$[NdI_2(thf)_5]$, the First Crystallographically Authenticated Neodymium(II) Complex**

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Dedicated to Professor Glen Deacon
on the occasion of his 65th birthday

Over the last three years the series of molecular complexes of divalent lanthanides has been extended for three lanthanide metals. The well known complexes of divalent samarium, europium, and ytterbium were supplemented by the solvated diiodide complexes of divalent neodymium, dysprosium, and thulium, $[LnI_2(dme)_3]$ (Ln = Nd,[1] Dy,[1] Tm;[2] dme = 1,2-dimethoxyethane) and $[LnI_2(thf)_5]$ (Ln = Nd,[1] Dy[1]). The thulium and dysprosium compounds proved to be useful agents in inorganic[3] and organic syntheses.[4, 5] Apart from complexes of divalent samarium, europium, and ytterbium, $[DyI_2(dme)_3]$[5] and $[TmI_2(dme)_3]$[2] are the only two molecular lanthanide(II) complexes which have been studied by single-crystal X-ray diffraction methods. Crystals of $[DyI_2(dme)_3]$ contain two independent molecules with linear and bent I-Dy-I units; the dysprosium atoms are η^2-chelated by all three DME molecules. The molecules of $[TmI_2(dme)_3]$ consist of linear I-Tm-I fragments with the metal atoms being further coordinated by one terminal η^1-bonding and two chelating η^2-bonding DME molecules. Here we report on the first reliable structure determination of a molecular neodymium(II) complex, $[NdI_2(thf)_5]$ (**1**), as well as on the structure of a new thulium(II) complex, $[TmI_2(dme)_2(thf)]$ (**2**).

NdI_2 was prepared from neodymium powder and iodine according to the procedure recently reported by Bochkarev and Fagin.[1] Crystallization of NdI_2 from THF at −28 °C affords the molecular complex $[NdI_2(thf)_5]$ (**1**) as black crystals. All manipulations have to be carried out at low temperatures otherwise **1** reacts with THF. Cooling of solutions of $[TmI_2(dme)_x]$ in 1:1 mixtures of DME and THF to 0 °C causes precipitation of $[TmI_2(dme)_2(thf)]$ (**2**) as longish emerald green crystals.

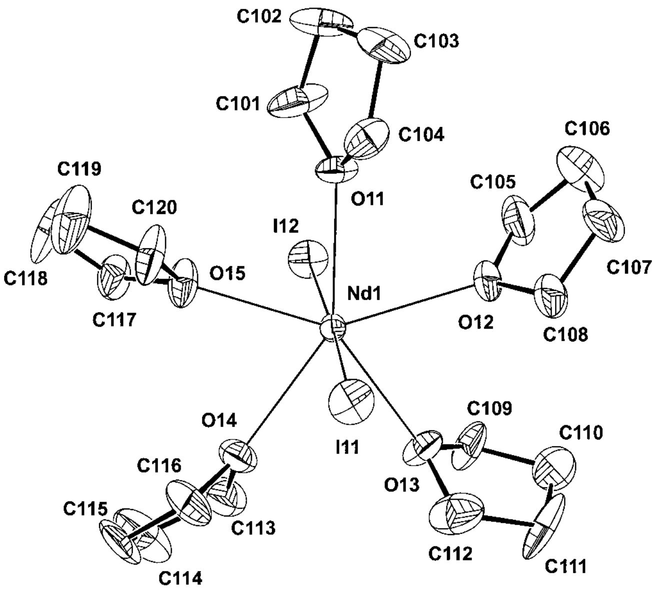

Figure 1. Structure of one of the four crystallographically independent molecules of **1** (ORTEP drawing; thermal ellipsoids with 30% probability. The hydrogen atoms are omitted for clarity). Relevant bond lengths [Å] and angles [°]: Nd1-I11 3.2566(10), Nd1-I12 3.2861(10), Nd1-O11 2.617(7), Nd1-O12 2.629(8), Nd1-O13 2.624(7), Nd1-O14 2.593(7), Nd1-O15 2.584(8); O11-Nd1-O12 71.8(3), O13-Nd1-O12 72.5(3), O14-Nd1-O13 71.8(3), O15-Nd1-O14 72.0(3), O15-Nd1-O11 72.8(3), I11-Nd1-I12 177.60(3), O11-Nd1-I11 94.44(17), O12-Nd1-I11 87.3(2), O13-Nd1-I11 93.60(18), O14-Nd1-I11 86.79(19), O15-Nd1-I11 89.91(19), O11-Nd1-I12 87.35(17), O12-Nd1-I12 94.8(2), O13-Nd1-I12 85.90(18), O14-Nd1-I12 90.82(19), O15-Nd1-I12 89.10(19).

