Controlling Complexation Behavior of Early Lanthanides via the Subtle Interplay of their Lewis Acidity with the Chemical Stability of 5,5’-(Azobis)tetrazolide

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Abstract: Two novel nitrogen-rich lanthanide compounds of 5,5’-(azobis)tetrazolide (ZT) were synthesized and structurally characterized. The dinuclear, isostructural compounds [Ce₂(ZT)₂CO₃(H₂O)₁₂]·4H₂O (1) and [Pr₂(ZT)₂CO₃(H₂O)₁₂]·4H₂O (2) were synthesized via two independent routes. Compound 1 was obtained after partial Lewis acidic decomposition of ZT by Ce⁴⁺ in aqueous solution of (NH₄)₂Ce(NO₃)₆ and Na₂ZT. Compound 2 was obtained by crystallization from aqueous solutions of Pr(NO₃)₃, Na₂ZT, and Na₂CO₃. By X-ray diffraction analysis at 200 K, it was found that the trivalent lanthanide cations are bridged by a bidentate carbonato ligand and each cation is further coordinated by six H₂O ligands and one ZT ligand thus being ninefold coordinated.

Introduction

Tetrazole derivatives are nitrogen-rich compounds that exhibit interesting properties both for application as energetic materials[1] as well as for coordination chemistry.[2] In particular, inorganic compounds of 5,5’-(azobis)[1H-tetrazol-1-ides] (vulgo 5,5’-(azobis)tetrazolides or 5,5’-azotetrazolates, ZT²⁻) have been studied to great extent.[3]

The free acid 5,5’-(azobis)tetrazole (H₂ZT) is highly unstable.[4] Thus, the ZT²⁻ ion is highly sensitive against acidic attack. Upon acidic decomposition, it forms 5-hydrizinotetrazole, formic acid, and N₂ gas.[4]

Water of crystallization plays a crucial role in the stabilization of inorganic ZT compounds.[5] Hence, not all ZT compounds are accessible through simple synthetic routes. It is difficult to generalize the behavior of inorganic compounds of ZT throughout the periodic table of elements. In any case, an often observed general pattern is that alkali and alkaline earth metal compounds of ZT[4] crystallize with a sufficient amount of water of crystallization, thus making them stable and allowing for the growth of sufficiently large crystals for X-ray diffraction structure analysis. Divalent ions of transition metals, e.g. Cu²⁺ or Cd²⁺, however, often precipitate immediately upon addition of Na₂ZT solution as a fine precipitate that explodes violently at the slightest touch when dried. It required some special preparative skills and complexation of the cation with NH₃ ligands to allow for the synthesis of the ZT compounds.[6] Trivalent salts of lanthanides (Ln) crystallize with a sufficient amount of constitutional water,[7] which makes them safe to handle. The same is true for the UO₂²⁺ compound.[8]

The Ln₂ZT₃ series are neat examples to illustrate the “Gadolinium Break”, which predicts a slight change in the chemical/crystallographic behavior of a series of Ln compounds between the Gd(III) and Tb(III) compounds. In this case, in the light Ln₂ZT₃ series (Ln = Ce – Gd), the ZT ion acts as a ligand to the metal,[9] whereas in the heavy Ln₂ZT₃ series (Ln = Tb – Lu), the compound crystallizes as a salt with isolated hydrated cations and anions.[10]

In general, the aforementioned changes in the chemical environment greatly affect the crystallization behavior of ZT compounds. Crystallization in supercritical CO₂/H₂O yields a Dy₂ZT₃ compound with lower H₂O content.[5] Crystallization under presence of CO₂ also yields an isotypic series of lanthanide ZT carbonates.[11] Lastly, presence of ppb amounts of foreign actinides, e.g. Am(III), results in a Tb(Am)₂ZT₃ compound[12] that crystallizes in the crystal structure type of the light Ln₂ZT₃ compounds,[9] rather than according of the series of the heavy Ln₂ZT₃s[10] to which Tb₂ZT₃ originally belongs.

