than 5 mg), both property of the University of Vienna; values in wt.-%. Due to the fact that elemental-analytical facilities are usually not calibrated for the analysis of high-N compounds, the respective anal. values may deviate from the calculated ones. This phenomenon has been reported in several previous studies [37][58–61]. For the ZTs of the lanthanoids, we observed a very reproducible and systematic shift of slightly increased values for C, whereas the values found for H and N are generally slightly decreased.

General Procedure. For the synthesis of the compounds **2–5**, 100 mg of $\text{Na}_2\text{ZT} \cdot 2 \text{H}_2\text{O}$ (**1**) (0.41 mmol) were suspended in 3 ml of H_2O . Compound **1** was obtained as a pure product, suitable as a starting material for the attempted syntheses (elemental analysis: $\text{C}_2\text{H}_4\text{N}_{10}\text{Na}_2\text{O}_2$ (246.099) calc.: C 9.8, H 1.6, N 56.9; found: C 9.7, H 1.8, N 56.0). The mixture was stirred and heated to $> 90^\circ$ in the water bath. As soon as the powder had dissolved, a soln. of 0.27 mmol of the respective $\text{Ln}(\text{NO}_3)_3 \cdot 5$ or $6 \text{H}_2\text{O}$ in 1 or 2 ml of H_2O was added to the soln. After ca. 5 min of stirring in the water bath, the clear soln. was transferred to a 50-ml polyethylene (PE) vial and closed with an air-tight lid in order to prevent H_2O from evaporation. For easier crystallization of compounds **2** and **3**, the bottom of the PE vial was scratched several times with an injection needle. The PE vials were stored in a dark place, and for **2** and **3** after ca. 6–10 d, the crystallization was completed, eventually after slow evaporation of the solvent. Compound **2** was obtained in the form of thin needles, which decomposed in the mother liquid after two or three weeks of storage and recrystallized in the form of **3**. Compound **4** formed in the same procedure, when the La and ZT soln. was exposed to air. Although obtained with a very low yield, the brown crystals of **4** could be separated from **2** (lemon-yellow needles) or **3** (lemon-yellow blocks) under the microscope, even though all three eventually formed in one mixture. Compound **5** was synthesized according to the same procedure, but the vials with the sample soln. were allowed to stand for several months. During this time, the decomposition/oxidation reaction described above took place and **5** crystallized.

*$\text{La}_4(\text{ZT})_6 \cdot 43 \text{H}_2\text{O}$ (**2**).* Lemon-yellow needles. Yield: 65%. IR (Diamond-ATR): 3510 (sh), 3387 (sh), 2447vw, 2161w, 2150w, 1646vs, 1457w, 1407s, 1398vs, 1378m, 1207s, 1187m, 1168 (sh), 1068s, 1057m, 1045m, 771s, 737vs. Raman (14.5 mW, 25°): 1509 (23), 1488 (30), 1436 (14), 1396 (100), 1215 (1), 1104 (20), 1090 (22), 1073 (27), 937 (4). Anal. calc. for $\text{C}_{12}\text{H}_{86}\text{La}_4\text{N}_{60}\text{O}_{43}$ (2314.8): C 6.2, H 3.7, N 36.3; found: C 6.3, H 3.1, N 35.6.

*Lanthanum(III) 5,5'-Azobis[1H-tetrazol-1-ide] Octadecahydrate (**3**).* Yellow blocks or rhombi. IR (Diamond-ATR): 3510 (sh), 3393 (sh), 2448vw, 2160vw, 2110w, 1646vs, 1456m, 1407s, 1398vs, 1207s, 1187m, 1090w, 1068m, 1057m, 1045m 770s, 737vs. Raman (14.5 mW, 25°): 1507 (26), 1486 (31), 1435 (15), 1395 (100), 1213 (1), 1103 (21), 1089 (21), 1077 (25), 936 (4). Anal. calc. for $\text{C}_6\text{H}_{36}\text{La}_2\text{N}_{30}\text{O}_{18}$ (1094.35): C 6.6, H 3.3, N 38.4; found: C 7.0, H 3.0, N 37.9.