$[NdI_2(thf)_5]$ (**1**) (Figure 1) crystallizes in the monoclinic space group $P2_1/n$. The unit cell contains 16 molecules of **1** and noncoordinating THF solvent molecules.[6] The four crystallographically independent molecules of **1** show similar molecular parameters. $[TmI_2(dme)_2(thf)]$ (**2**) (Figure 2) crystallizes in the monoclinic space group $C2/c$ with four molecules in the unit cell.[6] The comparison of the crystallographic data of **1**

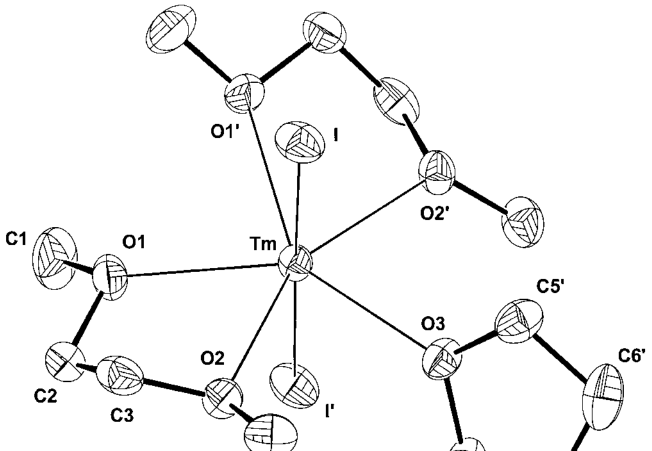

Figure 2. Structure of **2** (ORTEP drawing; thermal ellipsoids with 50% probability. The hydrogen atoms are omitted for clarity; symmetry transformations used to generate equivalent atoms: (′) $-x$, y, $0.5-z$). Relevant bond lengths [Å] and angles [°]: Tm-I 3.1511(5), Tm-O1 2.501(6), Tm-O2 2.551(6), Tm-O3 2.438(8); O1-Tm-O3 141.66(13), O1-Tm-O1′ 76.7(3), O2-Tm-O3 77.06(13), O1-Tm-O2 66.95(19), O1-Tm-O2′ 137.98(19), O2-Tm-O2′ 154.1(3), O1-Tm-I 96.65(15), O1-Tm-I′ 84.15(15), O2-Tm-I 80.00(13), O3-Tm-I 89.490(18), O2-Tm-I′ 99.77(13).

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with those of the analogous samarium complex $[SmI_2(thf)_5]$[7] (same space group, similar unit cell parameters, equal number of molecules in the unit cell), suggests that they are isotypic compounds. However, due to the limited quality of the crystallographical data of $[SmI_2(thf)_5]$, only the arrangement of the atoms, but no precise values for the bond lengths and bond angles could be established. Complex **2** is isostructural with $[SmI_2(dme)_2(thf)]$.[7] The molecules of **1** and **2** exibit a pentagonal-bipyramidal structure with the two iodine atoms in the axial positions. Similar seven-coordinate structures were reported for the solvent adducts of samarium and ytterbium diiodide $[SmI_2(dme)(thf)_3]$,[7] and $[YbI_2(\eta^2\text{-dme})_2(\eta^1\text{-dme})]$.[8] Furthermore, the structures of the cationic lanthanide(III) complexes $[SmI_2(thf)_5]^+$,[9a] $[LaI_2(thf)_5]^+$,[9b] $[CeCl_2(thf)_5]^+$,[9c] $[TbCl_2(thf)_5]^+$,[9d] $[YbCl_2(thf)_5]^+$,[9e,f] $[GdCl_2(thf)_5]^+$,[9e,g] $[DyCl_2(thf)_5]^+$,[9h,i] $[ErCl_2(thf)_5]^+$,[9b,g] and $[LuCl_2(thf)_5]^+$,[9j] show an analogous arrangement, whereas for $[YbI_2(thf)_4]$[10] a six-coordinate and for $[SmI_2(dme)_3]$[11] an eight-coordinate structure was ascertained. Depending on the crystallization conditions, $[SmI_2(dme)_3]$ crystallizes either as an enantiomer (Δ or Λ) or as a racemic mixture. The only crystallographically completely characterized penta(tetrahydrofuranato)metal(II) complex is the strontium compound $[SrI_2(thf)_5]$.[12]