Cations with higher valence, however, such as Th(IV) or Ce(IV),[4] partly destroy the ZT²⁻ anion due to their Lewis acidic properties. Hammerl et al. reported the formation of a brown precipitate and gas when combining Ce(IV) and...
ZT$^{2-}$.[4] In this study, we wanted to take a deeper look into this reaction – with unexpected results.

Results and Discussion

The HSAB concept (Pearson’s acid-base concept)[13] classifies trivalent lanthanides as hard Lewis acids, water as a hard solvent and the carbonate anion as a hard base. The lanthanide’s ionic radii decrease from La$^{3+}$ to Lu$^{3+}$ by 16% influencing their Lewis acidity and their reactivity towards complexation substantially. This can be monitored by the dianionic ZT ligand, which represents a peculiar ligand in rare earth element (REE) coordination chemistry being a rather weakly coordinating ligand. However, it is known to form a coordinative bond for the lighter REEs. Furthermore, recent work by Klamm et al.[14] employed the inherent Lewis acidity to generate bimetallic lanthanide complexes by cleavage of a cryptand ligand. This concept was used to prepare ($\mu$-carbonato)-dodeca-aquabis(5,5$'$-azobis(1H-tetrazol-1-ide))-di-cerium tetrahydrate, [ Ce$_2$(ZT)$_2$CO$_3$(H$_2$O)$_{12}$ ]·4H$_2$O (I) starting off from Ce(IV) ammonium nitrate, which is a well-known and efficient Lewis acid for one-pot syntheses.[15] In our case we used the starting material as an efficient Lewis acid partially decomposing the ZT thus reducing Ce(IV) to Ce(III) and allowing for a slow complexation as hexaquo-coordinated dinuclear complex. The decomposition of some of the ligand yields among others foraminated ninefold in a distorted capped square anti-prismatic fashion. Both compound I and ( $\mu$-carbonato)-dodeca-aquabis(5,5$'$-azobis(1H-tetrazol-1-ide))-di-praseodymium tetrahydrate (2) crystallize isostructural in the monoclinic space group $\overline{2}a$ with four molecules in the crystallographic unit cell (see Table 1). Both Ce and Pr are coordinately ninedinefold in a distorted capped square anti-prismatic fashion being rather common for Ln complexes. The coordination sphere comprises of the ZT moiety, six H$_2$O molecules and the bidentate carbonato ligand (see Figure 1). The asymmetric unit consists of half of the [Ln$_2$(ZT)$_2$CO$_3$(H$_2$O)$_{12}$]·4H$_2$O with the $\pi$(3)-O(1) bond representing a twofold rotation axis.

There is a manifold of stabilizing hydrogen-bonding network among the coordinating H$_2$O molecules as well as a total of four non-coordinating water molecules per compound molecule, and the ZT moiety, which are known to be crucial to stabilize the potentially explosive ZT compounds.[5] The ZT moieties are aligned almost parallel to the ac plane with the carbonato bridge between the two coordination centers being perpendicular to it. The Ce–O–Ce angle of 1 measures 165.06° compared to the 168.8° of the dinuclear carbonato-bridged Ce-compound of the previously investigated series,[11] whereas the Pr–O–Pr angle of 2 measures 165.10° compared to the 169.6° of the dinuclear carbonato-bridged Pr-compound.[11] In contrast to the earlier reported series, which features a wave-like alignment of the 5,5$'$-azobis(tetrazolide) ligands, our title compounds are aligned coplanar to the ac plane with parallel-displaced $\pi$–$\pi$ stacking of the (azobis)(tetrazolide) moieties of adjacent molecules. Distances of the N8 of the azo-bridge to the N10 of the tetrazole ring of the adjacent molecule range between 3.299 Å and 3.381 Å.

Figure 2 shows the packing of 1, viewed normal to (010) which is characterized by the stacking of ZT moieties, intercalated with dinuclear [Ce$_2$(ZT)$_2$CO$_3$(H$_2$O)$_{12}$] moieties. Crystal structure and refinement data for 1 and 2 are listed in Table 1.