*Lanthanum(III) 5,5'-Azobis[1H-tetrazol-1-ide] Carbonate Dodecahydrate (**4**).* Brownish prisms. IR (Diamond-ATR): 3724vw, 3700vw, 3535 (sh), 2652 (sh), 2453vw, 2361vs, 2339vs, 2161w, 2050w, 1980w, 1668m, 1538s, 1462 (sh), 1429w, 1404vs, 1359vs, 1210m, 1188m, 1099vw, 1062m, 1050m, 844s, 756s, 740vs, 696m, 689m. Raman (14.5 mW, 25°): 1481 (52), 1461 (33), 1429 (37), 1390 (100), 1210 (44), 1188 (41), 1180 (35, sh), 1099 (64), 1087 (53), 1076 (68), 1051 (39), 931 (31), 202 (26). Anal. calc. for $\text{C}_3\text{H}_{24}\text{La}_2\text{N}_{20}\text{O}_{15}$ (882.2): C 6.8, H 2.7, N 31.8; found: C 7.0, H 2.8, N 31.5.

*Octaaquadysprosium(3+)–5-azido-2H-tetrazole–5,5'-azobis[1H-tetrazol-1-ide]–water (2:4:3:8; **5**).* Brownish prisms. IR (Diamond-ATR): 3340vs (br.), 2148m, 1634s, 1393m, 1344m, 1106w, 726 (sh). Raman (14.5 mW, 25°): 2166 (2), 1504 (71), 1485 (24), 1433 (23), 1398 (100), 1107 (43), 1083 (30), 936 (20). Anal. calc. for $\text{C}_{10}\text{H}_{50}\text{Dy}_2\text{N}_{58}\text{O}_{24}$ (1691.9): C 7.1, H 3.0, N 48.0; found: C 9.7, H 2.8, N 41.8.

X-Ray Crystallography²⁾. Crystals were obtained as described above and measured at 200 K (for **2–4**) and 100 K (for **5**). Data for **2–4** were collected on a *Nonius KappaCCD* diffractometer (graphite monochromatized MoK_α radiation, $\lambda = 0.71073 \text{ \AA}$) equipped with a 0.3-mm moncap. optics collimator. For compound **5**, data collection was performed with an *Oxford Xcalibur* diffractometer equipped with a *CCD* area detector, using MoK_α radiation. For structure solutions by direct methods and the structure refinements, the programs SHELXS-97 [62] and SHELXL-97 [63] were used, resp. Absorption correction was done by evaluation of partial multi-scans. Thermal ellipsoids in ORTEP [64] plots represent a 50% probability. Unfortunately, crystals of **2** could not be obtained in higher quality, and as a consequence the respective structure refinement was of relatively poor quality. Nevertheless, we decided to present the preliminary results of this structure here, as they, at least, allow characterizing the principles of this highly interesting molecular structure. A full description of structural details

²⁾ CCDC-753318–753321 contain the supplementary crystallographic data for **2–5** including tabulated bond lengths and angles. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

(reasonable ATFs, positions of the H-atoms, twinning, cell/subcell relationships *etc.*) requires the availability of better single crystals.