The Nd–I distances of the four crystallographically independent molecules of **1** range from 3.2566(10) to 3.2910(10) Å. The average Nd–I distance of 3.276 Å is about 0.035 Å longer than the average metal–iodine distance in $[SmI_2(dme)_2(thf)]$ or $[SmI_2(dme)(thf)_3]$[7] and exceeds significantly the Tm–I distances in **2** (3.1511(5) Å) and in $[TmI_2(\eta^2\text{-dme})_2(\eta^1\text{-dme})]$[2] (3.141(2) and 3.186(2) Å). These data are consistent with the differences in the radii[17] of the respective metal(II) ions. The I-Nd-I angle in **1** (av 178.1°) and the I-Tm-I angle in **2** (178.98(4)°) are in accordance with a rather regular pentagonal-bipyramidal structure. The O-Nd-O angles in **1** are close together and range from 70.8(3) to 73.5(3)°. Also the Nd–O bond lengths vary only slightly and show an average value of 2.612 Å for the four crystallographically independent molecules. Because of the two different ligands the O-Tm-O angles in **2** deviate from the ideal value of 72°. The O(dme)-Tm-O(dme) angles formed by the two chelating DME molecules (66.95(19)°) are smaller than the O(thf)-Tm-O(dme) angle (77.06(13)°). A similar value (76.7(3)°) was determined between the two DME molecules. As in $[SmI_2(dme)_2(thf)]$,[7] the Tm–O(thf) distance (2.438(3) Å) is shorter than the [Tm–O(dme)] distances (2.501(6) and 2.551(6) Å). From the fact that the difference of 0.095 Å between the M–I distances in **2** and in $[SmI_2(dme)_2(thf)$ agrees well with the difference of 0.092 Å between the M–O(thf) and M–O(dme) bond lengths of these two compounds, it may be concluded that for the seven-coordinate compounds the difference in ionic radii of Sm^{II} and Tm^{II} will range between 0.092 and 0.095 Å.

Experimental Section

All manipulations were performed in vacuum and in a nitrogen atmosphere. The extreme sensitivity of **1** and **2** towards air and moisture and the low thermal stability of **1** prevented satisfactory elemental analysis.

1: After combustion of a mixture of neodymium (0.5 g) and iodine (0.5 g) in an evacuated glass tube (8 × 100 mm), the formed ingot of NdI_2 was broken down using an ultrasonic bath, and the powder formed was transferred under vacuum to a 50-mL Schlenk flask. While cooling the flask with liquid nitrogen, THF (ca. 25 mL) was condensed on to the NdI_2 powder. Subsequently, the flask was cooled with dry ice for 12 h and was then allowed to warm slowly to temperatures between −10 and −5 °C. Gentle stirring of the reaction mixture caused the formation of a deep violet solution which was then placed into a refrigerator (−28 °C). In the course of 36 h, black crystals of $[NdI_2(thf)_5]$ precipitated from the solution.

2: A mixture of thulium powder (3.0 g, 17.79 mmol) and iodine (0.5 g, 1.97 mmol) in DME (20 mL) was stirred at room temperature until the iodine color disappeared completely and colorless thulium triiodide precipitated. The mixture was sonicated at 70 °C for 30 min. The emerald green solution of TmI_2 formed was decanted from unreacted metal and concentrated in vacuum to a volume of 10 mL. Subsequently THF (10 mL) was added to the DME solution and the mixture was heated to 60 °C until the crystalline product was completely dissolved. Cooling of the solution to 0 °C gave **2** (0.97 g, 73 %) as large longish emerald green crystals. M.p. >90 °C (decomp); elemental analysis calcd (%) for $C_{12}H_{28}O_5I_2Tm$ (675.09): Tm 25.02; found: Tm 25.13.

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[6] X-ray structure data: Siemens SMART CCD diffractometer, ω scans, $Mo_{K\alpha}$ radiation ($\lambda = 0.71093$ Å), graphite monochromator, $T = 173$ K, SADABS[13] for absorption correction, structure solution with direct methods (SHELXS-97[14]), refinement against F^2 (SHELXL-97[15]) with anisotropic thermal parameters for all non-hydrogen atoms, hydrogen positions with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2) on calculated positions. Data collection for **1**: crystal dimensions 0.63 × 0.38 × 0.18 mm, monoclinic, space group $P2_1/n$, $a = 23.1057(3)$, $b = 26.1191(4)$, $c = 23.9426(1)$ Å, $\beta = 110.896(1)°$, $V = 13499.0(3)$ Å^3, $Z = 16$, $\rho_{calcd} = 1.688 \times 10^3\ kg\,m^{-3}$, $\mu = 3.401\ mm^{-1}$, $F(000) = 6736$, $2.1 \le 2\theta \le 50.0°$, $-27 \le h \le 27$, $-27 \le k \le 31$, $-27 \le l \le 28$, 76040 data collected, 23563 unique data ($R_{int} = 0.0867$), 11496 data with $I > 2\sigma(I)$, 1099 refined parameters, GOF(F^2) = 1.001, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$): $R_1 = 0.0643$, $wR_2 = 0.1277$, max/min residual electron density 1.186/−1.188 e Å^{-3}. The THF molecules coordinated to the metal center in **1** are disordered about multiple positions in a small range which results in large anisotropic displacement parameters of the atoms and shortening of the C–C and C–O bond lengths. It was not possible to find a satisfactory model for the disorder. The unit cell of **1** contains 22 noncoordinating THF solvent molecules of which only eight could be refined. The remaining 14 molecules occupy an area of 2354 Å^3 (17 %) in the unit cell. For further refinement the contribution of the missing solvent molecules was subtracted from the reflection data by the SQUEEZE routine of the PLATON[16] program. Data collection for **2**: crystal dimensions 0.40 × 0.24 × 0.16 mm, monoclinic, space group $C2/c$, $a = 12.9457(4)$, $b = 11.3172(2)$, $c = 15.3120(5)$ Å, $\beta = 114.900(1)°$, $V = 2034.81(10)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.204 \times 10^3\ kg\,m^{-3}$, $\mu = 7.407\ mm^{-1}$, $F(000) = 1260$, $5.0° \le 2\theta \le 55.0°$, $-16 \le h \le 16$, $-14 \le k \le 12$, $-18 \le l \le 19$, 7412 data collected, 2328 unique data ($R_{int} = 0.0538$), 1389 data with $I > 2\sigma(I)$, 94 refined parameters, GOF(F^2) = 1.050, final R indices ($R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$) $R_1 =$