Conclusions

In continuation of our endeavor to elucidate the coordination chemistry of the dianionic azobis[tetrazolide] within the lanthanides we prepared two novel compounds based on the dinuclear $\mu$-carbonato-bridged bis-lanthanide structural motif. Exploiting the intrinsic Lewis acidity of Ce and Pr under synthetic conditions complying with Pearson’s HSAB concept we
yielded the presented structures of ninefold coordinated complexes.

**Experimental Section**

**Caution!** ZT compounds are potentially explosive and should be handled with care, especially when anhydrous. Heating, complete drying and loss of water of crystallization should hence be avoided. They can react violently upon stimuli such as friction, heat, electric sparks or impact. Using appropriate safety equipment can drastically reduce the risk when handling these compounds (face shields, wrist protectors, Kevlar® gloves, conducting shoes, and ear protection).

**Syntheses:** Chemicals for the syntheses were purchased at Sigma Aldrich in p.a. quality and used without further processing or purification. Na₂ZT·2H₂O was synthesized by oxidation of 5-aminotetrazole with KMnO₄ in aqueous solution of NaOH, as outlined in literature. A preliminary approach for the synthesis of 2 with stoichiometric amounts of Pr(NO₃)₃·6H₂O (118 mg), Na₂ZT·2H₂O (66 mg), and Na₂CO₃ (14.4 mg) turned out unsuccessful, likely due to immediate quantitative precipitation or Pr₂(CO₃)₃.

**X-ray Crystallography:** Crystals were measured at 200 K. Data collection was performed with a Nonius Kappa CCD diffractometer (graphite monochromatized Mo-Kα 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 and SHELX-2018/3 were used, respectively. Absorption correction was done by evaluation of partial multiscan. Thermal ellipsoids in ORTEP plots represent a 50% probability.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-2038690 for 1 and CCDC-2038691 for 2 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

**Acknowledgements**

P. Weinberger acknowledges financial support by FWF F 31076. Open access funding enabled and organized by Projekt DEAL.

**Keywords:** Lewis acidity; Lanthanides; Dinuclear complex; X-ray diffraction / 5,5'-Azobis[tetrazolide]

**References**

[1] a) N. Fischer, K. Huell, T. M. Klapötke, J. Stierstorfer, G. Laus, M. Hummel, M. Froshauer, K. Wurst, H. Schottenberger, Dalton Trans. 2012, 41, 11201–11211; b) D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Chem. Eur. J. 2013, 19, 4602–4613; c) J. Stierstorfer, T. M. Klapötke, A. Hammerl, R. D. Chapman, Z. Anorg. Allg. Chem. 2008, 634, 1051–1057; d) A. Hammerl, T. M. Klapötke, R. Rocha, Eur. J. Inorg. Chem. 2006, 2210–2228; e) A. Hammerl, T. M. Klapötke, H. Noto, M. Warchold, G. Holl, M. Kaiser, U. Tincanisc, Inorg. Chem. 2001, 40, 3570–3575; f) H. Gao, J. M. Shreeve, Chem. Rev. 2011, 111, 7377–7436; g) A. M. W. Dufter, T. M. Klapötke, M. Rusan, J. Stierstorfer, Z. Anorg. Allg. Chem. 2020, 646, 580–585; h) M. Benz, T. M. Klapötke, J. Stierstorfer, Z. Anorg. Allg. Chem. 2020, 646, 1380–1388; i) N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, J. Mater. Chem. 2012, 22, 20418–20422.

[2] a) D. Müller, C. Knoll, B. Stöger, W. Artner, M. Reissner, P. Weinberger, Eur. J. Inorg. Chem. 2013, 2013, 984–991; b) L. Ga- jecki, D. J. Berg, J. Hoenisch, A. G. Oliver, Dalton Trans. 2018, 47, 15487–15496; c) N. Szimhardt, M. H. H. Wurzenberger, A. Beringer, L. J. Daumann, J. Stierstorfer, J. Mater. Chem. A 2017, 5, 1740–1748.

**Figure 2.** Packing of 1, viewed on (010).