REFERENCES

- [1] C. Auer von Welsbach, *Sitzungsberichte der Akademie der Wissenschaften* **1885**, 92, 317.
- [2] C. Auer von Welsbach, *Sitzungsberichte der mathematisch-naturwissenschaftlichen Klasse der kaiserlichen Akademie der Wissenschaften* **1907**, 116, 1425.
- [3] C. Auer von Welsbach, *Chemiker-Zeitung* **1926**, 128, 990.
- [4] C. Auer von Welsbach, *Sitzungsberichte der Akademie der Wissenschaften* **1910**, 119, 1011.
- [5] J. Chadwick, *Nature (London)* **1932**, 129, 312.
- [6] F. Joliot, I. Curie, *Nature (London)* **1934**, 133, 201.
- [7] L. Meitner, O. R. Frisch, *Nature (London)* **1939**, 143, 239.
- [8] O. Hahn, F. Straßmann, *Naturwissenschaften* **1939**, 27, 11.
- [9] G. Hevesy, H. Levi, *Nature (London)* **1936**, 137, 185.
- [10] G. Steinhauser, *Sitzungsberichte der Abteilung II (Transactions of the Austrian Academy of Sciences)* **2008**, 217, 3. doi: <http://dx.doi.org/10.1553/SundA2008sIII3>; available online free of charge under http://epub.oeaw.ac.at/0xc1aa500d_0x002298d5.pdf.
- [11] G. Steinhauser, G. Giester, C. Wagner, N. Leopold, J. H. Sterba, B. Lendl, M. Bichler, *Helv. Chim. Acta* **2009**, 92, 1371.
- [12] G. Steinhauser, G. Giester, N. Leopold, C. Wagner, M. Villa, *Helv. Chim. Acta* **2009**, 92, 2038.
- [13] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem., Int. Ed.* **2006**, 45, 3584.
- [14] G. Steinhauser, T. M. Klapötke, *Angew. Chem., Int. Ed.* **2008**, 47, 3330.
- [15] T. Abe, Y.-H. Joo, G.-H. Tao, B. Twamley, J. M. Shreeve, *Chem.–Eur. J.* **2009**, 15, 4102.
- [16] G.-H. Tao, B. Twamley, J. M. Shreeve, *Inorg. Chem.* **2009**, 48, 9918.
- [17] T. M. Klapötke, S. M. Sproll, *J. Polym. Sci., Part A: Polym. Chem.* **2010**, 48, 122.
- [18] Y. Huang, H. Gao, B. Twamley, J. M. Shreeve, *Chem.–Eur. J.* **2009**, 15, 917.
- [19] Y.-H. Joo, J. M. Shreeve, *Angew. Chem., Int. Ed.* **2009**, 48, 564.
- [20] J.-M. Lin, Y.-F. Guan, D.-Y. Wang, W. Dong, X.-T. Wang, S. Gao, *Dalton Trans.* **2008**, 6165.
- [21] Y.-H. Joo, J. M. Shreeve, *Org. Lett.* **2008**, 10, 4665.
- [22] G.-H. Tao, Y. Guo, Y.-H. Joo, B. Twamley, J. M. Shreeve, *J. Mater. Chem.* **2008**, 18, 5524.
- [23] G.-H. Tao, Y. Huang, J. A. Boatz, J. M. Shreeve, *Chem.–Eur. J.* **2008**, 14, 11167.
- [24] Y. Guo, H. Gao, B. Twamley, J. M. Shreeve, *Adv. Mater.* **2007**, 19, 2884.
- [25] C. Ye, J.-C. Xiao, B. Twamley, J. M. Shreeve, *Chem. Commun.* **2005**, 2750.
- [26] M. Quesada, H. Kooijman, P. Gamez, J. Sánchez Costa, P. J. van Koningsbruggen, P. Weinberger, M. Reissner, A. L. Spek, J. G. Haasnoot, J. Reedijk, *Dalton Trans.* **2007**, 5434.
- [27] A. Absmeier, M. Bartel, C. Carbonera, G. N. L. Jameson, P. Weinberger, A. Caneschi, K. Mereiter, J.-F. Létard, W. Linert, *Chem.–Eur. J.* **2006**, 12, 2235.
- [28] C. M. Grunert, J. Schweifer, P. Weinberger, W. Linert, K. Mereiter, G. Hilscher, M. Müller, G. Wiesinger, J. van Koningsbruggen Petra, *Inorg. Chem.* **2004**, 43, 155.
- [29] E. S. Andreiadis, R. Demadrille, D. Imbert, J. Pécaut, M. Mazzanti, *Chem.–Eur. J.* **2009**, 15, 9458.
- [30] M. Giraud, E. S. Andreiadis, A. S. Fisyuk, R. Demadrille, J. Pécaut, D. Imbert, M. Mazzanti, *Inorg. Chem.* **2008**, 47, 3952.
- [31] P. J. Eulgem, A. Klein, N. Maggiorosa, D. Naumann, R. W. H. Pohl, *Chem.–Eur. J.* **2008**, 14, 3727.
- [32] G. Nocton, J. Pécaut, M. Mazzanti, *Angew. Chem., Int. Ed.* **2008**, 47, 3040.
- [33] B. C. Tappan, M. H. Huynh, M. A. Hiskey, D. E. Chavez, E. P. Luther, J. T. Mang, S. F. Son, *J. Am. Chem. Soc.* **2006**, 128, 6589.
- [34] T. M. Klapötke, B. Krumm, F. X. Steemann, G. Steinhauser, *Safety Sci.* **2010**, 48, 28.
- [35] J. Thiele, *Justus Liebigs Ann. Chem.* **1898**, 303, 57.
- [36] G. Singh, R. Prajapati, R. Frohlich, *J. Hazard. Mater.* **2005**, 118, 75.
- [37] A. Hammerl, G. Holl, T. M. Klapötke, P. Mayer, H. Nöth, H. Piotrowski, M. Warchhold, *Eur. J. Inorg. Chem.* **2002**, 834.