0.0473, $wR_2 = 0.0917$, max/min residual electron density 2.057/ -1.062 e Å^{-3}. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-163342 (**1**) and CCDC-163343 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Mass-Spectrometric Monitoring of a PNA-Based Ligation Reaction for the Multiplex Detection of DNA Single-Nucleotide Polymorphisms[**]

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The genetic variation that occurs most frequently is the exchange of single nucleobases (single-nucleotide polymorphisms, SNP).[1, 2] These single-base mutations are associated with diseases, such as cystic fibrosis,[3] familial hypercholesterolemia,[4] cancer,[5] and many others. DNA diagnostic assays depend on a binding event between the target DNA and a complementary oligonucleotide probe. The hybridization alone, however, barely exhibits sufficient selectivity in distinguishing matched from single-base mismatched DNA targets. An enhancement of the discriminatory power is possible by accommodating a probe-modifying event such as oligonucleotide ligation[6] or primer extension.[7] There is an increasing demand for the development of assay systems in which a single analysis is able to report on more than one diagnostic event (multiplexing). Most commonly fluorescence-based techniques, such as fluorescent dye-terminator-extension,[7] TaqMan assays,[8] molecular beacons,[9, 10] or scorpion probes[11] are used. A drawback is the need for labor- and cost-intensive fluorescence labeling. More importantly, the degree of multiplexing that can be achieved is limited by the number of spectrally resolved fluorophores. In contrast, matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass-spectrometry (MS) offers unparalleled resolution and has been demonstrated to enable a genotyping of single-base mutations.[12, 13] However, the fragmentation and the known tendency to form DNA metal-salt adducts can impede the resolving power of MALDI-based detection when oligonucleotides are used as probes.[14, 15] Herein, a novel approach for single-base-mutation detection is proposed that capitalizes upon the use of peptide nucleic acids (PNAs)[16]—a chemically stable and nonionic DNA analogue that combines superior base-pairing properties with ease and accuracy of detection.[17, 18] Contrary to previous reports on PNA-based MALDI-TOF genotyping[19, 20] it is a DNA-controlled chemical ligation of two short probes that is monitored rather than the hybridization of one long probe.[21]

PNA exhibits an unparalleled suitability for MALDI-TOF MS analysis in terms of molecular-weight resolution and accuracy.[19, 20] The discriminative power of PNA-hybridization itself, however, depends on base content, sequence, and particularly on the length of the oligomer. Oligomers that are longer than 16 base pairs are required to provide a unique sequence. However, the longer PNA segments are relatively unselective as DNA binders.[22] Conversely, short-length PNA oligomers exhibit a sufficiently high DNA affinity combined with a very good discrimination for single-base mismatches. We thought that a highly specific sequence analysis of a unique gene segment should be possible by employing a PNA-ligation strategy. Since PNA is not a substrate of any known ligase, any attempt to employ PNA as a ligation probe has to rely solely on chemical methods.

PNA is a pseudopeptide and ligation chemistry can easily be implemented by using amide-bond forming reactions.[21] For the development of a sequence-specific PNA-based ligation reaction we examined the all-PNA model system shown in Scheme 1 and the carbodiimide-mediated condensation of PNA-fragments **1a** and **2a** was investigated. It became apparent that the addition of the complementary template **3a** increased the rate and the yield of the ligation reaction (Figure 1 A). Surprisingly, the presence of template **3b**, which contained a single-base mismatch, gave an even higher increase in the ligation yield.

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