- [38] W. J. Evans, E. Montalvo, T. M. Champagne, J. W. Ziller, A. G. DiPasquale, A. L. Rheingold, *J. Am. Chem. Soc.* **2008**, *130*, 16.
- [39] G. Giester, Z. Žák, P. Unfried, *J. Alloys Compd.* **2009**, *481*, 116.
- [40] H.-K. Fun, A. Sinthiya, S. R. Jebas, B. R. D. Nayagam, S. A. C. Raj, *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2008**, *64*, 1436.
- [41] G. Steinhäuser, K. Karaghiosoff, T. M. Klapötke, *Z. Anorg. Allg. Chem.* **2008**, *634*, 892.
- [42] Z. Chen, J. Fan, H. Xiao, *J. Mol. Struct. (THEOCHEM)* **1999**, *458*, 249.
- [43] A. Hammerl, T. M. Klapötke, H. Nöth, M. Warchhold, G. Holl, *Propellants, Explos., Pyrotech.* **2003**, *28*, 165.
- [44] J. Stierstorfer, T. M. Klapötke, A. Hammerl, R. D. Chapman, *Z. Anorg. Allg. Chem.* **2008**, *634*, 1051.
- [45] N. E. Brese, M. O’Keeffe, *Acta Crystallogr., Sect. B: Struct. Sci.* **1991**, *47*, 192.
- [46] I. D. Brown, D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.* **1985**, *41*, 244.
- [47] A. Trzesowska, R. Kruszynski, T. J. Bartczak, *Acta Crystallogr., Sect. B: Struct. Sci.* **2005**, *61*, 429.
- [48] A. Trzesowska, R. Kruszynski, T. J. Bartczak, *Acta Crystallogr., Sect. B: Struct. Sci.* **2004**, *60*, 174.
- [49] G. Socrates, ‘Infrared and Raman Characteristic Group Frequencies’, John Wiley & Sons, Chichester, 2001.
- [50] A. W. A. M. van der Heijden, V. Bellière, L. E. Alonso, M. Daturi, O. V. Manoilova, B. M. Weckhuysen, *J. Phys. Chem. B* **2005**, *109*, 23993.
- [51] Y. S. Sklyarenko, I. S. Sklyarenko, T. M. Chubukova, *Zh. Anal. Khim.* **1961**, *16*, 417.
- [52] A. Ben Ali, V. Maisonneuve, S. Houlbert, G. Silly, J. Y. Buzaré, M. Leblanc, *Solid State Sci.* **2004**, *6*, 1237.
- [53] J. C. Lavalley, *Catal. Today* **1996**, *27*, 377.
- [54] O. V. Manoilova, S. G. Podkolzin, B. Tope, J. Lercher, E. E. Stangland, J.-M. Goupil, B. M. Weckhuysen, *J. Phys. Chem. B* **2004**, *108*, 15770.
- [55] V. S. Kamenetsky, M. B. Kamenetsky, Y. Weiss, O. Navon, T. F. D. Nielsen, T. P. Mernagh, *Lithos* **2009**, *112*, 334.
- [56] A. G. Mayants, V. N. Vladimirov, N. M. Razumov, V. A. Shlyapochnikov, *Zh. Org. Khim.* **1991**, *27*, 2450.
- [57] E. M. A. Ali, H. G. M. Edwards, I. J. Scowen, *Talanta* **2009**, *78*, 1201.
- [58] T. M. Klapötke, C. M. Sabaté, *Chem. Mater.* **2008**, *20*, 1750.
- [59] W. Pan, in ‘24th Int. Annu. Conf. ICT’, 1994, p. 77.
- [60] A. Hammerl, G. Holl, M. Kaiser, T. M. Klapötke, P. Mayer, H. Piotrowski, M. Vogt, *Z. Naturforsch. B* **2001**, *56*, 847.
- [61] M. M. Williams, W. S. McEwan, R. A. Henry, *J. Phys. Chem.* **1957**, *61*, 261.
- [62] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Germany, 1997.
- [63] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany, 1997.
- [64] L. J. Farrugia, *J. Appl. Crystallogr.* **1997**, *30*, 565.

Received November 5, 2009